Dynamics of Diffusion-Limited Kinetic Aggregation

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We study the dynamics of diffusion-limited cluster-cluster aggregation of aqueous colloids using quasielastic light scattering. Scaling behavior is found for the dependence of the mean cluster size on both time and initial concentration, and limits are placed on the scaling exponents of the cluster mass distribution. The fractal nature of the resultant clusters directly affects the exponents, illustrating the inherent relationship between the dynamic and static properties of kinetic aggregation processes.

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The process of kinetic growth of small particles to form larger clusters has attracted considerable attention recently,[1] aroused in part by the practical importance of such phenomena, and in part by our generally incomplete understanding of these nonequilibrium processes. Particular interest has been focused on the structures of these clusters when the growth is limited by diffusion.[2] A general feature of this type of aggregation appears to be the dilation symmetry exhibited by the resultant clusters, whether they are formed by accretion of single particles[2-4] or by cluster-cluster aggregation.[5-8] Most of the work to date has been concerned with the fractal structure of the resultant clusters. However, the growth process is inherently kinetic, and there have been several very recent theoretical treatments of the dynamics of cluster-cluster aggregation.[9-11] Scaling forms, reminiscent of those found in describing critical phenomena, are found for the cluster distributions and their time dependence. However, there is some disagreement about the extent to which a mean-field approach can successfully describe the results.

In this Letter, we present an experimental study of the dynamics of diffusion-limited kinetic aggregation of aqueous metal colloids, using quasielastic light scattering. Previous studies[7,12] with transmission electron microscopy (TEM) have shown that the structures of the clusters formed is self-similar, with a fractal dimension $d_f \sim 1.75$. Here we show that the mean cluster size also exhibits scaling in time as well as in initial colloid concentration. This is a direct consequence of the fractal nature of the structures formed, and when this is explicitly included in a mean-field cluster-cluster model, we can account for the measured aggregation dynamics quite well. The dynamic behavior provides an alternative experimental measure of the fractal dimension. Furthermore, we are able to set limits on the scaling exponents of the cluster mass distribution. These experiments probe the inherent link between the dynamics of the aggregation and the resultant structures, a determination of which is essential for a complete understanding of the underlying physics.

The gold colloids[13] consist initially of very uniformly sized spheres with a radius $R_0 \sim 7.5$ nm and a concentration of $\sim 10^{12}/\text{cm}^3$. The aggregation is initiated by adding an uncharged organic molecule (pyridine) which adsorbs to the surface of the colloidal particles, displacing the negatively charged ions which had stabilized the colloid. In these experiments, we ensure that the particles stick on virtually every collision by adding a saturating amount of the organic adsorbate. By carefully controlling the colloid preparation, we obtain highly reproducible results, allowing both time and angle dependences of the scattering to be measured. We use a He-Ne laser operating at 632.8 nm, and measure the autocorrelation function[14] of the scattered light with a digital correlator.

The measured autocorrelation functions are quite nonexponential, reflecting the distribution of cluster sizes. We analyze them by calculating the initial logarithmic derivative, or the first cumulant,[14] K_1, which, at any point in time in the aggregation process, is given by[15]

$$K_1(q) = [I(q,0)]^{-1} \int M^2 N(M) S_M(q) \times [Dq^2 + A]\, dM. \quad (1)$$

Here q is the scattering vector, D and A are respectively the translational and rotational diffusion constants of a cluster of mass M, and $I(q,0)$ is the time-averaged total scattered intensity. The distribution of clusters is represented by $N(M)$ and the scattering from each cluster has a structure factor given by[16] $S_M(q) \sim M^{-1} q^{-d_f}$, for $qR \gg 1$. The radius of gyration of the cluster, R, is assumed to be fairly well defined and is given by $M = M_0 R^{d_f}$. Except at the earliest times, all our measurements are performed in the regime where $qR \geq 1$. To determine the dominant mechanism causing the decay of the intensity autocorrelation function, we plot the first cumulant, measured at the same

elapsed time, as a function of q^2 in Fig. 1. The large error bars at the smallest angle reflect the possibility of additional scattered light reaching the detector, causing a heterodyne measurement. As shown in Fig. 1, the data are well described by a linear fit in q^2, with an intercept near the origin. Thus the decay is dominated by translational rather than rotational diffusion, or internal modes. With the assumption that $D \sim R^{-1}$, the scaling behavior of the first cumulant,

$$K_1 \sim \int M^{1-1/d_f} N(M)\, dM, \tag{2}$$

is a moment of the cluster mass distribution function. From this, we obtain the effective hydrodynamic radius, R_H, which is well represented[17] by R. The time dependence of R will match that of the moment of the distribution probed by K_1, allowing us to study the dynamics of the aggregation.

We measure R as a function of time and show the results in a logarithmic plot in Fig. 2. These data are obtained at a scattering angle of 120°, but similar results are obtained at other angles. As indicated by the data in Fig. 2, we find a scaling behavior of the mean cluster size in time. We can obtain a reasonable description of our observations by explicitly including the fractal structure of the clusters in a mean-field treatment of the dynamics. We calculate the growth rate for a mean cluster mass, dM/dt. On the assumption of cluster-cluster aggregation, the dominant growth occurs by aggregation of two clusters of roughly equal size, so that $dM \sim M$. The rate of aggregation is determined by the diffusion equation, from which we obtain $dt \sim 1/8\pi RCD$, where C is the particle concentration. Furthermore, $D = kT/6\pi\eta R$, where k, T, and η are Boltzmann's constant, the temperature, and the viscosity, respectively. The number of particles is conserved, and is determined by the initial concentration, $C = C_0/M$. Thus, both the R and M dependences are eliminated and $dM/dt =$ constant, independent of the fractal nature of the clusters. We note that a more rigorous treatment of this type of aggregation using the Smoluchowski equations[18] gives this same result. After integration, however, we explicitly use the fractal scaling of the mass with radius, and obtain

$$R \sim \left(\frac{4C_0kT}{3\eta M_0}\right)^{1/d_f} t^{1/d_f}, \quad R \gg R_0. \tag{3}$$

The scaling exponent, 0.56, obtained from a least-squares fit to the data in Fig. 2 is in excellent agreement with the predicted value of $1/d_f = 0.57$. We can also estimate the value of the proportionality constant, as C_0 is known from the preparation conditions and M_0 can be determined from the TEM study of these clusters.[7] We obtain a value of ~ 1.1 in units where the radius is measured in microns and time in hours. This is to be compared with the value of 0.60 obtained from the fit. Considering all the approximations made in this calculation, the agreement is quite good.

Further confirmation of the accuracy of this model can be obtained by measuring the dependence of the aggregation kinetics on the initial particle concentration, C_0. We obtain both the prefactor and the exponent from a linear least-squares fit. The exponent is found to be independent of C_0, while the variation of the prefactor is shown in a logarithmic plot in Fig. 3. A least-squares fit to the data yields a slope of 0.56, again in excellent agreement with the behavior predicted by Eq. (3). As is the case for the time dependence, the observed scaling exponents of R with C_0 are a direct consequence of the fractal nature of the clusters formed.

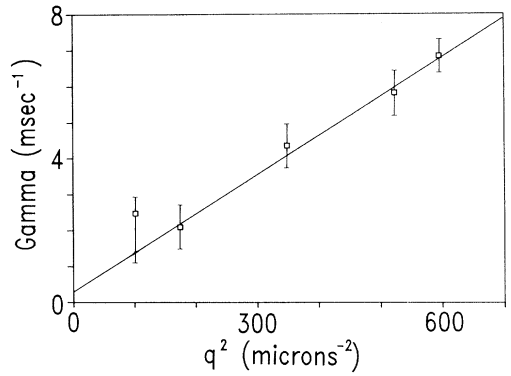

FIG. 1. The dependence of the first cumulant of the intensity autocorrelation function on q^2. The solid line is a least-squares fit to the data.

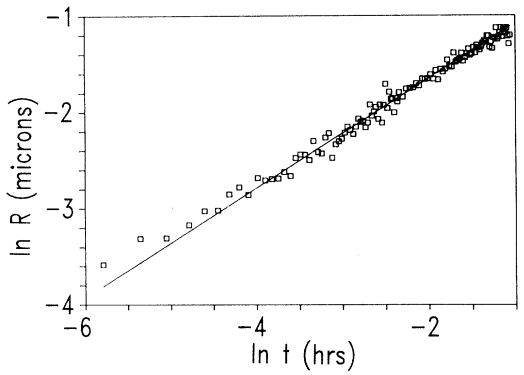

FIG. 2. Logarithmic plot showing the scaling of the mean cluster radius with time. The solid line is a least-squares fit to the data and corresponds to $R = 0.60t^{0.56}$.

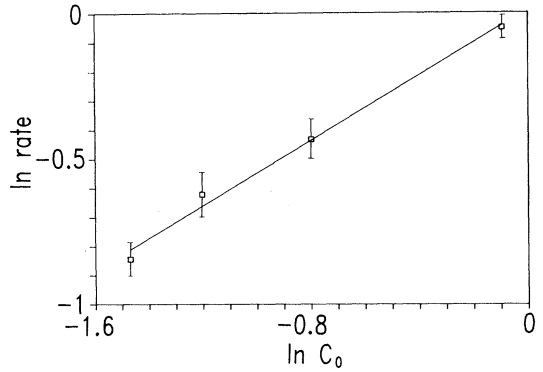

FIG. 3. Logarithmic plot showing the scaling of the aggregation rate with colloid concentration, normalized to the initial concentration of $1.7\times10^{12}/\text{cm}^3$. The straight line is a least-squares fit to the data and has a slope of 0.56.

We also monitor the average intensity of the scattered light, which rises very rapidly initially, but when R becomes comparable to q^{-1} (~ 50 nm), the intensity remains constant in time, despite the fact that the characteristic cluster size is growing. Since $d_f < 2$ and the total scattered light is a small fraction of the incident light, we assume $S_M(q) \sim M^{-1}$. Thus, when $qR > 1$, the total intensity scales as $I(q,0) \sim \int MN(M)\,dM$. This is simply the total mass in the system, which remains constant, independent of time. Physically, this behavior arises because of the ramified structure of the fractal clusters, which allows the total mass of the aggregate to contribute to the scattering. By contrast, a solid gold sphere with $qR > 1$ exhibits the traditional Mie scattering which has a very complicated behavior as the size increases, and the total scattering intensity would not remain constant.

The scaling behavior of the mean cluster radius with time offers an additional experimental method of measuring the fractal dimension. It is particularly noteworthy that this dynamic measurement yields important static structural information, and this emphasizes the kinetic nature of the aggregation process. However, these results are only valid for the case of diffusion-limited aggregation. When substantially smaller concentrations of organic adsorbates are added to the colloid, we find that the aggregation proceeds much more slowly and has an entirely different character.[12] Instead of scaling with time with an exponent less than 1, the behavior of the mean radius with time is better described by an exponent that is greater than 1, $R \sim R_0 t^{2.5}$. Furthermore, TEM studies suggest that the fractal dimension of the resultant clusters is somewhat larger than that measured for the rapid aggregation considered here. Under the conditions of slow aggregation, many collision attempts are required before the clusters stick, and the aggregation rate is no longer limited by diffusion. A more detailed description of this realm will be presented elsewhere.[19]

Although the autocorrelation functions are highly nonexponential, they retain an identical shape at all times when scaled with the delay time. This reflects the fact that each moment of the distribution function is growing at the same rate and is direct evidence that $N(M)$ exhibits a scaling behavior. In general, we expect[9,10] $N(M) \sim M^{-\tau}$, with a faster cutoff above some characteristic mass, M_c, whose value increases with time. The exponent, τ, is thought to depend on the scaling of D with M. If the scattering were dominated by a larger number of more weakly scattering small clusters, there would be no effective length scale in the distribution[15] and $K_1 \sim q^3$. Thus the observed q^2 dependence means that the effective length scale is set by M_c, and Eq. (2) requires $\tau < 2 - 1/d_f$ for the integral to depend on M_c. This sets an upper limit of ~ 1.4 on the value of τ, which is consistent with the value obtained by use of the Smoluchowski equations.[20]

The success of this simple model in accounting for our results suggests that a mean-field approach to the dynamics, as embodied by the Smoluchowski equations, is adequate. The essential addition that we make is the inclusion of the explicit dependence on the fractal structure of the resultant clusters. The Smoluchowski equations cannot account for the fractal structure of the aggregates, yet it plays a pivotal role in determining the dynamics of the aggregation. Two recent theoretical treatments attempt to account for the fractal structure in the aggregation process. Kolb *et al.*[10,11] use a mean-field approach and their results reduce to ours if diffusive motion of the clusters, with $D \sim R^{-1}$, is assumed. In contrast, Viscek and Family[9] use numerical simulations in 2 dimensions to find a scaling behavior that is quite different from the mean-field prediction. However, they start with considerably larger initial concentrations than we use in our experiments and use a different scaling of D, which may account for this discrepancy. The experimental results reported here can now serve as a physical test of the validity of any theoretical treatment.

The results reported in this Letter illustrate the crucial relationship between the dynamics and the static structure that is inherent in kinetic growth processes. The fractal nature of the clusters directly affects the scaling of their size with both time

and concentration, providing another experimental measure of d_f. Finally, our results suggest that changes in the short-range interactions between the particles, which can drastically alter the dynamics of the aggregation, may also cause changes in the long-range fractal structures that result. These important effects have yet to be fully investigated.

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