Evolution of the Cluster Size Distribution during Slow Colloid Aggregation

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We have made *in situ* dynamic light-scattering measurements to observe the real-time evolution to scaling of the light-scattering moments of a gold colloid cluster size distribution during aggregation in a slow aggregation regime. Quasi-monodisperse sols with significantly different aggregation rates evolved quickly to the same polydispersity in approximately equivalent reduced time units. This behavior and the experimental values of the asymptotic polydispersity agreed with numerical solutions to the coagulation equation and theoretical forms for the large-size part of the distribution. Numerical solutions showed, however, that the small-size part of the distribution does not reach its asymptotic scaling form in the time scales of our experiments.

INTRODUCTION

Considerable interest has been directed toward understanding the kinetics of aggregation in the recent past (1, 2). This has been incited by the discoveries that aggregates display a scale invariant symmetry and hence are described by fractals (3, 4), and that the cluster size distributions scale with time (5, 6). Furthermore, the kinetics of aggregation are relevant to a wide variety of natural phenomena. The Smoluchowski equation is the basic equation of aggregation and is given by (7, 8)

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} K(i,j)n_i n_j - n_k \sum_{j=1}^{\infty} K(k,j)n_j, \quad [1]$$

where $n_k(t)$ is the cluster size distribution describing the concentration of clusters with k monomers per cluster, and $K(i, j)$ is the aggregation kernel. For long aggregation times and for homogeneous kernels where

$$K(ai, aj) = a^{\lambda}K(i,j) \quad [2]$$

the Smoluchowski equation supports the fundamentally important result that the size distribution exhibits scaling (5, 9). That is,

$$n_k(t) \sim s^{-2}\phi(k/s), \quad [3]$$

where the time dependence is found solely in the mean size $s(t)$. This scaling implies that the relative shape of the distribution is constant and hence a universal function of the variable $x = k/s$, independent of the initial distribution.

Evidence for scaling exists in many forms. Friedlander's pioneering work showed the existence of self-preserving distributions in hydrosols and atmospheric aerosols undergoing Brownian coagulation (5, 10). These distributions were confirmed numerically by Hidy (11). The more recent simulations by Viscek *et al.* (6) have demonstrated scaling parameterized by exponents describing the power-law dependencies of $n_k(t)$ on k and t.

Recent experimental work includes that of von Schulthess *et al.* (12), who measured the cluster distribution for slowly aggregated latex spheres. In this slow, reaction-limited regime they found that the mean size increased exponentially with time and the size distribution was represented by a power-law $n_k \sim k^{-\tau}$ with $\tau = 1.4 \pm 0.15$. Weitz and Lin (13) coagulated gold hydrosols, collected the aggregates, and

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determined the size distribution with transmission electron microscopy. They found evidence for dynamic scaling and size distribution shape dependence upon the rate of aggregation. In the slow, reaction-limited aggregation regime, which was again characterized by an exponential growth, the size distribution followed a power-law $n_k \sim k^{-\tau}$ with $\tau \simeq 1.5$ for small $x = k/s$. Subsequently, Ball *et al.* (14) developed a reaction-limited aggregation kernel which successfully predicted this behavior. In another study Martin (15) used dynamic light scattering to study scaling in the slow aggregation regime in silica sols. He showed that the inverse relaxation time of the light-scattered correlation function and the Rayleigh linewidth scaled with different powers of the momentum transfer q when $qR \gg 1$, where R is the mean aggregate radius. Since the power by which these characteristic times scale is related to the size distribution through the exponent τ, he was able to find $\tau \simeq 1.85$ in the small-x regime. He also used the shape of the correlation function to infer $\tau \simeq 1.9$, a similar value. Finally, by fitting the long time tail of his scattered light autocorrelation function to a stretched exponential, he concluded that an exponential cutoff at large x was feasible.

One many conclude from these studies that in the reaction-limited regime exponential growth is seen and the small-x part of the distribution is power law. Some variation in the exponent τ currently exists. All these studies are concerned with the small-x part of the distribution: von Schulthess *et al.* (12) and Weitz and Lin (13) by direct observation, and Martin (15) by the fact that in the $qR \gg 1$ regime the scattered intensity per cluster varies as $I(k) \sim k$, hence the intensity weighted distribution is $n_k I(k) \sim k^{-0.85}$, which is dominated by small k. As mentioned above, Martin concludes that an exponential, large-x cutoff is consistent with his data, but this must be viewed with caution given this intensity weighting of the small-x part of the distribution.

In this paper we report real-time, *in situ* light-scattering measurements for an aggregating colloidal gold cluster distribution and verify the distribution's approach to a scaling form. Our light-scattering measurements were confined to the $qR < 1$ regime where the scattered intensity is proportional to the square of the cluster mass, i.e., $I(k) \sim k^2$. Hence for $\tau < 2$, the intensity-weighted distribution increases with k. This means that our results are sensitive to the large-x part of the size distribution. Thus, in contrast to the work above our measurements are real-time and large-x sensitive. We used dynamic light scattering and measured the time-dependent intensity-weighted moments of the aggregating distribution. These weighted moments are the first and second cumulants of the scattered-light intensity autocorrelation function (16, 17). They contain information regarding the mean cluster size and *relative shape* of the cluster distribution. From these, we were able to watch the relative shape of our cluster distribution evolve and then *stop* changing with time, indicating the distribution had scaled. It is important to realize that scaling can be observed without the absolute determination of the cluster distribution, $n_k(t)$. Moments can be used to classify a distribution uniquely. Here, we use intensity-weighted moments to classify the scaling behavior of our distribution.

Our experimental results demonstrate: (i) The evolution to and the maintenance of dynamic scaling from arbitrary initial distributions during aggregation. (ii) The quickness of the approach to scaling, within one to two characteristic aggregation times (defined below). (iii) The large $x = k/s$ limiting form, $\phi(x) = x^{-\lambda}e^{-ax}$, where λ is the kernel homogeneity (9), describes our data accurately. (iv) Comparison of our experimental results to numerical solution of Eq. [1] indicates that while the large-x part of the distribution establishes its asymptotic limiting form quickly, the small-x part of the distribution does not.

EXPERIMENTAL

Gold colloids were prepared by sodium citrate reduction of chloroauric acid as described

by Enustun and Turkevich (18). These sols were then carefully filtered through 0.2-μm filters to remove dust particles which could seriously interfere with our desire to measure the light-scattered second cumulant. Aggregation was initiated by addition of pyridine to $\sim 10^{-5}$ M. This caused a slow aggregation which leads to clusters with a fractal dimension of $D \simeq 2.05$, as described by Weitz *et al.* (19) in gold colloids and Schaefer *et al.* (20) in silica colloids. The faster diffusion-limited regime was not studied because light-scattering spectra with enough accuracy for determination of the second cumulant could not be obtained in a short time scale.

The dynamic light scattering or photon correlation spectroscopy (PCS) experiment was fairly standard (17), involving an argon ion laser operating at $\lambda = 488$ nm and a scattering angle of 90°. Spectra run times were 3 to 5 min in duration, which were short compared to the overall reaction rate, in order to avoid artificial broadening of the size distribution.

Some discussion has appeared in the literature regarding the optical properties of gold colloids (21, 22). Central to this contention is the question whether depolarized light scattering affects light-scattering results. For our colloids we found the depolarization ratio to be less than 1% and this small amount had no measurable effect on our PCS results.

Data analysis involved fitting the experimental correlation functions to

$$C(t) = B + A \exp(-\mu_1 t + \tfrac{1}{2}\mu_2 t^2), \quad [4]$$

where μ_1 and μ_2 are the first two cumulants. The ratio $Q = \mu_2/\mu_1^2$ is called the polydispersity index and is a measure of the relative width of the intensity-weighted size distribution. It has been extremely useful in the past for measurement of size distributions in particulate systems (23) and characterization of nonexponentiality in careful light-scattering measurements in critical fluids (24). Experimental determination of Q can be difficult due, in large part, to uncertainty in B. To measure B accurately we looked at $C(t)$ at large t where $C(t) \to B$ and calculated B from the photocount statistics. We were able to obtain reliable agreement between these two values. Other effects such as photomultiplier afterpulsing and heterodyning with stray light were checked and determined to be small. With careful experimental technique we were able to limit our experimental uncertainty in Q to ± 0.02.

Five different samples were studied. Initial radii and polydispersity indices ranged from 9.5 to 15 nm and 0.04 to 0.10, respectively. To make interpretation of our data straightforward and to weight the large-size part of the distribution, we constrained our data to the $qR < 1$ regime.

Time Evolution of Scaled Moments

As we stated previously, the light-scattering cumulants are moments of the cluster size distribution $n_k(t)$. The time evolution of the Nth moment, M_N, can be found by multiplying Eq. [1] by k^N, then summing over k to yield

$$\dot{M}_N = \tfrac{1}{2} \sum_{i,j} [(i+j)^N - j^N - i^N] \times K(i,j) n_i n_j. \quad [5]$$

Following Taylor and Sorensen (25), we now assume that the cluster size distribution has scaled, hence is represented by Eq. [3], and that the aggregation kernel is homogeneous with degree λ. Then,

$$\dot{M}_N = s(t)^{N+\lambda-2} M_1^2 I_N(K), \quad [6]$$

where $s(t)$ is the mass-weighted mean cluster size and $I_N(K)$ a constant dependent on $K(i, j)$. Equation [6] describes the time evolution of scaled moments according to Smoluchowski's equation. By setting $s = M_2/M_1$ in Eq. [6], an expression for s can be found (9) which upon substitution into Eq. [6] yields

$$M_N = M_N(0)(1 + t/t_c)^\beta. \quad [7]$$

Here, $\beta = (N-1)z$, where z has the well-known value (9) $1/(1-\lambda)$ and t_c is a characteristic aggregation time related to the initial size and kernel homogeneity.

We can now consider the time evolution of

the moments that describe the experimental light-scattering parameters. The first cumulant in the Rayleigh regime where $I \sim k^2$ is given by

$$\mu_1 = \sum_k D_k k^2 n_k / \sum_k k^2 n_k, \qquad [8]$$

where D_k is the hydrodynamic diffusion coefficient for a cluster of size k. Since D_k is inversely proportional to the cluster radius, we will assume $D_k \propto k^{-1/D}$, where D is the aggregate fractal dimension. Thus,

$$\mu_1 \sim \frac{M_{2-1/D}}{M_2} \qquad [9]$$

and from Eq. [7] we obtain

$$\mu_1(t) = \mu_1(0)(1 + t/t_c)^{-z/D}. \qquad [10]$$

In obtaining Eq. [10] we have assumed that the hydrodynamic diffusion coefficient varies as $D_k \sim k^{-1/D}$. This assumption may not be exact for very small k; the question is, How good is this assumption? Chen, Deutch, and Meakin (26), and Meakin, Lin, and Deutch (27) have studied the diffusion coefficient of fractal aggregates by computing the Kirkwood–Riseman drag. In their first study (26) they found for clusters with a fractal dimension of 2.5 an effective fractal dimension of 2.12 for drag on clusters as small as 10 particles. In their second work (27) clusters with a fractal dimension of 1.81 had an effective dimension of 1.84 for the diffusion coefficient for clusters larger than 50 particles. Neither study showed any systematic departure from the power-law dependence of the effective hydrodynamic radius with k even at small k. Furthermore, both results can be accurately extrapolated to the correct monomer ($k = 1$) value. These facts imply that use of $D_k \sim k^{-1/D}$ for small k might not be unreasonable. Our experiments began with monomeric spherical gold particles and were allowed to evolve until the radii were between 2.6 and 7.3 times the initial values. This implies that our final cluster sizes were between 7 and 53 particles per cluster for the five different sols. This is the range studied by Chen *et al.* and suggests that our approximation is good near the end of our runs. Near the beginning of our runs our assumption is unsubstantiated but certainly plausible.

RESULTS AND DISCUSSION

The first cumulant data were fit to Eq. [10] with $D = 2.05$, one example of which is shown in Fig. 1. Due to the limited time scales (to keep $qR < 1$) the fits were limited in the accuracy of t_c and z but had sufficient accuracy for our purpose, discussed below. The value of z led to values for the kernel homogeneity, for all sols, in the range $\lambda = 0.5 \pm 0.1$ for $D = 2.05$. The data could not be fit to an exponential dependence. This is surprising since earlier work on gold colloid aggregation using similar pyridine concentrations as a coagulant showed exponential growth (19). We cannot at this time offer an explanation for this difference. However, we point out that our homogeneities support the recent computer work of Meakin and Family (28, 29), who found kernel homogeneities of $\lambda = 0.5$–0.6 for slow cluster–cluster aggregation models. It is interesting to note that Eq. [9] approaches an exponential as $z \to \infty$, i.e., $\lambda \to 1$. Thus, Eq. [9] and an exponential are similar for large z. Our value for λ is corroborated by the Q measurements described below.

At this time we give a brief speculative argument on the origin of $\lambda \simeq 0.5$ in our aggre-

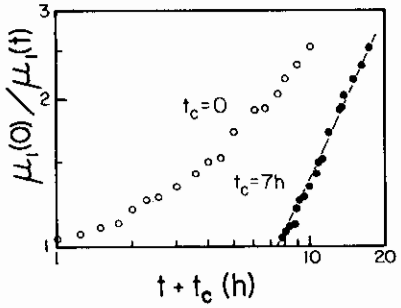

FIG. 1. Time evolution of the first cumulant for sol 3. The relative first cumulant, $\mu_1(0)/\mu_1(t)$, is plotted versus time t plus an adjustable parameter t_c. Unadulterated data are with $t_c = 0$. To fit to Eq. (10) a value of $t_c = 7$ h is required. This fit yields a straight line with slope equal to z/D on this graph.

gating colloid. The Brownian coagulation kernel has the functional dependence

$$K(i,j) \sim (i^{1/D} + j^{1/D}) \times (i^{-1/D} + j^{-1/D}). \quad [11]$$

For a slow aggregation processes, cluster diffusion is no longer the rate-determining step, hence the second term in Eq. [11] is ineffective since it is the diffusional term. Therefore, one can conjecture

$$K(i,j) \sim (i^{1/D} + j^{1/D}), \quad [12]$$

implying $\lambda = 1/D$. For $D = 2.05$, $\lambda \simeq 0.5$, consistent with our experimental value.

Q, the key parameter in this report, is a measure of the distribution's polydispersity (16, 23). For the scattering intensity proportional to the square of the cluster mass, $I \sim k^2$ ($qR < 1$ guarantees this), Sorensen and Taylor (30) derived the expression

$$Q_\infty = \frac{M_{2-2/D} M_2}{M_{2-1/D}^2} - 1, \quad [13]$$

which we refer to as the asymptotic polydispersity index. One recognizes the importance of this result by using the scaling distribution, Eq. [3], to calculate the moments in Eq. [13] and hence Q_∞. One finds that Q_∞ is not a function of time and therefore, if a distribution has scaled, the polydispersity index must be constant.

The experimental polydispersity index Q as a function of reduced time t/t_c for all five sols is displayed in Fig. 2. The characteristic time t_c was that obtained for each run from the first cumulant fit to Eq. [10]. A universal curve is seen despite the fact that t_c in the different sols ranged from 0.9 to 7 h. Note that in every case the Q value evolves to the same asymptotic value of $Q_\infty = 0.19 \pm 0.02$. This is a graphic demonstration of the evolution to and then the maintenance of dynamic scaling for the large-size part of the distribution. Furthermore, observe that the time scale to achieve this dynamic scaling is fairly quick, roughly 1.5 reduced-time units in all sols.

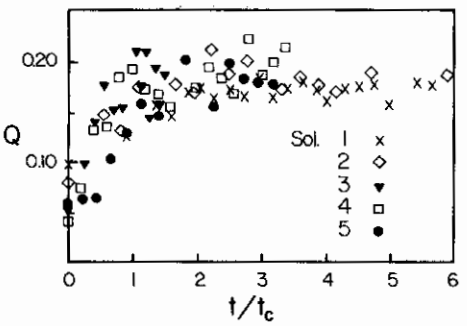

FIG. 2. Polydispersity index, Q, versus reduced time, t/t_c, for the five sols. Characteristic coagulation times are t_c = 1.1, 0.9, 7, 2.5, and 1.1 h for sols 1–5, respectively.

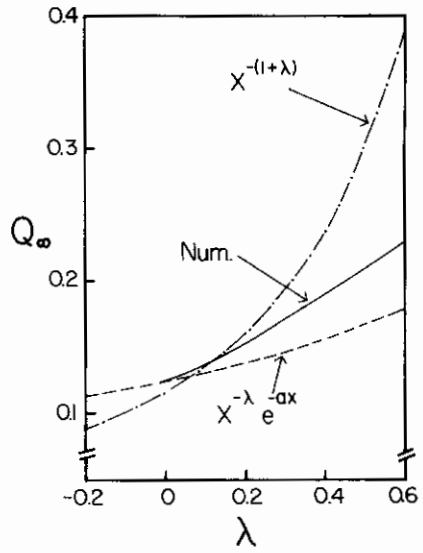

FIG. 3. Values of the asymptotic polydispersity ratio, Q_∞, versus kernel homogeneity for $D = 2.05$ for three different forms for the scaling distribution. "Num." is the numerical solution to the Smoluchowski equation.

The numerical value of Q_∞ can be calculated if a form for the scaling distribution is assumed. Due to the k^2 scattering dependence in the $qR < 1$ regime, we assume that only the large-x tail of the distribution affects Q_∞. With this assumption we choose the cutoff function valid for large x given by others (5, 9, 31, 32),

$$\phi(x) \sim x^{-\lambda} e^{-ax}, \quad [14]$$

where Botet and Jullien (31) give $a = 1 - \lambda$, but its exact value does not affect our results below.

Using Eqs. [13] and [14] we calculate Q_∞ as shown in Fig. 3 as a function of λ for $D = 2.05$. From the μ_1 time dependence above, we found $\lambda = 0.5 \pm 0.1$; hence from Fig. 3, we predict $Q_\infty = 0.17 \pm 0.01$. This is in good agreement with our experimental determination of $Q_\infty = 0.19 \pm 0.02$ and suggests the general validity of the large-x form in Eq. [14] and our analysis.

Proper calculation of Q_∞ would require an exact knowledge of the distribution at all x, not just the large-x tail, which is unavailable. Thus, to achieve a more detailed evaluation of Q_∞, we have numerically solved the Smoluchowski equation [1] with an initially monodisperse distribution for both sum, $K(i, j) = i^\lambda + j^\lambda$, and product, $K(i, j) = (ij)^{\lambda/2}$, kernels for a variety of λ's and have numerically determined both the size distribution and $Q(t)$. Sufficient accuracy was obtained using a numerical finite-difference technique where volume conservation was enforced.

We found that Q evolved to the same asymptotic Q_∞ at the same rate in reduced time units for kernels of the same homogeneity. That is, the evolution of $Q(t)$ was independent of the kernel type. The reduced time required to reach $0.9Q_\infty$ from a monodisperse distribution was a slightly increasing function of λ and, as shown in Fig. 4, was ~ 3 for $\lambda = 0.5$ for either kernel. This reduced time

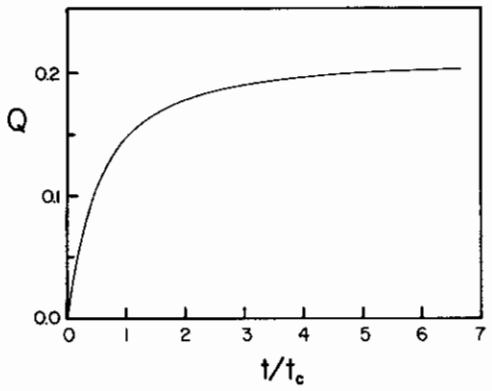

FIG. 4. Q calculated from the numerical solution to the Smoluchowski equation and Eq. (13) for $\lambda = 0.5$ and $D = 2.05$.

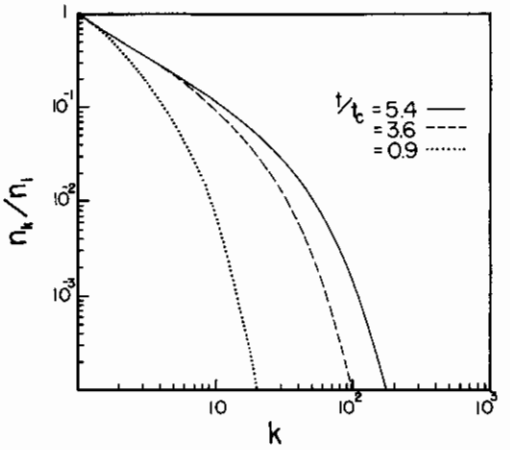

FIG. 5. Size distribution n_k versus k for three reduced time, t/t_c, obtained from numerical solutions to the Smoluchowski equation. Identical results were obtained for both sum and product kernels. The kernel homogeneity is 0.5.

of 3 is somewhat longer than our experimental runs which, however, started polydisperse. Given our experimental error, there is considerable similarity between Figs. 3 and 4. Thus our data substantiate the evolution of the size distribution as described by the Smoluchowski equation. The numerical Q_∞ values as a function of λ are also given in Fig. 3 and we consider these more realistic than those obtained from Eq. [14]. For $\lambda = 0.5 \pm 0.1$, $Q_\infty = 0.21 \pm 0.03$, again in good agreement with the experimental $Q_\infty = 0.19 \pm 0.02$.

We interpret the results above to indicate that the large-x tail of the distribution quickly establishes the form given in Eq. [14]. The small descrepancy between numerical results and those obtained from Eq. [14] does not indicate a problem in Eq. [14], but rather its improper use at small x. The exponential cutoff is consistent with the conclusion of Martin.

Further examination of our numerical results has shown that while the large-x tail quickly establishes its scaling form in Eq. [14], the small-x part of the distribution does not achieve its asymptotic scaling exponent over our experimental time scales. To demonstrate this we show in Fig. 5 the actual size distribution, n_k, as a function of k determined from

our numerical solutions of the Smoluchowski equation. Identical results were obtained for both sum and product kernels with $\lambda = 0.5$. As the reduced time increases, the small-x part of the graph becomes linear on the double logarithmic plot indicating the expected power-law, $n_k \propto k^{-\tau}$. The value for the exponent is found to be $\tau \simeq 1.0$. This compares poorly to the predicted asymptotic scaling value of $\tau = 1 + \lambda = 1.5$ for Class I kernels (9). Kang *et al.* (33) have also concluded that the scaling exponents do not obtain their asymptotic values very quickly after initiation of aggregation. They concluded that intermediate scaling regimes develop at short times in which scaling exponent relations hold, but the exponents themselves have not reached their asymptotic values.

As we have stressed, in the $qR < 1$ regime where we confined our experiments light scattering weights the large-x part of the size distribution. Thus the numerical result for Q in Fig. 4 indicates that the large-x part of the distribution evolves quickly to a near-constant value which indicates scaling for this part. The experimental value of Q_∞ is consistent with both the numerical solution in Fig. 4 and that calculated from Eq. [14] to indicate that asymptotic scaling as given by Eq. [14] has been achieved. On the other hand, analysis of Fig. 5 indicated that the small-x part of the distribution had a nonasymptotic value for the exponent τ, which implies that asymptotic scaling has not been achieved for small x. We conclude that the large-x and small-x parts of the distribution achieve their asymptotic forms at considerably different time scales during the aggregation process.

To stress the importance of the large-x cutoff in our results and the insensitivity of our results to the small-x form of the distribution, we have used Eq. [13] for the power-law $x^{-\tau}$ with $\tau = 1 + \lambda$ and a sharp cutoff. The results are also given in Fig. 3. For $\lambda = 0.5 \pm 0.1$, the theoretically predicted asymptotic value $Q_\infty = 0.31 \pm 0.07$ is in poor agreement with the data. If on the other hand we use $\tau = 1.0$ as found in our numerical solution, this corresponds to $\lambda = 0$, which yields $Q_\infty = 0.11$, again in poor agreement. Thus a power-law plus sharp cutoff description of the size distribution to determine Q_∞ does not appear to be satisfactory and we cannot make a comparison between our work and earlier experimental work (12, 13, 15) concerned with the small-x part of the distribution.

CONCLUSION

In conclusion, we have demonstrated the quick approach to scaling of the large-size tail of the distribution of a slowly aggregating colloid. Experimental values of the asymptotic polydispersity index agree with those calculated from Eq. [14] and numerical solutions to the Smoluchowski equation. These numerical solutions also indicate that the small-size regime does not establish its scaling form nearly as fast.

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