

Fractal Structures Formed by Kinetic Aggregation of Aqueous Gold Colloids

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We use transmission-electron micrographs to study the structure formed by the irreversible kinetic aggregation of uniformly sized aqueous gold colloids. The structures are highly ramified and exhibit a scale invariance that is well described as a fractal with a Hausdorff dimension of ~ 1.75 . This value is in excellent agreement with recent computer simulations of diffusion-limited aggregation when the clusters themselves are allowed to aggregate.

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The process of aggregation or flocculation of small particles to form larger clusters and the structures that result are important technologically and scientifically. The clusters formed by the aggregation of metal colloids, soot, or coagulated aerosols¹ are characterized by their tenuous, chainlike structure. Virtually all of our knowledge of the growth of these structures has come from computer simulations,²⁻⁵ which have suggested that the resultant structures exhibit scale invariance and can be well described as fractals.⁶ Thus, for example, the mass of the cluster is predicted to scale as L^D , where L is the size and D is the Hausdorff or fractal dimension and is typically less than the Euclidian dimension.

Two general classes of irreversible aggregation have emerged from the simulations. The first of these classes involves cluster formation by the accretion of single diffusing particles onto a seed aggregate.^{2,3} The diffusive nature of the particle motion appears to be essential,⁷ and the resultant structure has $D \sim 2.5$ in three dimensions. The second class involves cluster formation by the homogeneous aggregation of a collection of particles.^{4,5} In this case, most of the growth results from the aggregation of two clusters of comparable size rather than a small and a large cluster. In contrast to the first class, the nature of the transport does not seem to be important, and the resulting structure is characterized by a lower dimensionality, $D \sim 1.75$ in three dimensions.⁸

In contrast to the wealth of recent theoretical work, experimental studies that can test the validity and applicability of the modern theories have been rather sparse. In an early work, which stimulated much recent theoretical interest, Forrest and Witten⁹ analyzed electron micrographs of metallic smoke-particle aggregates formed in air and found what appeared to be long-range power-law correlations. In this paper, we study the irreversible, kinetic aggregation of a rather different system, highly uniform aqueous metal colloids. We charac-

terize the structure of the aggregates both by measuring the cluster-to-cluster variation in mass as their size increases, and by measuring the long-range density-density correlations within individual aggregates.¹⁰ We find that the resulting clusters are indeed scale invariant and are well described as fractals, with $D \sim 1.75$, in remarkable agreement with recent computer simulations.⁸ Since we are examining transmission electron-microscope (TEM) images, our analysis is performed for a two-dimensional projection of the clusters and makes use of the fact⁶ that the fractal dimension remains unchanged upon projection provided $D \leq 2$. Thus, while the results are unambiguous for the TEM images, the extension of our conclusions to the three-dimensional colloid clusters depends on the projection being close to geometric. However, we believe that the fractal nature of the clusters is established and that this work represents, to our knowledge, the first attempt to characterize the structure and growth mechanisms of colloidal aggregation using these quantitative techniques.

The gold particles are formed by the reduction of $\text{Na}(\text{AuCl}_4)$ by tri-sodium citrate,¹¹ and initially the sol consists of isolated, very uniformly sized, spherical particles ~ 14.5 nm in diameter, separated, on the average, by ~ 60 particle diameters. The surface-adsorbed citrate causes the gold particles to be highly charged, and the ionic strength of the solution creates a Debye-Hückel screening length of only a few atomic distances. The resulting repulsive double-layer interaction between the particles makes the sol very stable against aggregation. Aggregation is initiated by the addition of a small amount of pyridine to the solution.¹¹ The uncharged pyridine displaces the charged citrate on the surface, reducing the repulsion between colloidal particles, and allowing them to stick when they collide. Using surface-enhanced Raman scattering, we have shown that the pyridine displaces the citrate on the surface on a time scale of ≤ 1 min.¹³ By

contrast, the aggregation occurs on much longer time scales which can be controllably varied from ~ 30 min to several weeks.

We examine the structure of the clusters using a transmission electron microscope (TEM), and ensure that no additional aggregation occurs as the liquid is evaporated from the highly hydrophilic grid. However, while the aggregates are three-dimensional in solution, edge-on examination with the TEM shows that upon drying they collapse to form nearly flat, two-dimensional structures. By examining the full area of the TEM grid, clusters of widely varying sizes can be found and photographed, representing a snapshot in time of the aggregating colloid. A typical picture of a relatively large aggregate is shown in Fig. 1. It exhibits the tenuous, ramified appearance characteristically observed for colloidal aggregates.

To illustrate the scale-invariant nature of the aggregates as they grow, and to obtain an estimate of their Hausdorff dimension, we measure the number of particles in a cluster, N , as a function of the size L . Since there are relatively few overlapping particles, even in the largest cluster, N can be measured with high precision. As a measure of the size, we take the geometric mean of the longest linear dimension of the cluster and the length perpendicular to that axis. A logarithmic plot of N versus L is shown in Fig. 2 for nearly 100 different clusters on the grid. The data are very well described by a power-law behavior, as expected for a fractal.⁶ Similar results were obtained for pictures from other grids, and linear least-squares fits to the data sets

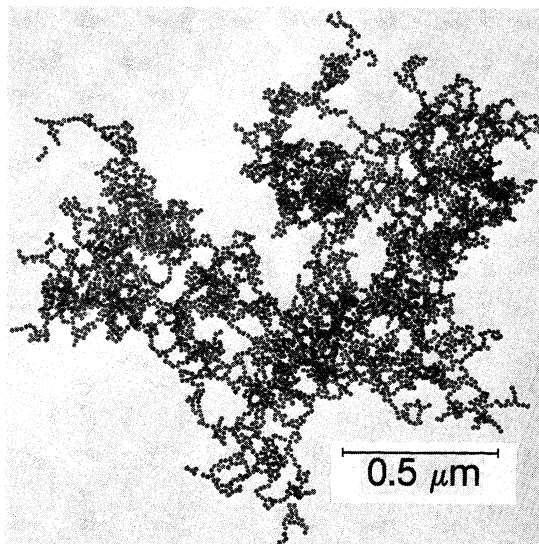


FIG. 1. TEM image of typical gold colloid aggregate. This cluster contains 4739 gold particles.

give an estimate of the Hausdorff dimension, $D = 1.7 \pm 0.1$.

The internal structure of each cluster also exhibits scale invariance. We show this by recording the center coordinates of each individual gold particle and calculating the point-to-point correlation functions of the images of the clusters, $c(r) \equiv \langle p(r)p(0) \rangle / \langle p(r) \rangle$. Here $p(r)$ is 1 at a particle center and 0 elsewhere, and the average is over position and orientation of the cluster. In our analysis, we account for the finite size of the clusters and correct for edge effects by finding the smallest circle that just encloses each cluster. Then, centered on each individual gold particle we find the largest circle which fits inside the outer circle, and include only other particles within the small circle in the calculation of $c(r)$. This ensures that for all directions there is an equal probability of finding a second particle a distance r from the first, but limits the maximum extent over which we can measure correlations to less than one quarter the cluster size.

For a two-dimensional projection of these fractals, we expect⁶ $c(r) \sim r^{-\alpha}$ for $r \ll L$, where $\alpha = 2 - D$. A representative series of correlation functions calculated for clusters of increasing size is shown by the solid lines in Fig. 3. For the very small clusters, the statistics are poor and the curves are noisy. However, once the number of particles in the cluster becomes greater than about 1000, the correlation functions exhibit an extended linear regime, with the slopes essentially independent of cluster size. The limiting slope, shown by the dashed line in Fig. 3, yields $\alpha = -0.23 \pm 0.1$, where the error reflects the cluster to cluster variation. The resulting Hausdorff dimension is $D = 1.77$

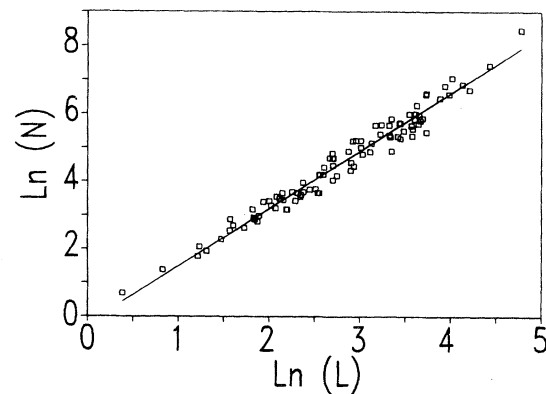


FIG. 2. N vs L , where the solid line is a least-squares fit to the data, with the slope giving $D \sim 1.75$. N can be converted to mass by multiplying by the mass of a single gold particle, $\sim 10^{-17}$ g, while L can be converted to nanometers by multiplying by 14.5.

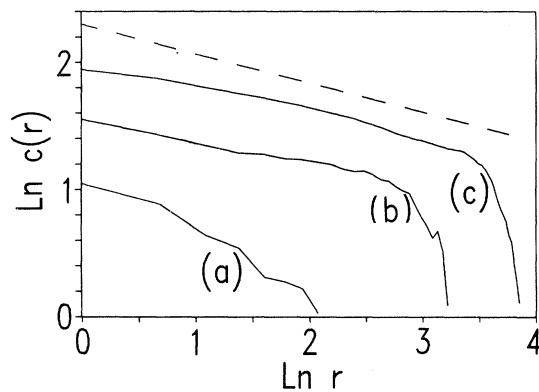


FIG. 3. Point-to-point correlation functions of TEM images of gold aggregates with (a) 125, (b) 1165, and (c) 4739 particles. The slope of the dashed line is -0.23 , and yields $D \sim 1.78$. r is scaled by the particle diameter, 14.5 nm.

± 0.1 , consistent with the value obtained from the number versus size behavior.

Several other consistency checks were performed on the data to confirm the value of D obtained. The digitized images were analyzed in a way that explicitly tests for their scale invariance.¹⁴ A grid was drawn over the data and a histogram was compiled of the number of squares in the grid containing n particles as a function of n . If the object were scale invariant, the second moment of the histogram would scale as $l^{2/D}$, where l is the grid square length. We indeed found power-law behavior and the value of D obtained was in excellent agreement with that obtained by the other techniques. We tested our analysis using a computer-generated fractal of the type Mandelbrot has called a curd.⁶ Using a curd generated in three dimensions, we measured the Hausdorff dimension of a projection using both our correlation function and our self-similarity analyses and established the validity and accuracy of our analysis techniques.

The value obtained for the Hausdorff dimension appears to be rather insensitive to the experimental conditions. To within experimental error, we obtained the same value for the structures produced when the rate of aggregation is varied over several orders of magnitude.¹⁵

Strictly speaking, our analysis is valid only for the two-dimensional images of the three-dimensional clusters that exist in solution. However, the most reasonable assumption to make about the collapse of the aggregates is that their structure is approximately projected geometrically from three to two dimensions, which would leave D unchanged. It is in fact difficult to conceive of any other form of

structural distortion occurring that would result in scale invariance with the same D for both the internal structure of the individual clusters as well as for the cluster-to-cluster variation of N versus L . Nevertheless, some distortion of the geometric projection, with an effect akin to "squeezing a horse,"¹⁶ may occur, particularly at short ranges, as a result of a slight attractive interaction between the gold particles and the grid surface. This would result in a slower decrease of the point-to-point correlation function at short ranges and might account for the flattening of $c(r)$ of the larger cluster observed in Fig. 3 at small r .

The relative offset in the magnitude of $c(r)$ for clusters of different sizes, shown in Fig. 3, also results from the projection of the aggregates. While the power-law behavior of $c(r)$ survives a projection if $D < 2$, if the fractal is of finite extent, there is a relative deficiency of projected points on the plane, resulting in a reduction in the magnitude of $c(r)$. For a cluster of size L , this reduction is independent of r and decreases in magnitude roughly as $L^{-\alpha}$. We observe a similar behavior for curds of different sizes, where we can calculate the asymptotic magnitude of $c(r)$ and find that the magnitude of the reduction does indeed scale as $L^{-\alpha}$.

We conclude that the three-dimensional structure of the aggregates is most likely also scale invariant, with a Hausdorff dimension of $D \sim 1.75$, and compare our results with computer simulations for three dimensions. Of the two general classes of computer simulation, the physics of the aggregation of the gold colloids is much better approximated by the model^{4,5} for homogeneous aggregation. In this case the main contribution to the growth process ultimately is the aggregation of clusters themselves. In three dimensions, the simulations predict⁸ $D \sim 1.75$, in remarkable agreement with the value obtained in these experiments.

These results offer an opportunity to compare the predictions of the recent computer simulations of irreversible, kinetic aggregation to real, physical systems. The agreement is certainly encouraging. This work also demonstrates the utility of using the scale-invariant description of the structure of colloidal aggregates and suggests that this may also lead to a better and more detailed characterization of the physical behavior of fractal objects such as the optical, transport, or diffusion properties. Furthermore, the structures formed by this aggregation process are likely rather insensitive to the details of the particle-particle interactions, and this type of analysis can be expected to apply equally well to many other aggregating systems.

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