In situ studies of colloidal aggregation induced by alternating electrical fields

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By means of *in situ* microscopy we have studied the irreversible aggregation of colloidal polystyrene particles induced by an external alternating electrical field, and observed a crossover from reaction-limited aggregation to diffusion-limited aggregation (DLA). In the DLA stage the time-dependent cluster-size distribution obeys dynamical scaling. A physical explanation is given.

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I. INTRODUCTION

The association of subunits to form large clusters is a phenomenon central to many natural and synthetic processes. Over the past decade there has been considerable interest in understanding such processes [1,2]. A prototype of these processes studied extensively is colloidal aggregation. The focus of the interest is on two fundamental aspects of the aggregation process: first the static geometry, which is the quantitative description of the static structure of the aggregates, and second the kinetics, which is the quantitative description of the evolution of their size. Significant advances have been made on these two aspects. Concerning the first aspect, experiments [2–4] and computer simulations [2,5] show that the clusters formed in many irreversible aggregations have scale-invariant, fractal structures. Concerning the second aspect, experiments [6–8], computer simulations [9], and theory based on the Smoluchowski equation [10] have established the existence of dynamic scaling of the size distribution. Two distinct aggregation regimes have been identified in computer simulations [5] and experiments [2–4]: (1) diffusion-limited aggregation (DLA) in which each collision between clusters results in bond formation; (2) reaction-limited aggregation (RLA) in which the probability of forming a bond in each collision is much less than 1. The morphologies of the clusters formed in them are different, which is reflected in the fractal dimension. The fractal dimension is 1.44 and 1.55 in two dimensions ($d=2$), 1.8 and 2.1 in three dimensions ($d=3$) for DLA and RLA, respectively. In addition to yielding different cluster structures, the two different aggregation regimes, RLA and DLA, also have different coagulation kinetics [7,8]. Recently much attention was given to the question concerning under what condition the aggregation processes are correctly described by corresponding mean-field equations such as the Smoluchowski equation. Computer simulations [11] and theoretical considerations [12] show that there exists an upper critical dimension, beyond which the Smoluchowski equation is valid perfectly and below which it is valid conditionally. But this has not been observed in experiments. So experimental studies in low dimensions are meaningful and interesting.

In this paper we present our experimental studies of the irreversible aggregation, induced by a uniform alternating electrical field perpendicular to the plane of the sample, of micrometer-diameter polystyrene colloidal particles confined to a quasi-two-dimensional film. It shows that the aggregates formed at a late stage of the process are fractals with fractal dimension 1.47, and that the aggregation process has two stages: RLA and DLA. A crossover from RLA to DLA is observed accompanied with a decrease in the growth rate of the mean cluster size. The cluster-size distributions have been measured, which obey dynamical scaling in late times of the aggregation. We explain the experimental results as biased Brownian coagulation and suggest that the crossover observed should be the crossover predicted theoretically.

II. THEORY

For discussing our experimental results conveniently, in this section we briefly recall the theory describing the aggregation kinetics. The most successful theory is the Smoluchowski rate equation (SE), which is

$$\frac{\partial C_k}{\partial t}=\frac{1}{2}\sum_{\substack{i,j\\ i+j=k}} K(i,j)c_i c_j - C_k\sum_i K(k,i)c_i \ , \qquad (1)$$

where C_k is the concentration of clusters composed of k monomers (called k-mers), $K(i,j)$ is the reaction probability of i-mers with j-mers to form $(i+j)$-mers, that is k-mers. So all physics is contained in the expression of the kernel $K(i,j)$.

It is commonly assumed [8] that the kernel $K(i,j)$ is a homogeneous function of the arguments i and j,

$$K(ai,aj)\approx a^{\lambda}K(i,j)\ ,\quad \lambda\leq 2\ , \tag{2}$$

$$K(i,j)\approx i^{\mu}j^{\lambda-\mu}\ ,\quad i\ll j\ ,\quad \mu\leq 1\ , \tag{3}$$

where the restrictions on λ and μ arise from the interpenetration of clusters. It can be shown (see Ref. [10]) that asymptotically the size distribution C_k approaches a scaling form

$$C_k(t)=Mk^{-2}\phi(k/S(t))\ . \tag{4}$$

Here M is the total number of monomers, and $S(t)$ is the mean cluster size [defined by $S(t)=\sum_k k^2c_k/M$] which obeys

$$S(t)\sim(1+t/t_c)^z \text{ with } z=1/(1-\lambda)\ . \tag{5}$$

Equation (2) is valid for large i and j. Hence the homogeneity parameter λ describes the reactivity of two big clusters and the tendency of the system to form large aggregates in a short time. While the homogeneity parameter μ characterizes the aggregation kinetics, and reflects whether the system favors small-large cluster aggregation or large-large cluster aggregation. For $\mu<0$, the small-large cluster aggregation dominates so the size distribution is monodispersed and the scaling function ϕ is bell shaped. For $\mu>0$ the large-large cluster aggregation dominates so the size distribution is polydispersed and the scaling function ϕ is monotonically decreasing. The scaling function forms for $\phi(x)$ with $\mu<0$ for small x and large x are

$$\phi(x\ll 1)\sim x^2\exp(x^{-|\mu|})\ , \tag{6}$$

$$\phi(x\gg 1)\sim x^{-\lambda}e^{-cx}\ . \tag{7}$$

Equation (1) is only a mean-field equation since the space fluctuations or the concentration gradients are not included. Recently by using a standard method developed for the reaction-limited process, van Dogen [12] has shown that there exists an upper critical dimension d_c. For $d>d_c$ the SE is valid perfectly all the time, while for $d<d_c$ the SE is only valid for times $t<t_d$; t_d marks a crossover from RLA to DLA and a slowdown in the growth rate of the second-order moment [defined as $M_2=\sum_k k^2c_k$, which is proportional to $S(t)$ in the mean-field approximation], the behavior of M_2 for $t>t_d$ can be approximately described by Brownian coagulation no matter what kernel the system originally has. Computer simulations [11] also show a crossover in Brownian coagulation.

III. EXPERIMENTAL SETUP

The polystyrene spheres suspended in an aqueous medium which we used in experiments are synthesized by emulsion polymerization method according to Ref. [13]. The diameter of the particles is about 1.5 μm and the polydispersity is about 4%. The suspension is confined to a quasi-two-dimensional thin film between two glass slides which are coated with a conductive substance. The thickness of the film defined by Mylar spacers is 50 μm. The particle number density (the number per unit area) is measured to be about 0.24, with the particle diameter used as the unit length. An alternating electrical field perpendicular to the film is applied to the system with the frequency fixed at 1500 Hz and the voltage at 1.3 V to induce aggregation. The aggregation process is *in situ* observed through an optical microscope equipped with a video system, by which the process can be recorded on videotapes and then analyzed by means of an image processor. Each pixel corresponds to approximately 0.5 μm^2.

IV. EXPERIMENTAL RESULTS AND DISCUSSIONS

The polystyrene latex we synthesized is charge stabilized. According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [14], the interaction between two particles includes two terms: the short-range van der Waals attraction and the screened Coulomb repulsion. It is the Coulomb repulsion between colloidal particles that prevents them from aggregating.

When an external alternating electrical field is applied perpendicular to the film, long-range interactions between particles will occur, which may be attractive or repulsive depending on the frequency of the field. The experiment shows that it is attractive for the frequencies around 1 kHz, and repulsive for frequencies higher than 10 kHz. The exact nature of the force is not clear. In a paper by Richetti, Prost, and Clark [15] the quadratic hydrodynamic interaction is proposed to explain the attractive force, and the dipole-dipole interaction to explain the repulsive force. The frequency and the voltage in our experiment were fixed at 1.5 kHz and 1.3 V to introduce an attractive force to initiate aggregation. Four aggregation trials were performed and the data of size distributions were averaged together.

First *in situ* observation shows that the aggregation process can be classified into two steps according to different coagulation kinetics: (1) reaction-limited cluster-cluster aggregation; (2) self-similar diffusion-limited aggregation. Typical photos of them are shown in Fig. 1(a) and 1(b). In the beginning of the aggregation process, clusters of different size exist due to local concentration fluctuations, but they are broken up into small parts and reformed unceasingly due to Brownian motions and thereby are not stable. When an external electrical field is applied, the aggregation starts. The clusters (including the monomers) move, and collide with each other to form large clusters. It is observed that the reacting small clusters collide and separate many times before they stick permanently. The characteristic distance between clusters now is small and the time scale for clusters and to diffuse to collide is less than the time scale for clusters to stick permanently, and this indicates that the aggregation rate now is controlled by the reaction probability of each collision between clusters. We call this time stage the RLA regime. It can be seen that the mobilities of clusters gradually go to zero as their sizes grow large. When the concentration of small clusters between large clusters is too low to form clusters larger than the critical size, the aggregation kinetics changes. The morphologies and spatial distribution of clusters at this time which can be seen from Fig. 1(b) is as follows: the large clusters become objects growing by consuming the small clusters

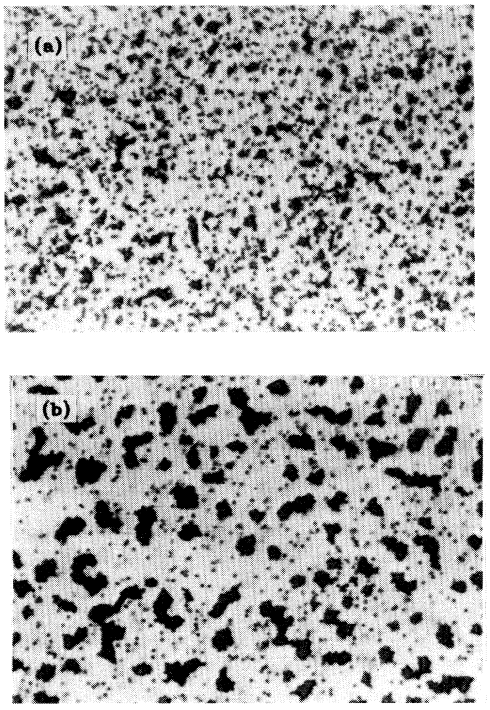

FIG. 1. Two typical photos in the aggregation process showing different coagulation kinetics. (a) $t=9.2$ s (RLA); (b) $t=75.1$ s (DLA).

diffusing between them, the characteristic time scale of the diffusion of small clusters is much larger than that of reaction between small and large clusters. This is indicative of that the coagulation rate at large times is limited by the diffusion of small clusters such as monomers, etc., and the aggregation is DLA. The time corresponding to this change from RLA to DLA is around 60 s after turning on the external field in our system. Qualitatively we conclude that the aggregation process has two regimes with different aggregation rates.

The cluster geometry and their size distribution have also been measured and analyzed quantitatively at regular time intervals. We have made the double logarithmic plot of cluster masses N vs their gyration radii r_g at different times and found that the data are very scattered in the first stage, but approximately align into a straight line in the late stage. Typical graphs are shown in Fig. 2. This implies that the clusters in the first regime are not self-similar, and that in the late regime are self-similar. In Fig. 2(b) it can be seen that for $\ln(R_g)>2$ the data fit onto a straight line rather well. Using the relation $N \propto R_g^{Df}$, we obtain the fractal dimension $D_f=1.47$, which is in accord with that of the two-dimensional DLA. For points with $\ln(R_g)<2$ the slope is larger than 1.47. The slope of the line to fit whole data is 1.82, which reflects the average dimension of all clusters. We denote it by d' ($=1.82$). There is thus a change in scaling behavior at $N\sim 90$ pixels, smaller clusters being more compact than larger clusters. In fact, this supports our qualitative result from direct observation that the aggregation process is dominantly diffusion limited, while it is reaction limited in the first stage. This is due to the fact that the compact structures at small scale result from the RLA between small clusters at the first stage, and the large cluster is the production of the aggregation between small clusters and large clusters at the late stage.

In Fig. 3 the size distribution $C_k(t)$ vs k is plotted, it can be seen that as the time increases the cluster-size distribution changes from monotonically decreasing form to a bell-shaped form whose peak shifts towards large k. A conclusion is that the size distribution evolves to a monodispersed one; in other words, the homogeneity exponent $\mu<0$. To see whether the dynamical scaling is obeyed, a plot of k^2C_k/M vs $k/S(t)$ at all times is made as shown in Fig. 4. The entire aggregation run is plotted in this

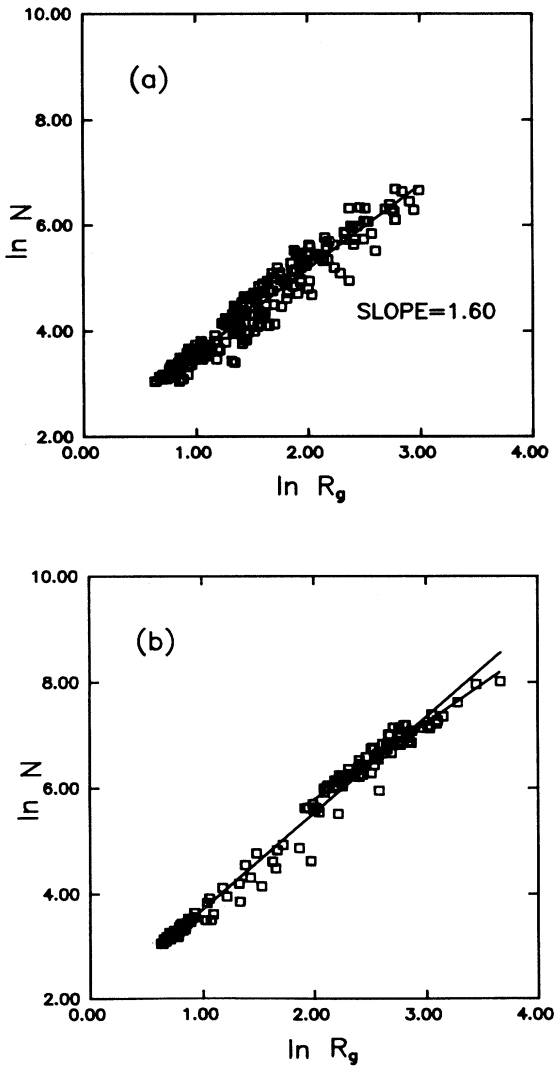

FIG. 2. Double logarithmic plot of the cluster masses as a function of gyration radii. (a) $t=9$ s; (b) $t=217$ s; the solid straight line fitting the data over the whole range has a slope of 1.82, and that fitting the data over the range $\ln(R_g)>2$ has a slope of 1.47.

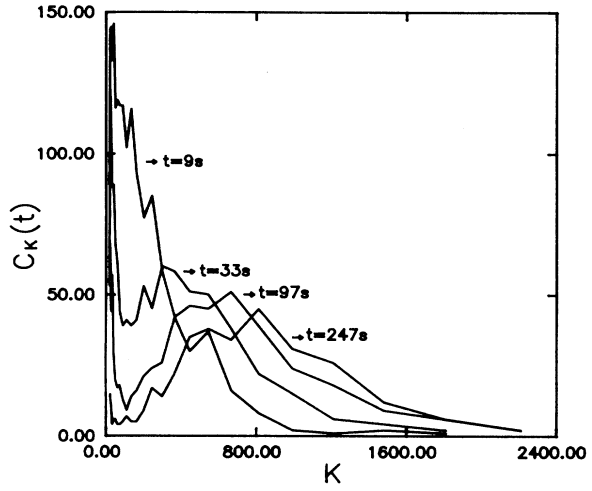

FIG. 3. The evolution of the cluster-size distribution measured at different times (to avoid overcrowding only four curves at different times are shown).

figure, from 3.6 to 310 s after turning on the electrical field. We can see that all data fall in a single curve when $t>60$ s. Also plots of other scaling forms such as $k^{\gamma}C_k/M$ vs $k/S(t)$ with $\gamma=0.5$, 1.0, 1.5, 2.5, 3.0 were tried, but only $\gamma=2$ scales the data the best. This implies that the size distribution C_k does approach asymptotically a scaling form expressed as $C_k \sim k^{-2}M\phi(k/S(t))$. Using the theoretical form [i.e., Eq. (6)] of $\phi(x)$ for small x: $\phi(x \ll 1)\sim x^2\exp(-x^{-|\mu|})$; the best fit of the master curve in Fig. 4 in small x values yields the homogeneity $\mu=-0.55$ (see the solid line in Fig. 4).

The mean cluster size $S(t)$ as a function of t is plotted in Fig. 5, from which we can obtain that asymptotically $S(t)\sim(1+t/t_c)$. This means the exponents z in Eq. (5) equals 1, that is to say $\lambda=0$. From Fig. 5 a decrease in the growth rate of $S(t)$ after about $t=60$ s is obvious. This is consistent with the observed crossover from RLA to DLA stated in the beginning of this section and indicates that the change accompanies a change in coagulation rate.

A physically reasonable kernel which is usually used to describe diffusion-limited aggregation is the Brownian kernel. At first we try to use it to explain our data, in two dimensions, which can be expressed as

$$K_{ij}\sim D_i+D_j\sim i^{-a}+j^{-a}\,. \tag{8}$$

Here relation $D_i\sim i^{-a}$ is used, which means that larger clusters move more slowly than smaller ones. The homogeneity exponents of the kernel are $\lambda=-a$, and $\mu=-a<0$, then the value of μ obtained from the behavior of scaling function $\phi(x)$ for small x implies that $\lambda=0.55$ and $z=1/(1-\lambda)=0.6$, which cannot explain the curve of $S(t)$ vs t in Fig. 5. This suggests that the two-dimensional Brownian kernel is not appropriate to describe our system.

Then we try a kernel, which is proportional to the product of the cross section and the relative diffusion coefficient of two reacting clusters, to interpret our data. It is written as

$$K_{ij}\sim(R_i+R_j)(D_i+D_j)\sim(i^{1/d'}+j^{1/d'})(i^{-a}+j^{-a})\,, \tag{9}$$

where relation $D_i\sim i^{-a}$ and $R_i\sim i^{1/d'}$ are used; R_1 is the characteristic radius of cluster i, and d' is the average dimension of all clusters due to reaction including clusters of all sizes, which is equal to 1.82. The homogeneity exponents of this term is $\lambda=1/d'-a$, $\mu=-a$. If it applies to our system, the values $\lambda=0$ and $d'=1.82$ imply that $a=1/d'=0.55$, which is in accord with the value ($\mu=-0.55$) obtained from the small-x limit of scaling

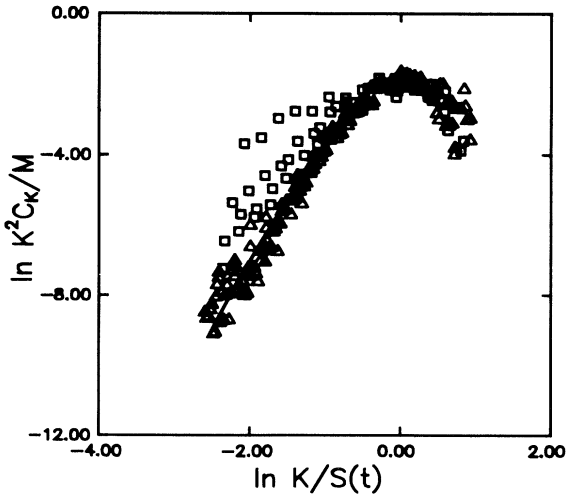

FIG. 4. Scaling plot of the size-distribution data. The cluster-size distribution at early times ($t<57$ s) does not scale into a single curve. □, $t<57$ s; △, $77<t<310$ s. The solid line is the theoretical prediction for the small x behavior of $\phi(x)$ with $|\mu|=0.55$.

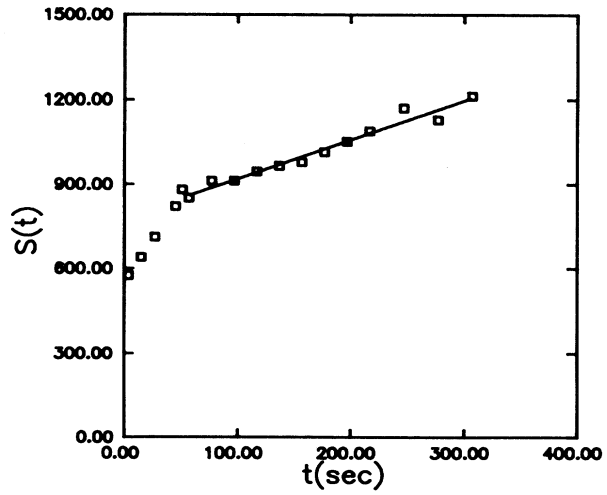

FIG. 5. Plot of the mean cluster size as a function of t. The solid straight line shows that $S(t)$ grows linearly with time at late time.

function $\phi(x)$. The self-consistency of the exponents indicates that the asymptotical behavior of the aggregation initiated by electrical field can be described by SE with this kernel.

Generally, the kernel describing the aggregation process with a fractal trajectory of the clusters (of dimension d_W) can be expressed as $K_{ij} \sim (i^{1/d'} + j^{1/d'})^{d-d_W}(i^{-a} + j^{-a})$. Brownian coagulation corresponds with $d_W = 2$. In our system the length scale of mutual interactions (long-range attraction) is about the order of distance between clusters in our system, so the diffusion of clusters is biased Brownian motion, not Brownian, and the dimension of its trajectory is approximately 1. In fact Eq. (9) is the extension of the Brownian kernel to a fractal trajectory of dimension $d_W = 1$.

The kernel [Eq. (9)] is similar to the Brownian kernel in three dimensions, including two competing effects: First, the more massive the cluster is, the less mobility the cluster has and thereby the less the reaction rate is of such clusters reacting with other clusters. On the other hand, the larger the cluster is, the larger the collision cross section is and thereby the larger the reaction rate is of such clusters reacting with other clusters. The growth kinetics of this kernel should be similar to that of Brownian coagulation. Theory [12] based on SE and computer simulations [11] have revealed that due to fluctuations the two competing effects may result in a crossover phenomenon in Brownian coagulation: in short times the coagulation is close to constant kernel coagulation because the clusters are about the same size. This corresponds to RLA observed in our experiment; in the late time stage the coagulation is dominated by small-large cluster aggregation, this corresponds to DLA observed in our experiment.

It must be noticed that the kernel [Eq. (9)] describing the aggregation process in the late stage is different from that [Eq. (8)] proposed by Dogen, with $d_W = 1$ replacing $d_W = 2$.

A similar work by Richetti, Prost, and Clark [15] gives a fractal dimension of 1.74, which is higher than the fractal dimension (1.47) in our system. We think that the only difference between their system and ours is the particle density. The particle density in their system is around 0.5, higher than that in two systems (0.24). Two different results for the fractal dimension may correspond to two aggregation regimes: aggregation in the particle density near percolation threshold, emerging sol-gel transition; aggregation in low particle density, which is diffusion limited.

It is worth pointing out that it is reasonable to use the dimension d', not the fractal dimension of large clusters, to interpret the aggregation kinetics. This is due to the fact that in the DLA regime of the aggregation process, in which the cluster-size distribution obeys dynamical scaling, the aggregation of large clusters and small clusters dominates, and it is natural using d' to interpret data, which describes how the characteristic radii of clusters including small ones vary with their masses in average. In fact, d' is an average dimension and cannot be called a fractal dimension because clusters have compact structure and do not share the same scaling with large clusters. So d' is different from the fractal dimension D_f although d' is close to the result of Rechetti, Prost, and Clark. It only reflects the compact structure of small clusters that d' is greater than the fractal dimension D_f.

Recently Robinson and Earshaw [16] reported their result on the experimental study of colloidal aggregation in two dimensions, which shows that under all experimental conditions the kinetics exhibited a crossover from slow to rapid growth. This is opposite to the result of ours. The reason, we think, is that the diffusion coefficient in their system increases with increasing mass of clusters. As the clusters grow larger, the aggregation rate (proportional to the product of the sticking probability and the diffusion coefficient) grows larger. This results in the crossover from slow to rapid growth. The theory of van Dogen [12] only took into consideration the case that the diffusion coefficient increases with increasing mass of the cluster, so it leads to a crossover from slow to rapid growth. In fact, the crossover observed by Robinson and Earshaw result from the same reason as the crossover proposed by van Dogen which is the spatial fluctuation in low-dimensional systems.

V. CONCLUSIONS

In summary, the aggregation of polystyrene particles induced by an electrical field is studied systematically. A crossover from RLA to DLA accompanied by a slowdown in the growth rate of the mean cluster size is observed, which is identified according to the growth kinetics observed. In the first stage, the clusters are not scale invariant, and the size distribution does not obey dynamical scaling. The aggregation in this time is reaction limited, which is identified according to direct observation. In the late stage, the clusters are scale invariant, the fractal dimension is 1.47, which is in agreement with the theoretical value of DLA (1.45), and the size distribution obeys dynamical scaling. All these and direct observation show that the growth kinetics is diffusion limited.

The growth can be explained self-consistently by applying Smoluchowski theory with a kernel of Eq. (9), however, with $d' = 1.82$, which is an average dimension of all clusters. The crossover is explained as that observed in computer simulations and predicted in theory, but the kernel is different from that predicted by the theory of van Dogen.

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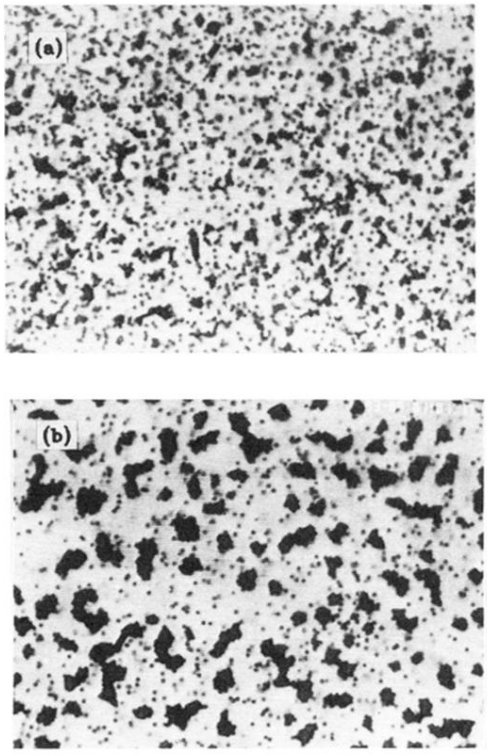
[1] F. Family and D. P. Landau, *Kinetics of Aggregation and Gelation* (North-Holland, Amsterdam, 1984).
[2] L. Pietronero and E. Tosatti, in *Fractals in Physics,* Proceedings of the Sixth International Symposium on Fractals in Physics, ICTP, Trieste (North-Holland, Amsterdam, 1986).
[3] D. A. Weitz and M. Oliveria, Phys. Rev. Lett. **52**, 1433 (1984).
[4] D. W. Schaefer, J. E. Martin, P. Wiltzius, and D. S. Cannel, Phys. Rev. Lett. **52**, 2371 (1984).
[5] P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983); P. Meakin and Z. Wasserman, Phys. Lett. **103A**, 337 (1984).
[6] S. K. Friedlander, *Smoke, Dust and Haze* (Wiley, New York, 1977).
[7] D. A. Weitz and M. Y. Lin, Phys. Rev. Lett. **57**, 2037 (1986).
[8] M. L. Broide and R. J. Cohen, Phys. Rev. Lett. **64**, 2026 (1990).
[9] T. Vicsek and F. Family, Phys. Rev. Lett. **52**, 1669 (1984); P. Meakin, T. Vicsek, and F. Family, Phys. Rev. B **31**, 564 (1985).
[10] P. G. J. van Dogen and M. H. Ernst, Phys. Rev. Lett. **54**, 1396 (1985).
[11] K. Kang and S. Redner, Phys. Rev. A **30**, 2833 (1984); K. Kang, S. Redner, P. Meakin, and F. Leyvraz, *ibid.* **33**, 1171 (1986).
[12] P. G. J. van Dogen, Phys. Rev. Lett. **63**, 1281 (1989).
[13] J. Ugelstad, K. H. Kaggerud, F. K. Hansen, and A. Berge, Makromol. Chem. **179**, 815 (1978). F. K. Hansen and J. Ugelstad, J. Polym. Sci. **17**, 3033 (1979).
[14] H. Sonntag, K. Strenge, and B. Vincent, *Coagulation Kinetics and Structure Formation* (Plenum, New York, 1987).
[15] F. Richetti, J. Prost, and N. A. Clark, in *Physics of Complex and Supermolecular Fluids,* edited by S. A. Safran and N. A. Clark (Wiley, New York, 1987).
[16] D. J. Robinson and J. C. Earshaw, Phys. Rev. A **46**, 2045 (1992).



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