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# Universality laws in coagulation

D.A. Weitz \*

*Exxon Research and Engineering Co., Rt. 22E, Annandale, NJ 08801 (U.S.A.)*

M.Y. Lin \*

*Department of Physics, Princeton University, Princeton, NJ 08544 (U.S.A.)*

H.M. Lindsay

*Department of Physics, Emory University, Atlanta, GA 30322 (U.S.A.)*

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## Abstract

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We show that the process of irreversible, kinetic colloid aggregation exhibits universal behavior, independent of the detailed chemical nature of the colloidal particles. Modern methods of statistical physics, applied to a kinetic growth process, provide a good basis to model the observed behavior. Two limiting regimes of colloid aggregation are identified: rapid aggregation, limited solely by the diffusion of the growing clusters; and slow aggregation, limited by the reaction rate that leads to the formation of bonds between the clusters. In each regime the cluster structure is fractal, with fractal dimension  $d_f \sim 1.8$  for diffusion-limited clusters and  $d_f \sim 2.1$  for reaction-limited clusters. A scaling method is used to compare dynamic light scattering data obtained from completely different colloids aggregated under the two limiting conditions. These data provide a critical comparison of the behavior of the different colloids, and confirm the universality of each limiting regime of colloid aggregation.

## INTRODUCTION

The aggregation of colloidal particles to form larger clusters is a process of wide technological importance and of great scientific interest. It has been the subject of serious scientific study for well over one hundred years. However, until recently

the great complexity of the problem has limited the extent of our understanding of the process. The structure of the clusters is highly random and disordered, making a quantitative analysis of their shape quite difficult. Furthermore, a wide variety of different types of behavior can be seen for even a single colloid. This has precluded the development of a simple theoretical understanding of this complex, yet important process.

More recently, however, significant progress has been achieved in our understanding of irreversible

\* Present address: National Institute of Standards and Technology, React A106, Gaithersburg, MD 20899, U.S.A.

colloid aggregation [1–3]. The impetus for much of this progress has been the recent developments in statistical physics. Scaling concepts, which have found so much success in describing such reversible processes as phase transitions, have now also been applied with similar success to irreversible kinetic growth processes, such as colloid aggregation. Indeed, recent work has shown that irreversible colloid aggregation exhibits universal behavior, which transcends the chemical details of the particular colloid system, and which provides a unified, and relatively simple, description of this complex process [4,5]. In this paper, we present a brief review of the recent applications of these concepts of modern statistical physics to colloid aggregation, and discuss the universal features that have emerged.

There are two general classes of colloid aggregation which have been widely studied [1]. Both begin with a monodisperse suspension of small, solid particles undergoing Brownian motion. When the aggregation is initiated, the diffusive motion of the particles leads to collisions between them, causing them to stick together and form larger clusters. In the first class of aggregation, the clusters, once formed, no longer diffuse, and all aggregation is due to the accretion of single particles. This class is called single particle aggregation. By contrast, in the second class, the clusters themselves continue to diffuse, collide and form yet larger clusters. As the clusters grow, what began as a monodisperse distribution of single particles evolves into a very complex distribution of clusters of different sizes. This class is called cluster-cluster aggregation. Both types of aggregation have been extensively studied theoretically. However, most experimental studies of colloid aggregation have focused on the cluster-cluster class, as it is by far the most commonly encountered.

Several key features characterize any aggregation process [3]. These include: the structure of the clusters, the kinetics of the aggregation and the shape of the cluster mass distribution and its evolution in time. It is in the description of each of these features that the application of modern methods of statistical physics and the concepts of scaling has provided such progress. The first application of these techniques was to the descrip-

tion of the structure of the clusters. The cluster structure is highly random and disordered, and had long defied any quantitative description. However, the cluster structure can, in fact, be quantitatively parameterized by means of a type of symmetry, that of invariance under a change in length scale, or dilation symmetry. Thus colloidal aggregates can be characterized as fractals [6], and their structure can be quantitatively parameterized by means of their fractal dimension [7]. The aggregation kinetics, and the shape and time evolution of the cluster mass distribution can both be addressed through the application of scaling, in this case, in time. The shape of the cluster mass distribution is found to be invariant in time, with all the time dependence described by the evolution of the average cluster mass [8,9].

The fundamental property which determines the nature of cluster-cluster aggregation is the form of the interaction potential between two colloidal particles as they approach one another [10]. Colloidal particles which are stable against aggregation have some form of repulsive interaction which prevents two approaching particles from touching and sticking together. This repulsion is often due to charged groups adsorbed on the surface of the colloidal particles, but can also arise from other sources, such as a thin coating of polymer on the particle surface. The height of the resultant repulsive barrier,  $E_b$ , must be much greater than  $k_B T$  for the colloid to be stable against aggregation. If  $E_b$  is reduced, colliding particles can surmount the barrier, and stick together, thus initiating the aggregation process. The rate of aggregation will be determined by the probability,  $P$ , that two particles will stick upon colliding. This is determined by the height of the remaining barrier, and is given by  $P \sim \exp(-E_b/k_B T)$ .

The exponential dependence of the sticking probability on  $E_b$  makes the aggregation rate very sensitive to the value of the repulsive energy barrier, and a very wide range of aggregation rates can be obtained with any colloidal suspension. However, there are two characteristic, limiting regimes of aggregation [11]. In the first, the repulsive barrier is removed completely, so that  $E_b \ll k_B T$  and  $P \approx 1$ . In this case, every collision results

in the particles or clusters sticking to one another, and the aggregation rate is limited solely by the time between diffusion-induced collisions. This class of aggregation is called diffusion-limited colloidal aggregation (DLCA). In the second regime, the repulsive barrier is reduced only a small amount, so that  $E_b > k_B T$ , and  $P$  is very small. In this case, a large number of collisions are required before two particles or clusters stick to one another, which limits the aggregation rate. This regime is called reaction-limited colloid aggregation (RLCA). The two regimes lead to very rapid and very slow aggregation respectively, and have been recognized as such in the traditional colloid literature [10]. However, they also form two limiting types of behavior, with distinct, and universal features characteristic of each.

The ‘rules’ which determine the aggregation in each regime are quite simple. In DLCA, two clusters stick immediately upon contact, and the diffusive nature of the motion of the clusters plays an important role in determining both their structure and the aggregation kinetics. The diffusive motion ensures that the clusters always stick to one another at the edges, making the resultant aggregates significantly more tenuous. By contrast, in RLCA, the sticking probability is so low that, on an average, statistical basis, two clusters can adopt any bonding configuration that is physically possible, since the clusters have sufficient opportunity to explore all possible configurations. Thus the diffusive nature of the cluster motion does not play a significant role in the aggregation process, and the clusters no longer stick solely at the edges, making their structure significantly less tenuous. In both regimes, the bonds between particles, once formed, are assumed to be both permanent and rigid, so that no further change in their structure occurs as the aggregation proceeds.

The nature of the interparticle interactions determines the kinetics of the aggregation process; the kinetics in turn play a significant role in determining the structure of the clusters formed, and the shape of the mass distribution of clusters. Furthermore, since a very large number of clusters are involved in any aggregation process, and since the details of the structure of each clusters are not as important as the overall features, a statistical

description is well suited to describing the physics. The basic simplicity of the underlying physics facilitates modeling the aggregation process. The models developed deal solely with the nature of the interaction and the resultant “rules” which determine how clusters move and stick to one another. Thus, these models are independent of the detailed chemical nature of each colloid, and should apply equally well to all colloids. It is in this sense that the description of colloid aggregation should be universal.

## THEORY

The two limiting regimes of cluster–cluster aggregation have been studied extensively, and an elegant and detailed picture of their behavior has now been developed [1,3]. The theoretical work has entailed two basic approaches: the simplicity of the rules of the aggregation make computer simulation a very powerful method for studying both regimes, and considerable knowledge has been obtained about the structure of the clusters and the shape and time evolution of the cluster mass distribution [12]. The aggregation kinetics and the cluster mass distribution have also been studied extensively through the use of the Smoluchowski equations [13]. These are a set of rate equations which assume that the aggregation rate between two clusters depends solely on their masses. Scaling techniques have proven to be well suited to the study of these equations [8,9]. Experimentally, a wide range of colloid systems have been studied using many different techniques. Excellent agreement is obtained between the experimental observations and the theoretical predictions [14,15].

Each regime is distinguished by several distinct characteristics: the clusters formed in each regime are fractal, so that their mass scales with their radius as  $M = (R/a)^{d_f}$ , where  $a$  is the radius of a single particle and  $d_f$  is the fractal dimension, which is non-integral and less than the dimension of space. For DLCA,  $d_f \sim 1.8$  while for RLCA,  $d_f \sim 2.1$ . The cluster mass distribution in each regime exhibits dynamic scaling and can be written as  $N(M) = \bar{M}^{-2} \psi(M/\bar{M})$ , where the scaling

function,  $\psi(M/\bar{M})$  describes the shape of the cluster mass distribution and is independent of time, while  $\bar{M}$  is the mass of the average cluster and reflects all of the time dependence of the aggregation. For DLCA,  $N(M)$  is slightly peaked around the average mass with an exponential cutoff at larger masses. For RLCA, the cluster mass distribution has a power-law form with an exponential cutoff at large mass,  $N(M) \sim \bar{M}^{\tau-2} M^{-\tau} \exp(-M/\bar{M})$ . The kinetics of the aggregation are determined by the time dependence of  $\bar{M}$ : for DLCA,  $\bar{M}$  grows linearly with time, while for RLCA it grows exponentially with time.

## EXPERIMENTAL

To experimentally demonstrate the universal features of colloid aggregation, we compare the behavior of three completely different colloids: gold, silica and polystyrene latex [4]. Each colloid is comprised of a different material; each colloid is initially stabilized by completely different functional groups on their surfaces; the aggregation for each colloid is initiated in a different manner; the interparticle bonds in the aggregates for each colloid are different; and each colloid has a different primary particle size. However, each colloid can be made to aggregate by either diffusion-limited or reaction-limited kinetics.

The colloidal gold has a particle radius of  $a = 7.5$  nm and an initial volume fraction of  $\phi_0 = 10^{-6}$ . It is stabilized by citrate ions adsorbed on the surface. The aggregation is initiated by addition of pyridine, which displaces the charged ions, reducing the repulsive barrier between the particles. The amount of pyridine added determines the aggregation rate: for DLCA, the pyridine concentration is  $10^{-2}$  M, while for RLCA, it is about  $10^{-5}$  M. The interparticle bonds are metallic.

The colloidal silica used is Ludox SM obtained from DuPont. It has particles with  $a = 3.5$  nm, and is diluted to  $\phi_0 = 10^{-6}$ . It is initially stabilized by  $\text{OH}^-$  or  $\text{SiO}^-$  on the surface. The pH is kept  $\leq 11$  by addition of NaOH and the aggregation is initiated by addition NaCl, which reduces the Debye-Hückel screening length, thereby reducing the repulsive barrier between the particles. For

DLCA, the salt concentration is  $0.9$  M, while for RLCA, it is  $0.6$  M. The interparticle bonds are believed to be silica bonds.

The polystyrene latex has  $a = 19$  nm and is diluted to  $\phi_0 = 10^{-6}$ . It is initially stabilized by charged carboxylic acid groups on the surface of the particles. Addition of HCl to a concentration of  $1.2$  M is used to neutralize the surface charges and decrease the screening length to initiate the aggregation for DLCA. For RLCA, NaCl is added to a concentration of  $0.2$  M, to reduce the screening length and initiate the aggregation. The particle surfaces deform on bonding leading to large Van der Waals interactions between the bound particles.

To study the aggregation of each colloid and to critically compare their behavior in the two regimes, we use light scattering [16]. Static light scattering is used to measure the fractal dimension of the clusters, while dynamic light scattering is used to follow the aggregation kinetics. In addition, the dynamic light scattering data obtained from each colloid in each regime can be scaled onto a single master curve. The shape of this master curve is very sensitive to the features of the aggregation process, depending on the detailed structure of the clusters and the shape of the clusters mass distribution. However, all features particular to the individual colloids are scaled out of the master curve, allowing the curves from the different colloids to be compared directly, with no free parameters, providing a critical test of the universality of colloid aggregation in each of the two limiting regimes [4].

## RESULTS

Static light scattering measures the time averaged scattering intensity from the sample,  $I(q)$ , as function of the scattering wavevector,  $q = (4\pi n/\lambda)\sin(\theta/2)$ , where  $\lambda$  is the incident wavelength in vacuo,  $n$  is the index of refraction of water, and  $\theta$  is the scattering angle. Dynamic scattering measures the temporal autocorrelation function of fluctuations in the scattering intensity resulting from the diffusive motion of the clusters. We measure both the total scattered intensity and the

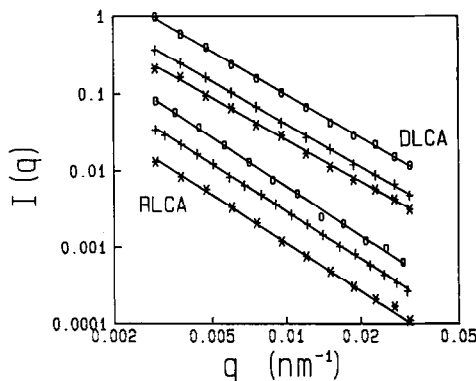


Fig. 1. Static light scattering from the three colloids aggregated in each of the limiting regimes. The linear behavior in the logarithmic plot demonstrates the fractal structure of the clusters, and the fractal dimensions determined from the slopes are: for DLCA, 1.86 for gold ( $\circ$ ), 1.85 for silica ( $+$ ) and 1.82 for polystyrene ( $*$ ); for RLCA, 2.14 for gold ( $\circ$ ), 2.07 for silica ( $+$ ) and 2.09 for polystyrene ( $*$ ).

autocorrelation function concurrently as functions of the scattering angle, and hence the scattering wavevector. The excitation source is the 488-nm line of an  $\text{Ar}^+$  laser, and the accessible scattering vectors are  $0.003 \leq q \leq 0.03 \text{ nm}^{-1}$ .

Static light scattering probes the internal structure of the aggregates. Because the fractal clusters are self-similar in structure, the scattered intensity from each cluster depends only on the product  $qR_g$ , where  $R_g$  is the radius of gyration of the cluster. At low  $qR_g$ , the internal structure of the aggregate is not resolved, and the scattered intensity is isotropic, independent of  $q$ . At high  $qR_g$ , however, the internal fractal structure is resolved and the scattered intensity scales as  $(qR_g)^{-d_f}$ . The measured intensity is a weighted average over the cluster mass distribution. However, for aggregates that are sufficiently large, the total measured intensity also exhibits the fractal scaling in  $q$ , allowing  $d_f$  to be determined directly. The static light scattering obtained from all the colloids in each regime is shown in Fig. 1. In each case, the data were collected only after the clusters were sufficiently large that  $q\bar{R} \gg 1$ , where  $\bar{R}$  is an average cluster size. The linear behavior in the double logarithmic plots confirms the fractal structure of the aggregates. The upper three data sets are obtained from clusters prepared under DLCA condi-

tions; and have  $d_f = 1.86$  for the gold,  $d_f = 1.85$  for the silica and  $d_f = 1.82$  for the polystyrene. To within the experimental error of roughly  $\pm 0.05$ , these results are identical. By contrast, the lower three data sets, which are obtained from clusters prepared under RLCA conditions, have consistently higher values of the fractal dimensions, with  $d_f = 2.14$  for the gold,  $d_f = 2.07$  for the silica and  $d_f = 2.09$  for the polystyrene. These values are again equal to within experimental error. Thus these results demonstrate the universal behavior of the structure of the fractal colloid aggregates in each of the two regimes.

Dynamic light scattering probes the diffusive motion of the clusters. When the clusters are large enough that their internal fractal structure can be resolved, both their translational and rotational diffusion contribute to the fluctuations [17]. Here, we consider only the first cumulant [18], or the initial logarithmic derivative of the autocorrelation function of the intensity fluctuations. This is given by  $\Gamma_1 = q^2 D_{\text{eff}}(qR_g)$ , where the effective diffusion coefficient reflects the contribution of both translational and rotational diffusion. When  $qR_g \ll 1$ , only translational diffusion contributes and  $D_{\text{eff}}(qR_g) = D = \zeta/R_H$ , where  $\zeta = k_B T / 6\pi\eta$  and  $\eta$  is the fluid viscosity. The hydrodynamic radius is related to the radius of gyration of the cluster,  $R_H = \beta R_g$ , with  $\beta \sim 1$ . For  $qR_g \gg 1$ , rotational diffusion also contributes and  $D_{\text{eff}} \sim 2D$ .

The effective diffusion coefficient determined from the measured first cumulant is again a weighted average over all the clusters in the distribution. It is given by

$$\bar{D}_{\text{eff}} = \frac{\sum N(M) I(qR_g) D_{\text{eff}}}{\sum N(M) I(qR_g)} \quad (1)$$

In the limit of  $q\bar{R} \rightarrow 0$ ,  $\bar{D}_{\text{eff}} = \bar{D}$ , providing a good measure of the average cluster size,  $\bar{R} = \zeta/\bar{D}$ .

The combination of the sensitivity to the cluster mass distribution and rotational diffusion leads to a pronounced  $q$  dependence in the measured  $\bar{D}_{\text{eff}}$ , and provides a very sensitive probe of the aggregation process [4,16]. However, to fully explore this  $q$  dependence at a single point in time during the aggregation process would require an experimentally inaccessible range of scattering angles. In-

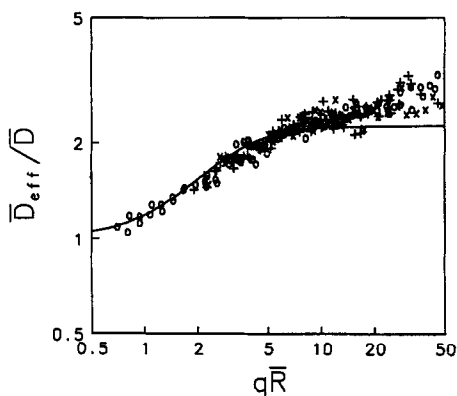


Fig. 2. Master curves obtained independently from dynamic light scattering data from each of the three colloids aggregated under diffusion-limited conditions. The curves are indistinguishable, demonstrating the universality of DLCA. The solid line is the calculated behavior.  $\circ$  = Gold,  $+$  = silica,  $\times$  = polystyrene.

stead, we exploit the dynamic scaling of the cluster mass distribution to measure  $\overline{D}_{eff}$  over a much wider range of  $q\overline{R}$ . Thus, we determine  $\overline{D}_{eff}$  over the range of  $q$  experimentally accessible and repeat the measurements during the aggregation process, as  $\overline{R}$  increases, while the shape of the cluster mass distribution remains unchanged. The values measured at each  $q$  are interpolated to obtain a series of data sets, each consisting of  $\overline{D}_{eff}(q)$  evaluated at the same time. We normalize  $\overline{D}_{eff}$  by  $\overline{D}$ , and plot the data as a function of  $q\overline{R}$ , where the required parameter,  $\overline{D} = \zeta/\overline{R}$ , for each set is determined empirically by scaling the data onto a single master curve. With sufficient data, there is always a substantial overlap between data from different sets, making the scaling unambiguous. All material parameters are scaled out, so that these master curves provide a means to critically compare the behavior of completely different colloids.

The master curve obtained for each colloid aggregated under DLCA conditions are shown in Fig. 2, while the master curves for each colloid aggregated under RLCA conditions are shown in Fig. 3. The shape of the master curve for DLCA is quite different from that of RLCA. This reflects the different shapes of  $N(M)$  for each regime, with the power-law form for RLCA leading to a considerably stronger  $q$ -dependence of the master

curve. In each regime, the master curves for the three colloids are indistinguishable. We emphasize that the master curves for each colloid are obtained independently, and there is no free parameter in comparing them. This is striking evidence of the universality of each of the regimes of colloid aggregation.

The solid lines drawn through the master curves are the calculated values using eq. (1), with the forms for  $N(M)$  expected for each regime and a form for  $I(qR_g)$  obtained from computer simulated clusters for the appropriate regime [19]. The agreement is very good, except for DLCA at large  $q\overline{R}$ . The calculation for the RLCA regime allows us to determine the cluster mass exponent,  $\tau = 1.5$ , which is in accord with theoretical predictions based on the Smoluchowski equations [20].

The scaling values of  $\overline{R}$  also allow us to determine the aggregation kinetics of each colloid in each regime. We show the results for the DLCA regime in Fig. 4, where we plot  $\overline{R}$  as a function of aggregation time  $t_a$  in a double logarithmic plot [14]. The linear behavior exhibited by each colloid confirms the power-law kinetics; the slopes, combined with the measured fractal dimensions, give the power law for the growth of the average mass. In all cases, this exponent is 1 to within experimental error. The different offsets of the three curves reflect the differences in the initial con-

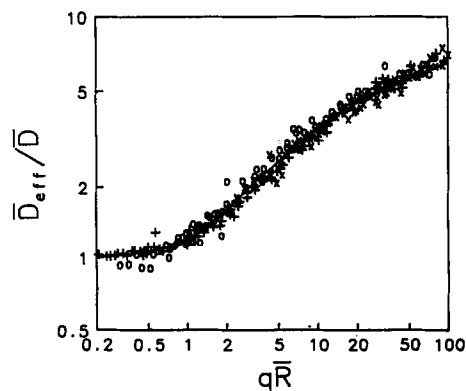


Fig. 3. Master curves obtained independently from dynamic light scattering data from each of the three colloids aggregated under reaction-limited conditions. The curves are indistinguishable, demonstrating the universality of RLCA. The solid line is the calculated behavior.  $\circ$  = Gold,  $+$  = silica,  $\times$  = polystyrene.

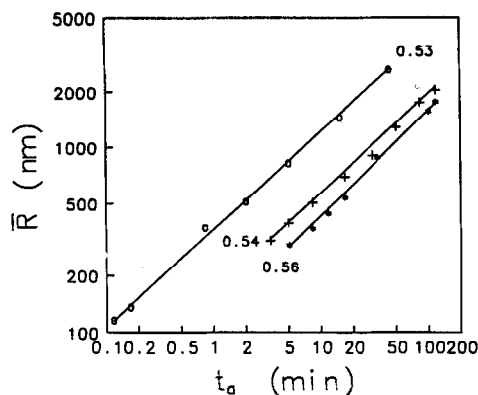


Fig. 4. The aggregation kinetics of the diffusion-limited aggregation of each of the three colloids obtained from the scaling of the data onto the master curves. The slopes of the power-law kinetics and the fractal dimensions show that the average cluster mass grows linearly with time in all cases.  $\circ$  = Gold,  $+$  = silica,  $*$  = polystyrene.

centrations. The results for the RLCA regime for each of the colloids are shown in Fig. 5, where we now use a semilogarithmic plot to show the exponential growth observed for each colloid [15]. In this case, the different slopes reflect the different initial aggregation rates of each colloid, which do depend on the details of the chemistry. Indeed, for the polystyrene, some time apparently elapses before the final aggregation rate is achieved. We believe that this is caused by the deformation of the particles which occurs on bonding and which

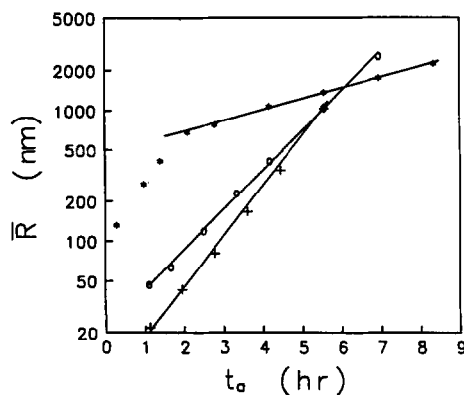


Fig. 5. The aggregation kinetics of the reaction-limited aggregation of each of the three colloids, demonstrating the exponential kinetics in each case.  $\circ$  = Gold,  $+$  = silica,  $*$  = polystyrene.

modifies the sticking probability at early time. Nevertheless, all colloids display exponential growth of the radius of the average cluster, and hence of the mass, as expected.

### CONCLUSIONS

In summary, we have shown experimental evidence to demonstrate the universal features of colloid aggregation. Two limiting regimes are observed: fast, diffusion-limited and slow, reaction-limited colloid aggregation. Each regime follows universal laws that describe its behavior. In many experimental situations, these limiting regimes are not achieved. Nevertheless, the overall aggregation behavior can usually be described in terms of these two regimes. Typically the initial stages of the aggregation are controlled by some intermediate value of the sticking probability, and the aggregation is not strictly diffusion-limited. Instead, at the earliest times, it can be approximated as reaction-limited. However, as the aggregation proceeds, and the concentrations of clusters decreases, their spacing increases, and diffusion becomes increasingly important as a rate limiting step. Thus at longer times the aggregation crosses over to diffusion-limited. Thus, these two limiting, and universal, regimes provide the basis for describing a large range of behavior for colloid aggregation.

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