Fractal Geometry of Colloidal Aggregates

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Measurement of the fractal dimension, D, of colloidal aggregates of small silica particles is reported. We observe power-law decay of the structure factor [$S(k) \sim k^{-D}$] by both light and x-ray scattering showing that the aggregates are fractal. D is found to be 2.12 ± 0.05, which is intermediate between recent numerical results for the kinetic models of diffusion-limited aggregation ($D = 2.5$) and cluster aggregation ($D = 1.75$), but is rather close to the value for lattice animals ($D = 2.0$), which are equilibrium structures.

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Understanding aggregation has been a primary goal in the field of colloidal physics for many years.[1] In addition to its importance in commercial processes, aggregation is a prototypical example of a complicated random process which may display such features as self-similarity, scaling, and universality.[2] These features have been revealed by computer simulations.[3-6] It has been shown recently, for example, that the two most popular models, diffusion-limited aggregation[3,4] (DLA) and cluster-cluster aggregation[5,6] (CA), produce ramified structures that are self-similar in that the two-point density-density correlation function $\rho_2(r)$ is of a power-law form,

$$\rho_2(r) \sim r^{-A}, \tag{1}$$

for values of r intermediate between the lattice constant or monomer size a and the cluster size R. Structures described by Eq. (1) are self-similar and are known as fractals; their essential geometric properties are independent of length scale. In d-dimensional space, they are characterized by a fractal or Hausdorff-Besicovitch dimension D related to A by $D = d - A$. An immediate consequence of Eq. (1) is that the radius of gyration of a cluster R_G is related to the number of particles it contains N_c by

$$N_c \sim R_G^D. \tag{2}$$

A uniform object has $D = d$, while more open structures in which the density decreases with distance from the center have $D < d$. Numerical simulations have shown D to be $\sim 5d/6$ for DLA in d dimensions for both lattice ($2 \leq d \leq 6$) and nonlattice ($d = 2, 3$) diffusion, independent of sticking coefficient s ($0.1 \leq s \leq 1$). Cluster aggregation in which many particles diffuse and stick together to form clusters which also diffuse and stick yields self-similar aggregates having $D = 1.45$ and 1.75 in two and three dimensions, respectively.

Several experimental studies of the fractal nature of aggregates have been reported[7-9] but all involved rather severe sample preparation like depositing the aggregates on substrates or resuspending possibly compressed powders in water. Here we report what we believe to be the first definitive *in situ* measurements made directly by scattering from suspensions of the growing aggregates. In scattering experiments which measure $S(k)$, the Fourier transform of $\rho_2(r)$, power-law correlation is revealed by an equivalent power-law decay in $S(k)$,

$$S(k) \sim k^{-D}, \tag{3}$$

over the range $R_G^{-1} \lesssim k \lesssim a^{-1}$. For the system of colloidal silica particles we studied $a \simeq 27$ Å and $R_G \lesssim 10^4$ Å, and we were able to observe clear power-law behavior over more than two decades in k using light and x-ray scattering. This shows very clearly that the aggregates are of a fractal nature, but we find $D = 2.12 \pm 0.05$ which does not agree with either DLA or CA.

The silica monomers used were Ludox particles (Ludox SM, du Pont) which are stable as monomers and small clusters in basic solutions but which aggregate when the pH is reduced to 5.5 while the salt concentration (NaCl) is increased to $\gtrsim 0.5$ M. This reduces the charge on the particles and decreases the Debye-Hückel screening length to the point where particles become likely to approach each other sufficiently closely as to allow van der Waals binding to occur. Under these conditions the clusters grow to "enormous" sizes ($\gtrsim 1$ μm) and even sediment under gravity eventually. Figure 1 shows an electron micrograph of such a cluster.

Two concentrations were studied with light

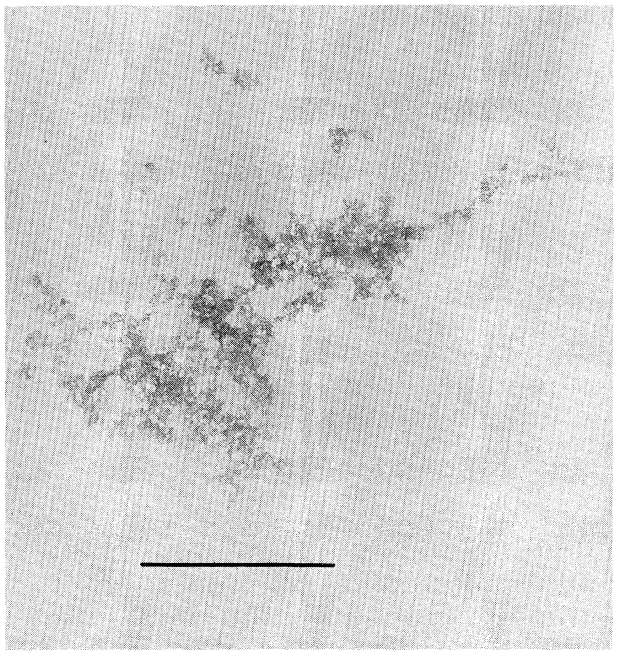

FIG. 1. Electron micrograph of a silica cluster. The bar is 5000 Å.

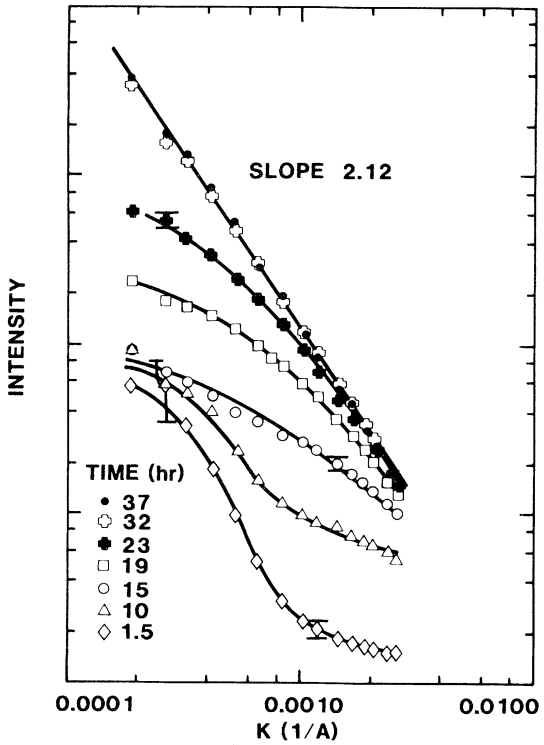

FIG. 2. Scattered light intensity profiles as aggregation proceeds.

scattering (0.1 wt.% at 1 M NaCl, 0.5 wt.% at 1 M NaCl) and one with x-ray scattering (1 wt.% at 0.5 M NaCl). Although aggregation rates were somewhat different, all three samples gave identical values of D. Using light-scattering instrumentation described previously,[10] we were able to measure $S(k)$ in the range $0.0002 \leq k \leq 0.002$ Å^{-1}, and hence, in addition to studying the power-law regime in $S(k)$, we could also determine the size of the clusters up to about 5000 Å. After about 25 h, the radius of gyration grew beyond this limit. This is reminiscent of the divergence observed with gelation, although the system was too dilute to actually gel.

Small angle x-ray scattering (SAXS) data were collected using a Kratky x-ray camera with a rotating-anode source (1.54 Å) and a linear, position-sensitive detector. The solvent background was subtracted, but no corrections were made for detector sensitivity or linearity. The Kratky system[11,12] is a line-source instrument, which means the data are "slit-smeared." Because of this slit smearing, the observed intensity $I_x(k)$ differs[13] from Eq. (3) by a factor of k:

$$I_x(k) \sim kS(k). \tag{4}$$

In order to measure D directly from $I_x(k)$, $k^{-1}I_x(k)$ is plotted. Equation (4) is not correct outside the power-law regime, but this problem is of no concern here.

Figure 2 shows the temporal development of the scattered light intensity $I(k)$. During the early stages of aggregation, the intensity showed a pronounced maximum at small angles. This was not observed in measurements on unaggregated Ludox, although SAXS measurements gave a radius of gyration of 55 Å prior to aggregation, indicating some clustering of the 27-Å feed stock. However, after aggregation for about an hour, a few large clusters were visible in the scattering volume when inspected in the forward direction through a telescope. These clusters, which form quite early in the aggregation process, are almost certainly responsible for the observed maximum and for the large error bars associated with the small-k data. The error bars decrease as aggregation proceeds, and the maximum at small angles grows two decades in intensity until 37 h after initiation $I(k)$ is power-law over the entire range of k. After ~ 40 h, Fig. 3 shows that $I(k)$ remains power-law but decreases in amplitude as very large aggregates sediment. Note that the slope is essentially unchanged as clusters grow and settle.

Power-law behavior for $I(k)$ is a signature of fractal structures. It is clear from Fig. 3 that these clusters are fractal over 5000 Å $> k^{-1} >$ 500 Å. In fact, if these are combined with x-ray results, as

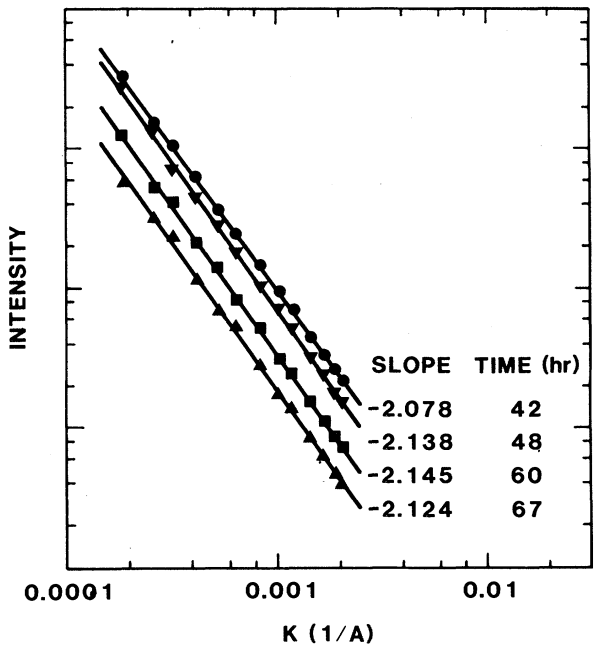

FIG. 3. Development of light scattering profiles with concurrent sedimentation and aggregation.

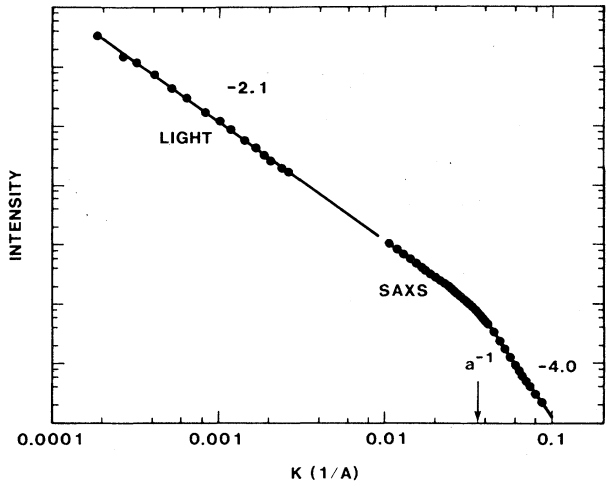

FIG. 4. Combined SAXS and light scattering results. Data are shifted vertically by an arbitrary factor to match smoothly.

shown in Fig. 4, it is clear that self-similarity extends over two decades in k. To our knowledge, this measurement represents the most definitive confirmation of fractal behavior in either simulated or laboratory clusters.

The fractal dimension was obtained from the slope of the curves in Figs. 2 and 3. Since the curves at the beginning of aggregation do not demonstrate power-law behavior, no exponents have been determined in this regime. As the clusters grow, however, the power-law domain invades the entire observable regime and the slope is then legitimately interpreted as the fractal dimension D. By averaging over ten measurements in this regime, we find $D = 2.12 \pm 0.05$.

At very large k, there is a distinct crossover to a second power-law regime with an exponent of -4 (see Fig. 4). This slope was originally calculated by Porod for two-phase systems with sharp boundaries.[12] The crossover occurs at a value of k^{-1} equal to the nominal radius of gyration, $a \simeq 27$ Å, of the colloidal feedstock as indicated in Fig. 4. The fact that fractal behavior is observed up to the crossover and the limiting slope of -4 indicate that the monomers remain intact in the aggregate and that the "width" of the arms of the cluster is just the diameter of the monomers.

The fact that scattering occurs from a broad distribution of particle sizes could possibly lead to artifacts in the determination of D from the slope of $I(k)$. At stages of the aggregation where a substantial amount of light is scattered by clusters with $R_G \lesssim k^{-1}$, Eq. (3) is not valid. However, as aggregation proceeds, more and more material from the low end of the particle size distribution is incorporated into the clusters and the largest grow to the point where they sediment. Since this occurs without change in D (see Fig. 3), we conclude that polydispersity has not affected our result for D.

The fractal dimension of 2.12 observed here is not consistent with either diffusion-limited aggregation (DLA)[3,4] for which $D = 2.5$ or cluster aggregation (CA)[5,6] for which $D = 1.75$. These two models depend on kinetic processes whereby the monomers and, in the case of CA, other clusters approach an existing seed by a random-walk trajectory. In these models, a fractal structure results because it is improbable for a random trajectory to penetrate the interior of an existing cluster. A process that has not, however, been included in the simulations is rearrangement with the clusters. This would lead to denser structures with a higher Hausdorff dimension. Hence the more realistic of the two models (CA), with the addition of rearrangment, could be consistent with our experimental results.

We note that the measured value of D is quite close to that of equilibrium structures called lattice animals[14] (LA) for which $D = 2$. Elsewhere[15] an equilibrium model is developed for cluster structure, analogous to Flory's calculation[16] for linear chains. It is suggested that cluster structure results from a balance of entropic effects, which favor a branched random-walk structure, and excluded-volume forces, which favor cluster expansion. This

model should apply when the repulsive part of the electrostatic potential between particles is strong enough to limit cluster-cluster contact and to guarantee the self-avoiding structure of the LA. In addition, the short-range attraction must be comparable to kT so equilibrium is realized. A range of structures from dense clumps to DLA/CA clusters is predicted for colloids depending on the balance of long-range repulsive forces and short-range attractive forces.[15]

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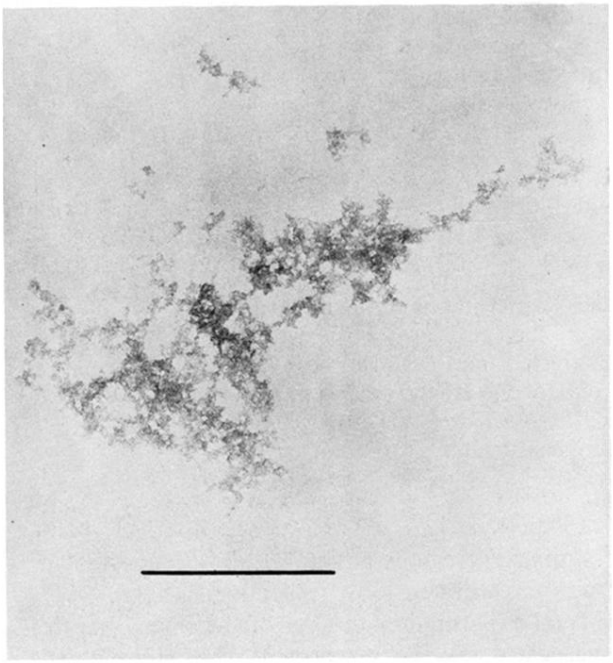

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