Gelation of Colloidal Silica

Giovanni Dietler, Claude Aubert, and David S. Cannell

Department of Physics, University of California at Santa Barbara, Santa Barbara, California 93106

and

Pierre Wiltzius

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Classical light-scattering studies of colloidal silica gels show that they have a fractal structure for length scales shorter than a concentration-dependent crossover length ξ, and behave like a collection of nearly randomly distributed scattering centers for length scales greater than ξ. Our data show that ξ has a power-law concentration dependence, $\xi \propto c^{-1.17 \pm 0.1}$.

PACS numbers: 82.70.Gg, 82.70.Dd

Aggregation of many small units leading to the formation of increasingly large clusters plays an important role in many different areas including physics, chemistry, biology, and materials science. Following the discovery by Forrest and Witten[1] that smoke-particle aggregates can have a fractal geometry, with the density-density correlation function $g(r)$ exhibiting power law decay within the aggregates, a substantial effort has been devoted to computer simulation of various aggregation models.[2-4] This work has shown that kinetic processes can produce clusters having such power law correlations, indicating that such aggregates are very likely scale invariant. Scattering and other experiments on aggregating silica[5-7] and gold colloids[8,9] have shown that such systems generate clusters with a fractal geometry and have explored the dependence of the Hausdorff dimensionality of the clusters on aggregation conditions. Both simulation and experiment have focused on the low-concentration limit to permit the clusters to grow as large as possible and allow the fractal geometry to manifest itself over the widest possible range of length scales.

In this Letter we present the results of classical light-scattering studies of the aggregation of colloidal silica for silica concentrations great enough to result in the formation of gel networks, before the growing clusters sediment significantly. We find that while the clusters are growing, but before the gel point is reached, the static structure factor $S(q)$ closely resembles that observed previously for clusters formed by slow aggregation at low silica concentration,[5] i.e., it exhibits power-law decay, $S(q) \propto q^{-2.16 \pm 0.10}$ for $q\xi \gtrsim 1$, and is approximately q independent for $q\xi \lesssim 1$. Here ξ is a length scale characteristic of the range of density fluctuations occurring in the solution. As the clusters grow and ξ increases, the crossover to power-law behavior occurs at ever smaller values of q. At some point, however, the growing clusters form a gel, and after this takes place very little further evolution of $S(q)$ occurs. The higher the silica con-

centration, the smaller is the value of ξ when gelation occurs. Consequently, the gels are characterized by a concentration-dependent crossover length ξ, such that $S(q)$ shows power-law decay for $q\xi \gtrsim 1$, with nearly the same exponent previously observed for slow aggregation, in the dilute limit,[5] and for $q\xi \lesssim 1$, $S(q)$ is nearly constant. These observations are consistent with the gels' exhibiting fractal geometry on length scales smaller than ξ, with that geometry apparently being characteristic of the aggregation process that produced the clusters.

The small-q behavior of $S(q)$ is that which would be expected from a collection of scattering objects, each of size $\lesssim \xi$, randomly positioned in space. A similar structure factor has been observed for silica aerogel by Schaefer and Keefer,[10] using x-ray scattering, but no other comparable measurements exist, to our knowledge. It is tempting to identify ξ with a characteristic cluster dimension at gelation, and this simple picture is generally consistent with our data for the concentration dependence of ξ ($\xi \sim c^{-1.17 \pm 0.1}$). However, this picture may be too naive since it ignores "screening" of the fluctuations associated with the largest clusters by the presence of smaller clusters which may occupy much of the internal void spaces of the largest clusters.

The samples were prepared from colloidal silica spheres 70 Å in diameter (Ludox SM, graciously provided by E. I. Du Pont de Nemours & Co.). The stock silica solution (30 wt.% silica) was diluted directly (while stirring) into (0.5–0.75)M NaCl solution, containing enough HCl to produce a final solution of the desired silica concentration in 0.45M NaCl, at pH 7.0 ± 0.1. Under these conditions aggregation occurred slowly over a period of hours to days. The structure factors of the solutions containing the growing aggregates were measured *in situ* by means of classical light scattering with use of the apparatus described previously.[11] The range of scattering wave vectors used was $0.61 \ \mu m^{-1} \le q \le 23.6 \ \mu m^{-1}$.

Figure 1 shows the typical manner in which $S(q)$ evolved in time, at a silica concentration of 2.4 wt.%. Initially ($t = 1$ h) there appeared to be a few larger particles present, yielding the peak at low q; however, the aggregation process was independent of these aggregates, and their scattering was soon overwhelmed by the scattering from the aggregating colloidal particles ($t \gtrsim 3$ h). The scattering was characterized by a steadily increasing value for $S(q=0)$, coupled with a slower increase in ξ. In a dilute solution $S(q=0)/c$ would be directly proportional to the weight-average molecular weight of the growing clusters, while ξ^2 would be $R_G^2/3$, where R_G^2 is the z-averaged square of the radius of gyration. At a certain time, dependent upon concentration, the samples became mechanically rigid as judged simply by shaking, and $S(q)$ changed very little after that time, which was ~20 h for the data of Fig. 1. At this point the larger clusters, at least, ceased to diffuse, and time averaging of the scattered intensity was not adequate to provide accurate results. This was expected, and improved statistics could be obtained by an averaging over different spatial locations in the sample, or by an averaging over different orientations of the sample relative to the scattering wave vectors. The latter approach was used to obtain the data shown as open circles, which are the result of our rotating the sample continuously while keeping the position of the scattering volume fixed. When fitted by a Fisher-Burford approximant,[12]

$$S(q) = \frac{S(q=0)}{[1+q^2\xi^2/(1+a)]^{1+a}},\tag{1}$$

these data yielded $a \approx 0.08$, corresponding to $S(q) \sim q^{-2.16}$ for $q\xi \gg 1$, which is close to the limiting slope (2.08 ± 0.05) previously observed[5] for clusters grown in dilute solution, under conditions of slow aggregation.

Figure 2 shows data obtained for gels of varying silica concentrations, together with the results of fitting the data by Eq. (1) (solid curves). Although there was a slight tendency for a to increase with increasing concentration, all of the data were consistent with $a = 0.08$, and this was imposed in obtaining the values of ξ, discussed below. It is interesting to note that for the gels, $S(q)$ tends to fall slightly at low q, which may indicate weak correlation between the gelling clusters. The results for ξ and a were not sensitive to this, however. It is also very noteworthy, as shown by the data for the lower concentrations, that $S(q)/c$ becomes concentration independent for $q \gg \xi^{-1}$. In fact the data show scaling behavior when plotted vs $q\xi$.

Figure 3 presents our results for ξ as a function of ϕ, the volume fraction of silica, which is related to c by $\phi^{-1} = \rho/c + 1 - \rho$, where $\rho = 2.51$ is the specific gravity of fused silica. The data for ξ were obtained as discussed above. The solid line is the best fit to the data for $\phi \le 10^{-2}$, where a limiting power law behavior appears to occur. The fit is given by

$$(\xi/b) = 0.22\phi^{-1.17 \pm 0.1},\tag{2}$$

where $b = 35$ Å is the radius of the individual colloidal particles. The fact that the data for ξ increasingly fall below this limiting form at higher concentration is consistent with the tendency for the fractal dimension d_f, obtained by fitting, to increase with silica concentration, but our data do not extend to sufficiently high q to deter-
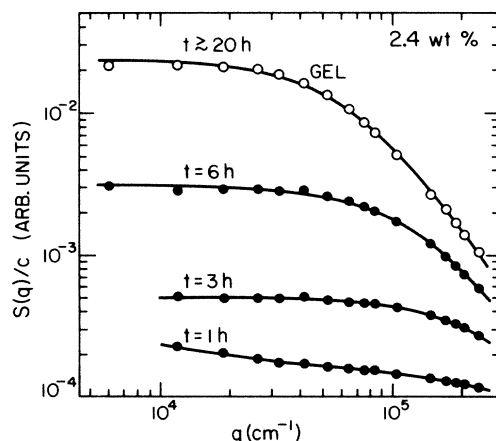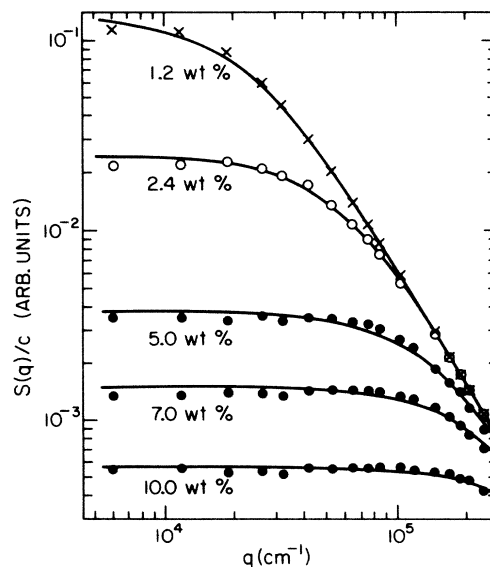

FIG. 1. The static structure factor divided by c vs the scattering wave vector for a solution of 70-Å-diam colloidal silica spheres (2.4 wt.% silica) in 0.45M NaCl at pH 7.0, at various times during the gelation process. Except for $t = 1$ h, the solid lines are fits by Eq. (1), as discussed in the text. The open circles correspond to data for the gel.

FIG. 2. The static structure factor divided by c vs the scattering wave vector q, for gels formed of 70-Å colloidal silica spheres in 0.45M NaCl at pH 7.0, for five different silica concentrations. The solid curves are fits, as discussed in the text. Note that $S(q)/c$ appears to become independent of c at high q.
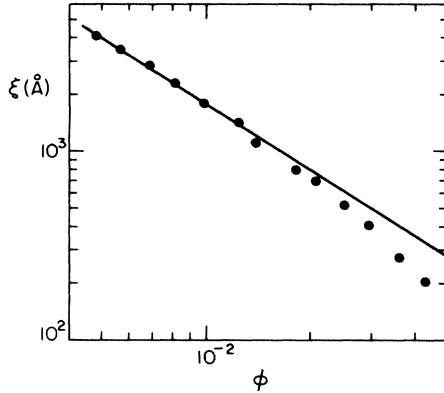
FIG. 3. The crossover length ξ as a function of silica volume fraction for gels formed of 70-Å silica spheres in 0.45M NaCl at pH 7.0. The solid line is a fit to the data for $\phi \leq 10^{-2}$, and corresponds to $\xi = 0.22 \, \phi^{-1.17 \pm 0.1}$.

mine d_f accurately for the higher concentrations.

Perhaps the simplest model one might construct for such colloidal gels would be that of a monodisperse collection of clusters, each of radius R, growing until their total volume V became equal to the container volume V_0. At this point gelation would occur, and ξ would equal R_0, the cluster radius at gelation. This model is consistent with our data for ξ, since it predicts $\xi \sim \phi^{-1/(3-d_f)}$, i.e., $\xi \sim \phi^{-1.19}$ for a fractal dimension $d_f = 2.16$. In this model $R = bs^{1/d_f}$, where b is a small characteristic length, e.g., the radius of the individual colloidal particles, and s is the number of particles per cluster. For a solution containing N_0 individual colloidal particles, $V = N_0 (4\pi b^3/3) s^{(3/d_f - 1)}$, and as s increases, a value s_0 will be reached for which $V = V_0$. At this point $R \equiv \xi = bs_0^{1/d_f} = b[V_0/(4\pi b^3/3)N_0]^{1/(3-d_f)}$, i.e.,

$$\xi/b = \phi^{-1/(3-d_f)}, \tag{3}$$

which is consistent with the data.

A similar, but possibly more realistic, model would relax the constraint of a monodisperse collection of clusters. On the basis of our limited knowledge concerning the actual cluster size distributions,[13,14] a power law distribution of the form

$$n(s) = A(\bar{s}) s^{-\tau} f(s/\bar{s}) \tag{4}$$

would appear to be the best choice. Here $n(s)$ is the number of clusters per unit volume, containing s colloidal particles, τ is an exponent, presumably dependent on aggregation conditions, and $f(s/\bar{s})$ is a large-s cutoff, such as $e^{-s/\bar{s}}$. The normalization $A(\bar{s})$ is necessary to conserve the total number of colloidal particles N_0. The total volume occupied by the clusters, again assumed to have radii $R(s) = bs^{1/d_f}$, is given by

$$V = \frac{4\pi}{3} b^3 A(\bar{s}) \sum_{s=1}^{\infty} s^{(3/d_f - \tau)} f(s/\bar{s}). \tag{5}$$

The measured length scale for the solution of growing clusters (assumed to be spatially uncorrelated) is given by

$$R_z^2(\bar{s}) = b^2 \sum_{s=1}^{\infty} s^{(2/d_f + 2 - \tau)} f(s/\bar{s}) / \sum_{s=1}^{\infty} s^{2-\tau} f(s/\bar{s}). \tag{6}$$

For an exponential cutoff the various sums can be approximated by incomplete gamma functions, enabling one to obtain analytic results.

For $\tau < 2$, the sums, including that expressing mass conservation, are dominated by the upper cutoff $\bar{s}$, and one obtains the same concentration dependence for ξ as found above for the monodisperse case. Since $\tau \simeq 1.5$ has been observed recently[13] for the slow aggregation of colloidal gold particles, it seems that polydispersity would not seriously affect the predicted concentration dependence of ξ.

In order to be consistent we examined the effect such a power-law distribution would have on the determination of d_f, assuming no spatial correlation between individual clusters. We consider a cluster of s particles to have a structure factor

$$S_s(q) = [1 + q^2 b^2 s^{2/d_f}]^{-d_f/2}, \tag{7}$$

since we are in a q range where the form factor of the individual colloidal particles is nearly unity. A collection of clusters yields an overall intensity

$$I(q) \propto \sum_{s=1}^{\infty} s^2 S_s(q) n(s). \tag{8}$$

We have approximated the sum in Eq. (8) by an integral and carried it out numerically for $\tau = 1.5$ and $d_f = 2.08$. When we fit the results for $I(q)$ using Eq. (1), over a range of q values comparable to that we employ experimentally, we find $d_f = 2.06$ ($16 \lesssim q\bar{R} \lesssim 524$), where $\bar{R} \equiv b\bar{s}^{1/d_f}$ is the radius of a cluster having the cutoff mass. Thus, even such power-law polydispersity should have little effect on our experimental determination of d_f. This finding appears to differ from that of Martin and Ackerson[15] who found $\mu = d_f(3 - \tau)$, where μ is the apparent fractal dimension which should be seen experimentally. Apparently, they only meant to consider the case $\tau > 2$, and their result does not hold[16] for $\tau < 2$. It is worth noting that the presence of small clusters can have the effect of reducing the slope with which $S(q)$ falls off at large q, but could never increase it, as a naive use of their result might suggest.

Although such models may be appealing in their simplicity, it is not necessary to make such specific assumptions in predicting the dependence of ξ on ϕ. If the gels have a unique fractal dimension for length scales below ξ, then the mass m_ξ of silica in a volume ξ^3 is proportional to ξ^{d_f}. The total number of such independent volumes in a system of volume V_0 is V_0/ξ^3, for a total silica mass $M \sim m_\xi V_0/\xi^3 \sim V_0 \xi^{d_f - 3}$. Thus $\phi \sim M/V_0 \sim \xi^{d_f - 3}$, as found for the simple models discussed above. Although

we cannot rule them out directly, we feel that they may be too naive because they do not recognize that in a concentrated colloidal solution undergoing aggregation in the reaction-limited regime small clusters would be very likely to be found in the void spaces of larger clusters, and this would result in "screening" of the fluctuations associated with the overall cluster size in dilute solution. In this case ξ, rather than reflecting cluster radius, would actually be a screening length, analogous to the correlation length in semidilute polymer solutions. Such an interpretation would be consistent with our data, and would raise the interesting question of the relationship, if any, between ξ and the distribution and sizes of void spaces in the gel.

[1]S. R. Forrest and T. A. Witten, Jr., J. Phys. A **12**, L109 (1979).

[2]T. A. Witten, Jr., and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).

[3]P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983).

[4]M. Kolb, R. Botet, and R. Jullien, Phys. Rev. Lett. **51**, 1123 (1983).

[5]D. W. Schaefer, J. E. Martin, P. Wiltzius, and D. S. Cannell, Phys. Rev. Lett. **52**, 2371 (1984).

[6]D. S. Cannell and C. Aubert, in *Proceedings of the NATO Advanced Study Institute on Growth and Form,* edited by H. E. Stanley and N. Ostrowsky (Martinus Nijhoff, Dordrecht, The Netherlands, 1986), p. 187.

[7]C. Aubert and D. S. Cannell, Phys. Rev. Lett. **56**, 738 (1986).

[8]D. A. Weitz and M. Olivera, Phys. Rev. Lett. **52**, 1433 (1984).

[9]D. A. Weitz, J. S. Huang, M. Y. Lin, and J. Sung, Phys. Rev. Lett. **54**, 1416 (1985).

[10]D. W. Schaefer and K. D. Keefer, Phys. Rev. Lett. **56**, 2199 (1986).

[11]H. R. Haller, C. Destor, and D. S. Cannell, Rev. Sci. Instrum. **54**, 973 (1983).

[12]M. E. Fisher and R. J. Burford, Phys. Rev. **156**, 583 (1967).

[13]D. A. Weitz, M. Y. Lin, J. S. Huang, T. A. Witten, S. K. Sinha, J. S. Gethner, and R. C. Ball, in *Scaling Phenomena in Disordered Systems,* edited by R. Pynn and A. Skjeltorp (Plenum, New York, 1985), p. 171.

[14]G. K. von Schulthess, G. B. Benedek, and R. W. DeBlois, Macromolecules **13**, 939 (1983), and **16**, 434 (1983).

[15]J. E. Martin and B. J. Ackerson, Phys. Rev. A **31**, 1180 (1985).

[16]J. E. Martin, private communication, and J. Appl. Crystallogr. **19**, 25 (1986).