Structure and kinetics of reaction-limited aggregation

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Several different models are used to investigate reaction-limited cluster-cluster aggregation and the crossover from diffusion-limited to reaction-limited aggregation. The results obtained from these models are consistent with each other, if finite-size and finite-concentration effects are taken into account. For reaction-limited aggregation in three dimensions we find, in the case where the probability that two clusters will combine depends only on the time that they spend in contact with each other, that the mean cluster size $S(t)$ increases exponentially with time t and that the cluster-size distribution $N_s(t)$ (of clusters of size s at time t) decays as $N_s(t) \sim s^{-\tau}$ with τ having a value larger than 1.5. For the case where the probability that two clusters will combine depends only on the number of times they collide with each other, we find a power-law growth in the mean cluster size, $S(t) \sim t^z$ with $z \sim 2.0$–2.5, and a cluster-size-distribution exponent τ close to 1.0. Our results indicate that the approach to asymptotic behavior may be quite slow and that the effective fractal dimensionality of the clusters depends both on the aggregation kinetics and on the extent of aggregation. We find that if the rate of bonding between two clusters depends on their collision frequency, then the exponent τ has a value close to 1 for the aggregation of small rigid clusters and close to 2 for the aggregation of large floppy clusters.

I. INTRODUCTION

In recent years considerable interest has developed in the aggregation[1–5] of particles to form large clusters which frequently have a fractal structure.[6] Although power-law mass-length scaling relationships were found in a variety of real systems and simulated aggregates more than a decade ago, much of the present high level of interest in fractal aggregates was stimulated by the observation of fractal geometry in iron particle aggregates[7] and the subsequent development of the diffusion-limited aggregation (DLA) model.[8] In the DLA model, particles are added, one at a time, to a growing aggregate of particles via random-walk trajectories. Although DLA does not provide a satisfactory description of colloidal aggregation, it has led to the development of other more realistic models. One of these models is the diffusion-limited cluster-cluster aggregation (DLCCA) model.[9,10] which (for the case of three-dimensional space or lattices) leads to clusters which have a fractal dimensionality D of about 1.78. This is in quite good agreement with experimental studies of colloidal aggregates.[11–14]

During the past few years a good understanding of both the structure[1–5] and kinetics of DLCCA has been developed. However, real systems only rarely come close to satisfying the conditions assumed in DLCCA (irreversible fast aggregation to form rigid clusters). In most aggregation processes many encounters between pairs of clusters are required before two clusters are combined to form a larger cluster. In the limit where the number of encounters required for permanent bonding is very large (a condition frequently satisfied in practice), all possible bonding configurations (or at least a representative sample of them) can be explored before combination occurs. Under these conditions the aggregation process is limited not by cluster diffusion but by "chemical" details which determine how many collisions are required for cluster-cluster bonding. Although relatively few examples of chemically limited cluster-cluster aggregation have been studied experimentally,[12,15–17] it seems apparent that chemically limited aggregation is more common than diffusion-limited aggregation. In dilute systems we might expect a crossover from chemically limited aggregation at short times (small clusters separated by relatively small distances) to diffusion-limited aggregation at long times (large clusters separated by large distances) providing that other processes (such as mechanical instability[18] and settling[19]) do not intervene.

A model for reaction-limited cluster-cluster aggregation (RLCCA) was proposed by Kolb and Jullien[20] and Family, Meakin, and Vicsek,[20] which was a generalization of DLCCA. In this model[20] the reactivity of the clusters is dependent on a sticking probability which depends on the product of the masses of the reacting clusters. The results indicated that for a small sticking probability cluster-size distribution and its moments asymptotically scale with the same exponents as for the case when the sticking probability is unity. Only in the limit $p \to 0$, does the model reduce to RLCCA. A hierarchical model for RLCCA was developed by Jullien and Kolb.[21] In this lattice model 2^n particles are combined in stages so that after the nth stage the system contains 2^{n-m} clusters each consisting of 2^m particles (or occupied lattice sites). In this model all possible ways of joining pairs of

clusters are found and one of these is selected at random. Using clusters containing up to 512 occupied lattice sites effective fractal dimensionalities of 1.53±0.04, 1.98±0.04, and 2.32±0.04 were found for hypercubic lattices with Euclidean dimensionalities d of 2, 3, and 4, respectively. Jullien and Kolb also determined the number of possible configurations C_N for two contacting clusters containing N occupied lattice sites. They found a power-law relationship between C_N and N,

$$C_N \sim N^{\lambda} . \tag{1}$$

Values for λ of 0.74, 1.16, and 1.44 were found for $d=2$, 3, and 4, respectively. For the most important three-dimensional case the fractal dimensionality of about 2.0 is in quite good agreement with experimental results, but most experiments[12,15–17] give a slightly higher value for the effective fractal dimensionality (2.05–2.15).

Brown and Ball[22] have investigated a model in which pairs of clusters are selected and placed at random on a cubic lattice. Only if the two clusters are adjacent but not overlapping is a new cluster formed. Depending on how the clusters are selected, the cluster-size distribution may be monodisperse (in the case of a hierarchical model) or may evolve in a natural way into a polydisperse distribution if the clusters are selected at random, irrespective of their sizes. Brown and Ball found that the effects of polydispersity are much larger for RLCCA than for DLCCA. For $d=3$, fractal dimensionalities of 1.94±0.02 were found for the monodisperse case and 2.11±0.03 for the polydisperse case. For $d=2$, values of 1.53±0.01 and 1.59±0.01 were obtained. The exponent λ was also measured and values of 1.16±0.04 and 1.06±0.02 for $d=3$ and 0.75±0.01 and 0.73±0.02 for $d=2$ were found for the monodisperse and polydisperse cases, respectively.

A theoretical model for RLCCA has been proposed by Ball *et al.*[23] The analysis of Ball *et al.* is concerned with RLCCA under the conditions where all bonding configurations between any two pairs of clusters have an equal probability of being accepted to form a new cluster. They find that under these conditions the reaction kernel $K(i,j)$ can be described in terms of its scaling properties $K(i,j)\sim ij^{\lambda-1}$ for $i \gg j$ and $K(i,j)\sim i^{\lambda}$ for $i \simeq j$ with $\lambda=1$ in three dimensions. A reaction kernel with these scaling properties leads to exponential growth in the mean cluster size S defined by

$$S(t)=\frac{\sum_{s=1}^{\infty} s^2 N_s(t)}{\sum_{s=1}^{\infty} s N_s(t)} , \tag{2}$$

where $S(t)$ is the mean cluster size at time t and $N_s(t)$ is the number of clusters of size s at time t. A power-law cluster-size distribution $N_s(t)\sim s^{-\tau}$ is also predicted with τ having the value of 1.5.

In this paper we describe the results obtained from three different models. Model I is a modification of the time-dependent DLCCA,[24,25] in which the probability that two clusters will combine is proportional to the amount of time they spend in contact with each other. In this model, which is carried out at finite densities ρ, the reaction probability is reduced as far as is practical to approach the chemically controlled limit. Model II is closely related to model I, except that the chemically controlled limit is reached by allowing particles or clusters to move with equal probability to any set of unoccupied lattice sites after they have been selected. In model III, pairs of particles are selected at random from the entire system and brought into contact with each other. If the two particles are contained in clusters, the associated particles constituting the clusters are moved with them and the two particles are combined (to form a single cluster containing all of the particles associated with the two selected particles) only if there is no overlap between particles in the two clusters. This model, which was proposed by Leyvraz,[26] is closely related to the model of Brown and Ball.[22] Results from both lattice and nonlattice versions of this model will be presented.

In the simplest version of the RLCCA model the probability that two clusters will combine with each other is proportional to the amount of time that the two clusters spend in contact with each other. However, in real systems the reaction rates may depend on the cluster masses. We have explored the effects of such mass-dependent reactivities and find that the cluster-size distribution (and fractal dimensionality) is sensitive to such details.

The outline of this paper is as follows. In Sec. II we define the three models that we use to simulate reaction-limited aggregation, and present the results of the simulations. Discussion and conclusions are given in Sec. III.

II. MODELS AND RESULTS

A. Model I

Model I is based on the time-dependent cluster-cluster aggregation model which has been described previously.[25] In this model, clusters are selected at random and moved by one lattice unit in a randomly selected direction if a random number X uniformly distributed in the range $0<X<1$ satisfied the condition

$$X < \frac{\mathcal{D}(s)}{\mathcal{D}_{\max}} . \tag{3}$$

Here $\mathcal{D}(s)$ is the diffusion coefficient for the selected cluster of size s and $\mathcal{D}_{\max}$ is the maximum diffusion coefficient for any cluster in the system. In most cases we assume that the cluster diffusion coefficient depends only on its size or number of particles s (i.e., shape effects are ignored) and that $\mathcal{D}(s)$ is related to s according to

$$\mathcal{D}(s)\sim s^{\gamma} . \tag{4}$$

Scaling arguments and calculations[27] using the Kirkwood-Risemann theory[28] indicate that for the case of colloidal aggregation in a dense fluid the exponent γ is given by $\gamma=-1/D$.

After each cluster has been selected, the time is incremented by $1/(N\mathcal{D}_{\max})$ where N is the number of clusters in the system. The time is incremented whether or not the cluster is actually moved. This procedure (which is described in more detail in Ref. 25) introduces a time scale in units of the time required (on average) for a single particle to move by one lattice unit.

In the DLCCA model two clusters are combined as

soon as they come into contact with each other via nearest-neighbor occupancy. This model can be modified to include the effects of sticking probabilities P_σ smaller than 1 by allowing sticking to occur with a probability of P_σ each time one cluster attempts to move onto the lattice sites occupied by another cluster. In this model clusters would be selected at random and a direction in the lattice would also be selected at random. If movement of the cluster in the selected direction would cause it to overlap the sites occupied by one (or more) other cluster then these two (or more) clusters would be combined if $X > P_\sigma$ (where X is a random number uniformly distributed over the range $0 > X > 1$). If $X < P_\sigma$ the two (or more) clusters would remain side by side but would not be combined. In the limit $P_\sigma \rightarrow 0$, this model corresponds to reaction-limited aggregation.

Instead of testing for sticking after each cluster has been selected, we calculate the probability that two clusters will stick as soon as they move into contact with each other (or remain in contact after attempting to overlap). An estimate of the probability that two adjacent clusters will combine before one of them is randomly selected and moved is given by

$$P_1 = \frac{\sigma'}{[\sigma'(i)+\mathcal{D}(i)+\mathcal{D}(j)]} ; \tag{5}$$

a more detailed analysis gives

$$P_2 = \frac{\sigma}{\sigma+[\mathcal{D}(i)+\mathcal{D}(j)]/2-\sigma[\mathcal{D}(i)+\mathcal{D}(j)]/2} , \tag{6}$$

where $\mathcal{D}(i)$ and $\mathcal{D}(j)$ are the diffusion coefficients of the two contacting clusters. The parameter σ' in Eq. (5) can be regarded as a rate constant describing the rate at which two contacting clusters "react" to form a combined cluster. The limit $\sigma' \rightarrow \infty$ corresponds to DLCCA and the limit $\sigma' \rightarrow 0$ corresponds to RLCCA. The parameter σ in Eq. (6) is the probability that two clusters will combine after they either move into contact with each other or remain in contact after one of the two clusters has been randomly selected but not moved. In this case the limit $\sigma \rightarrow 1$ corresponds to DLCCA and $\sigma \rightarrow 0$ corresponds to RLCCA.

The procedure outlined above was adopted in the interest of reducing computer time requirements. For a typical simulation with 10 000 particles (occupied lattice sites) on a 128^3 lattice it is possible to reduce σ to values of about 10^{-3}. Such a simulation requires about 5 h of central-processing-unit (CPU) time on an IBM 3081 computer. It should be possible to reduce σ to about 10^{-4}, but very large amounts of computer time would be required to explore still smaller values of σ.

Simulations have been carried out using both Eqs. (5) and (6) to calculate the probability of combining two clusters after contact. For the smallest value of σ' or σ (10^{-3}) used in this work nine simulations were carried out using Eq. (5) and 16 simulations were carried out using Eq. (6) with 10 000 particles (sites) on 128^3 lattices. Very similar results were obtained using both Eqs. (5) and (6). Only results obtained using Eq. (6) are shown here.

Figure 1 shows the time dependence of the mean cluster size $S(t)$and the number of clusters $N(t)$ for several

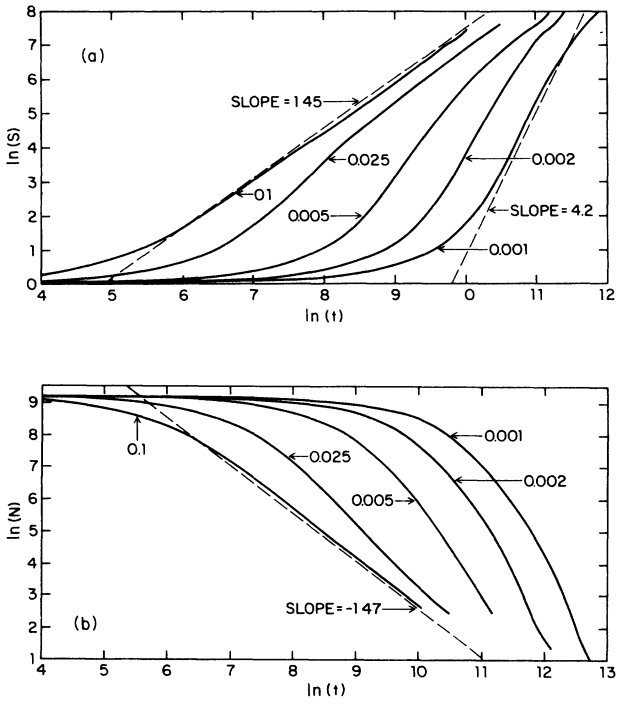

FIG. 1. Dependence of the mean cluster size (S) and number of clusters (N) on time obtained from three-dimensional simulations using model I. These simulations were carried out assuming that $\mathcal{D}(s) \sim s^{-1/2}$. Each curve was obtained using a different value for the parameter σ [Eq. (6)].

different values of the parameter σ in the range $0.1 \leq \sigma \leq 0.001$. In these simulations the parameter γ [Eq. (4)] was set to a value of $-\frac{1}{2}$ which is approximately equal to $-1/D$ for RLCCA. The results shown in Fig. 1 show a crossover from the behavior associated with DLCCA for large values of σ and/or short times [$S(t) \sim t^z$, $N(t) \sim t^{-z}$, where the exponent z has a value close to 1] to a quite different behavior for small values of σ and/or long times, which we associate with RLCCA. The results shown in Fig. 1 indicate that in the RLCCA limit $S(t) \sim t^z$ and $N(t) \sim t^{-z}$, where the exponent z has a large value > 4. However, such large exponents are difficult to measure accurately and we cannot, on the basis of these results, rule out either exponential growth or gelation [$S(t) \sim (t - t_g)^{-\omega}$, where t_g is the gel time]. For values of σ larger than 10^{-3}, the results from 20–30 simulations were averaged to obtain the results show in Fig. 1.

The time-dependent cluster-size distributions $N_s(t)$ were determined in all of our simulations. Figure 2 shows some of the results obtained using the lowest value for σ (10^{-3}). In Fig. 2(a) the cluster-size distribution is shown at several different times and Fig. 2(b) displays one of these size distributions. Figures 2(a) and 2(b) indicate that for intermediate times, which are accessible in both experiments and simulations the cluster, size distribution can be described approximately by the power law

$$N_s(t) \sim s^{-\tau} , \tag{7}$$

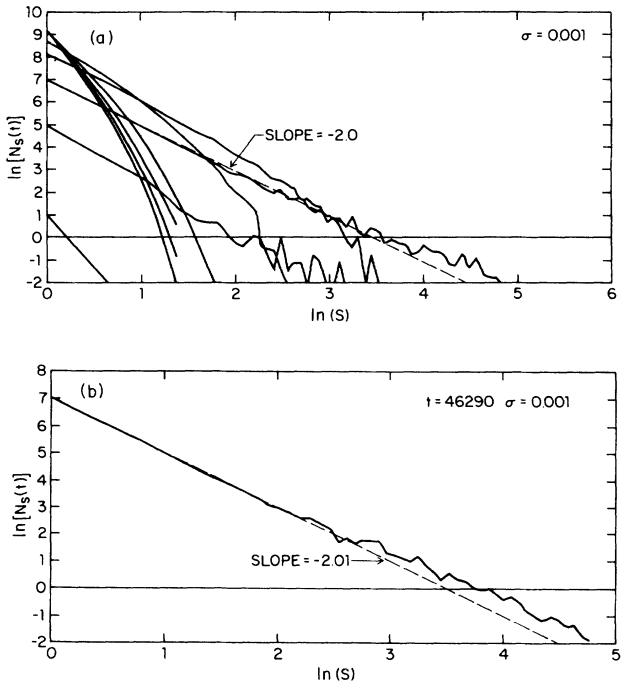

FIG. 2. Cluster-size distributions $N_s(t)$ obtained at various times (t) during simulations of DLCCA using Model I with $\gamma = -\frac{1}{2}$ and a value of 10^{-3} of σ [Eq. (6)]. (b) The cluster size distribution obtained for $t = 46\,290$.

where the exponent τ has a value of about 2.0.

Simulations carried out using model I suffer from several disadvantages. They must be carried out at finite densities ($\rho \sim 4.77 \times 10^{-3}$ particles per lattice site in our case) which do not closely approach the limit $\rho \to 0$ in which the simplest behavior is expected. They require large amounts of computer time so that it is not possible to reduce statistical uncertainties to very low levels or carry out simulations on very large systems. Also, it is not possible to closely approach the limit $\sigma \to 0$. However, the effects of nonzero densities ρ and reaction parameters σ are important in real systems and model I allows us to explore these effects.

In order to obtain information about cluster-cluster aggregation in the limit $\sigma \to 0$ (reaction-limited aggregation), two new models closely related to the models of Brown and Ball[22] and Leyvraz[26] were developed. These models and the results obtained from them are described in Secs. II B and II C of this paper.

B. Model II

In model II we retain a finite particle density but the simulation is carried out in the reaction-limited regime. The simulations are carried out on cubic lattices which typically contain 128^3 sites with periodic boundary conditions. A fixed number N_0 of sites are selected on cubic lattices at random and filled to represent single particles. In most of our simulations N_0 was set to a value of 10 000 on cubic lattices typically containing 128^3 sites with periodic boundary conditions. After the N_0 sites have been selected, clusters of sites joined by nearest-neighbor occupancy are identified. At this stage, the system consists mainly of single occupied sites with no occupied nearest neighbors, together with a few clusters containing two or more sites. Clusters are then selected at random and moved if a random number X satisfies the condition

$$X < \frac{G(s)}{G_{\max}} , \tag{8}$$

where

$$G(s) \sim s^{\delta} . \tag{9}$$

In this model the cluster is moved with equal probability to any set of unoccupied lattice sites in the system. If all of the sites occupied by the cluster in its new position are vacant, the move is accepted; otherwise, a new random position is selected. This process is repeated until a set of vacant sites has been found and the cluster remains in that new position. After a cluster has been successfully moved, its perimeter is examined and it is combined with any cluster with one or more occupied sites on the perimeter. Here the perimeter consists of all empty sites which are nearest neighbors to the occupied sites in the cluster. After a cluster has been moved and combined with any contacting clusters, a new cluster is randomly selected and moved if $X < G(s)/G_{\max}$. The whole process is repeated until only a few clusters remain in the system.

A time scale can be associated with this model by incrementing the time by $1/(NG_{\max})$ after each cluster has been selected (irrespective of whether or not it is actually moved). Except for the fact that a finite density of particles is used in this model, it is very similar to the model introduced earlier by Brown and Ball.[22] If the exponent δ in Eq. (9) has a value of 0, then each bonding configuration in the system has an equal probability of reacting to advance the aggregation process. Consequently, $\delta = 0$ corresponds to RLCCA. The definition of reaction-limited cluster-cluster aggregation in terms of an equal reaction probability is equivalent to assuming that the probability that two clusters will combine depends only on the amount of time they spend in contact with each other. However, it is possible that the probability that two clusters will combine will depend also on the number of times that they move into contact with each other. Under these conditions it is reasonable to assume that the effective reaction rate between two clusters of size i and j will be given by

$$K(i,j) \sim [\mathcal{D}(i) + \mathcal{D}(j)] K_0(i,j) , \tag{10}$$

where $K_0(i,j)$ is the number of possible bonding configurations between the two clusters. The quantity $K_0(i,j)$ is automatically included in our simulations using model II. The dependence on the cluster diffusion coefficients is included by using a nonzero value for the exponent δ in Eq. (9).

The appropriate choice for the exponent δ will depend on the physical details of the aggregation process. For relatively small rigid clusters with a short-range activation barrier, it is reasonable to use a value of $-1/D$ for

the exponent δ. For larger or more floppy clusters, the collision frequency between two clusters will depend on internal motions in the two clusters, and a value of 0 for the exponent δ seems to be more reasonable. Since all clusters will become floppy in the limit $s \rightarrow \infty$, it might be argued that $\delta = 0$ is the appropriate value to use if we are interested in the asymptotic (long-time) behavior of the system.

As has been pointed out by Brown and Ball,[22] the structure of clusters formed by reaction-limited cluster-cluster aggregation is sensitive to the reaction kinetics. This effect can be more clearly seen in two-dimensional than in three-dimensional simulations. Figure 3 shows the results obtained using 10 000 particles on 512×512 site square lattices with periodic boundary conditions. This figure shows results obtained at or near the end of simulations carried out using four values for the exponent δ (-1.0, -0.5, 0.0, and 0.5). Under these conditions only one or a few clusters remain. For the case $\delta = 0.5$, the very broad cluster size distribution can be seen.

The dependence of $\ln(R_g)$ on $\ln(s)$ is shown in Fig. 4 for all of the intermediate clusters formed in two-dimensional simulations carried out using three different values for the exponent δ. Here R_g is the cluster radius of gyration. The results from more than 100 simulations were averaged for each value of δ. Figure 4 shows that for clusters in the size range $20 \leq s \leq 1000$ the dependence of $\ln(R_g)$ on $\ln(s)$ is quite linear, indicating that a single fractal dimensionality D_β, defined by

$$R_g \sim s^\beta, \quad D_\beta = 1/\beta , \tag{11}$$

can be used to describe the structure of the clusters in the above size range. Figure 5 shows the dependence of the effective exponent β [obtained by least-squares fitting straight lines to the dependence of $\ln(R_g)$ on $\ln(s)$ for clusters in the size range $25 < s < 2500$ lattice sites] on eight values of δ in the range -1 to 0.75. The results shown in Fig. 5 indicate that β decreases continuously as δ is increased. However, because of finite-size and finite-

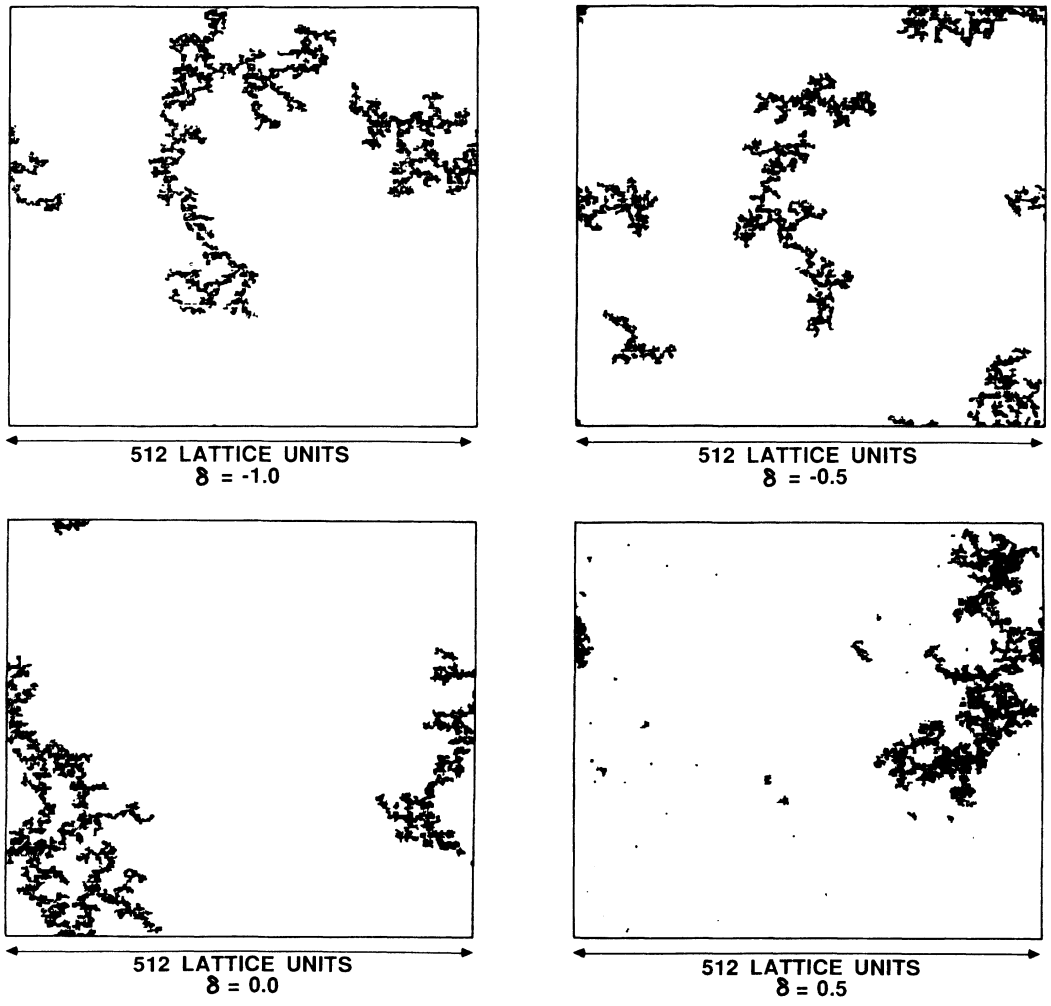

FIG. 3. Some results obtained from a two-dimensional version of model II. Here the system is shown near the end of simulations carried out using 10 000 occupied sites on 512×512 lattices with periodic boundary conditions. Results are shown for four different values of the parameter δ [Eq. (10)]. This figure illustrates the increase in fractal dimensionality and increasing breadth of the cluster-size distribution with increasing δ.

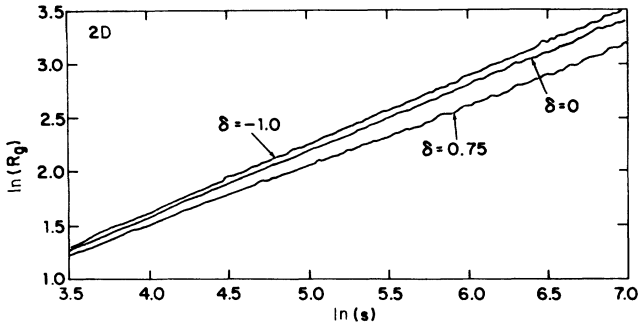

FIG. 4. Dependence of the radius of gyration (R_g) on cluster size (s) obtained from 2D simulations carried out using model II with δ set to values of -1, 0 and 0.75.

concentration effects we cannot be certain that the variation of β with δ is continuous over the whole range of δ values. In the limit $\delta \to \infty$ this model becomes equivalent to an Eden[29] model (random addition of single particles to large clusters) in the limit of zero density, so that we expect the exponent β to approach a value of $\frac{1}{2}$ in the limit $\rho \to 0$, $\delta \to \infty$. Although β has not approached closely this limiting value for $\delta = 0.75$, our results are consistent with this idea. Similarly, in the limit $\rho \to 0$, $\delta \to -\infty$, we expect β to have a value close to that found in the hierarchical model of Kolb and Jullien[20,21] who found that $D_\beta = 1.53 \pm 0.04$ or $\beta = 0.65 \pm 0.02$. Our results indicate a limiting value of about 0.64 for β, in good agreement with those of Jullien and Kolb. The value for β obtained from the hierarchical model should be an upper limit for our model and our results are certainly consistent with this. Results similar to those shown in Fig. 5 were presented earlier[30] for the three-dimensional (3D) version of model III.

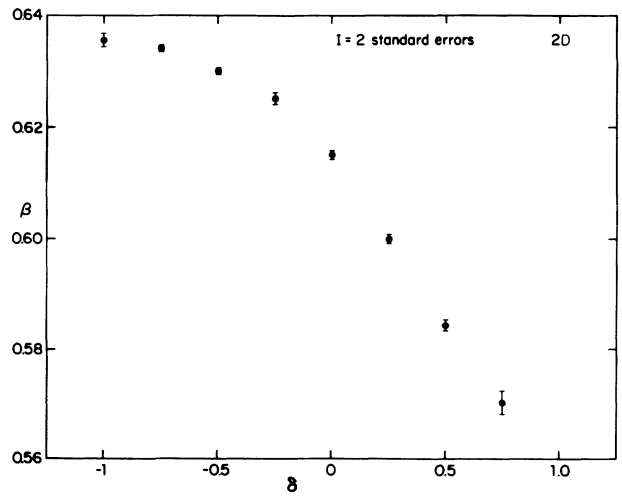

FIG. 5. Dependence of the radius of gyration exponent (β) on δ obtained from the dependence of $\ln(R_g)$ on $\ln(s)$ (see Fig. 4) using two-dimensional versions of model II with eight values of δ in the range $-1 \leq \delta \leq 0.75$.

Although the structure of fractal aggregates is still a subject of considerable interest, our main motivation for carrying out the work described in this paper was to explore the kinetics of reaction-limited aggregation. Simulations were carried out for values of δ in the range -1.0 to 0.75. Only results for the cases which seem to be the most important ($\delta = 0$ and $\delta = -1/D = -0.5$) are reported here. Figure 6 shows the dependence of the mean cluster size $S(t)$ on time t for the case where $\delta = 0$. These simulations were carried out using 10 000 sites on 128^3 lattices. The results shown in Fig. 6 are equally consistent with a power-law or exponential increase in the mean cluster size with increasing time. It also seems possible that the time dependence of the mean cluster size could be represented by an expression of the form $S(t) \sim (t - t_g)^{-\gamma}$ for times close to t_g (the gel time). In our simulations the growth of $S(t)$ saturates at long times as a result of the finite system size. In addition, the effects of the initially almost monodisperse distribution take some time to decay. For this reason the range of times over which $S(t)$ displays reasonable power-law or exponential behavior is at best quite narrow and we cannot distinguish between them.

The time-dependent cluster-size distributions obtained from the same simulations are shown in Fig. 7. Each of the curves in Fig. 7(a) shows the number of clusters of a particular size as a function of time and the curves shown in Fig. 7(b) are the cluster-size distributions at various times. The results shown in Fig. 7(b) indicate a power-law cluster-size distribution [Eq. (8)] with a value close to 2.0 for the exponent τ at intermediate times. The results obtained from model I (with $\delta = -\frac{1}{2}$) and from model II

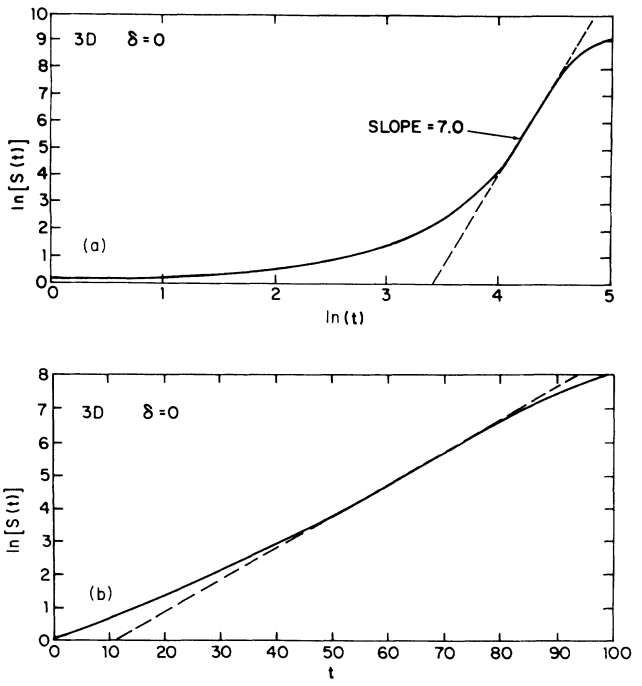

FIG. 6. Dependence of the mean cluster size (S) on time obtained from model II with $\delta = 0$. These results were obtained from 3D simulations using 10 000 particles on 128^3 lattices.

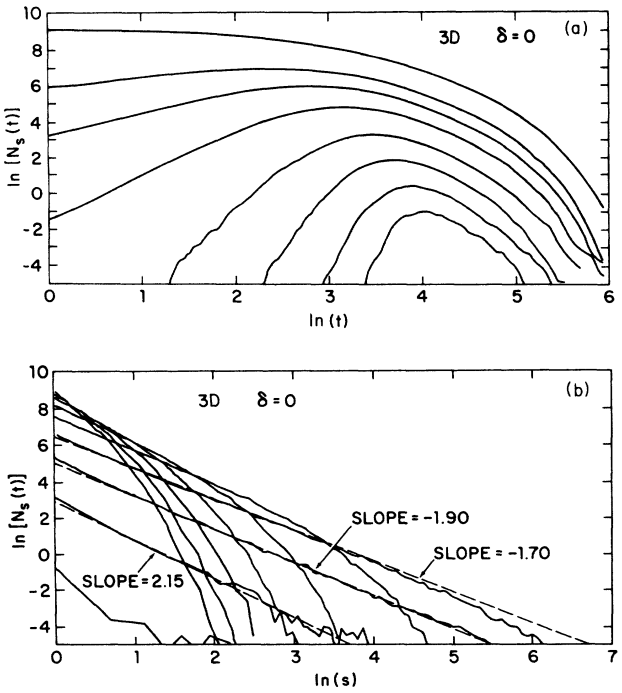

FIG. 7. Time-dependent cluster-size distributions obtained from the simulations used to generate Fig. 6. (a) The number of clusters of size 1, 2, 3, 5, 10, 19–20, 38–40, and 75–80 as a function of time. (b) The cluster-size distributions at nine different times ($t=1.72$, 3.12, 5.68, 10.4, 18.8, 34.3, 62.4, 114, and 207).

(with $\delta=0$) which both represent reaction-limited cluster-cluster aggregation are qualitatively very similar. They are also in reasonably good quantitative agreement. In particular, both models indicate effective values for the cluster-size distribution exponent τ which are larger than 1.5.

Simulations have been carried out at several different concentrations from model II with $\delta=-0.5$. This value for the exponent δ is close to $-1/D$ [measurement of the radius of gyration for clusters of different sizes for simulations carried out using model II with $\delta=-0.5$ indicate that $\beta\simeq 0.470(D_\beta\simeq 2.13)$]. Figure 8 shows the dependence of $\ln[S(t)]$ on $\ln(t)$ obtained from simulations carried out using 5000, 10 000, and 20 000 particles on lattices containing 128^3 sites. The corresponding densities are 2.38×10^{-3}, 4.77×10^{-3}, and 0.54×10^{-3} occupied sites per lattice site, respectively. The results shown in Fig. 8 indicate that the effective value for the exponent z [$S(t)\sim t^z$] increases with increasing particle concentration. However, these results also indicate that the effective value of z is probably not more than about 10% larger than the value which would be obtained in the zero concentration limit for $\rho=4.77\times10^{-3}$ (10 000 particles).

Figure 9 shows the cluster-size distributions obtained from simulations with $\delta=-0.5$ and 10 000 particles per 128^3 lattices. Figure 9 shows that at intermediate times the cluster-size distribution can be described in terms of a power law with an exponent τ of about 1.0. Consequently, it appears that the exponent τ can have an effective value in the range $1.0\leq\tau\leq2.0$ at intermediate times in reaction-limited cluster-cluster aggregation, depending on the physical details associated with the aggregation process.

The reaction kernel describing reaction-limited cluster-cluster aggregation processes is a quantity of considerable interest.[23] Simulations such as those described above can be used to determine the values of the elements in our effective reaction kernel (K_{ij}) by measuring how often clusters of size i combine with clusters of size j to form clusters of size $i+j$.[31] Results from a large number of simulations are required to reduce statistical uncertainties to reasonable levels. Figure 10 shows elements of the reaction kernel (K_{ij}) of the type K_{ii} [Fig. 10(a), diagonal elements] and of the type K_{1j} [Fig. 10(b), the most off-diagonal elements] as a function of time during the simulations. Additional details concerning the determination of an effective reaction kernel from such simulation results are given in Refs. 30 and 31. The results shown in Fig. 10 were obtained from 1650 simulations, each carried out with 10 000 particles on 128^3 lattices (i.e., a total of 1.65×10^7 particles). The results shown in Fig. 10 indicate that the elements of the binary reaction kernel are time-independent quantities at all times for which data with reasonably small statistical uncertainties exist. In the case of diffusion-limited aggregation an ini-

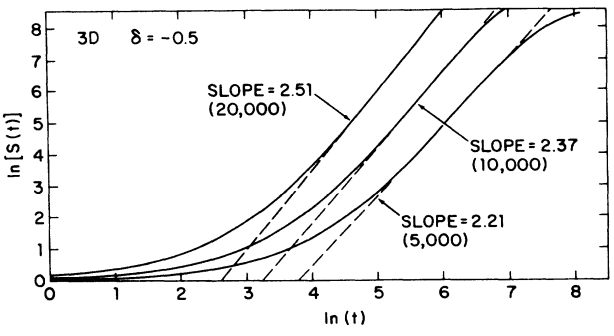

FIG. 8. Dependence of the mean cluster size (S) on time obtained from 3D simulations carried out using model II with three different particle densities (5000, 10 000, and 20 000 particles on 128^3 lattices).

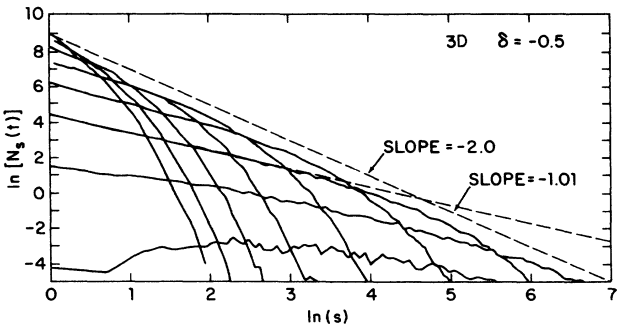

FIG. 9. Time-dependent cluster-size distributions obtained from 3D simulations carried out using model II with $\delta=-0.5$ (approximately $-1/D$). Results are shown for the times (t) of 2.75, 8.44, 25.9, 79.7, 245, 752, 2310, and 7100.

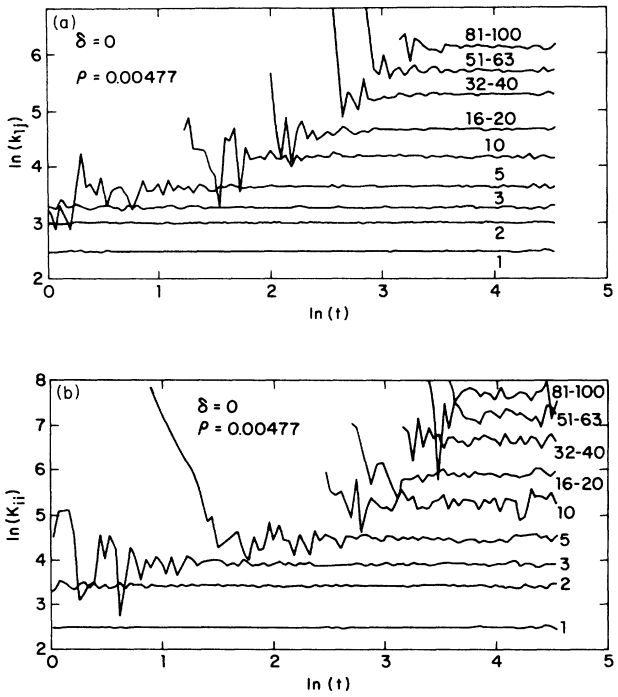

FIG. 10. Time dependence of the elements K_{ii} (a) and K_{1j} (b) obtained from 3D simulations using model II with 10 000 particles on 128^3 lattices. A value of 0 was used for the exponent δ in Eq. (10).

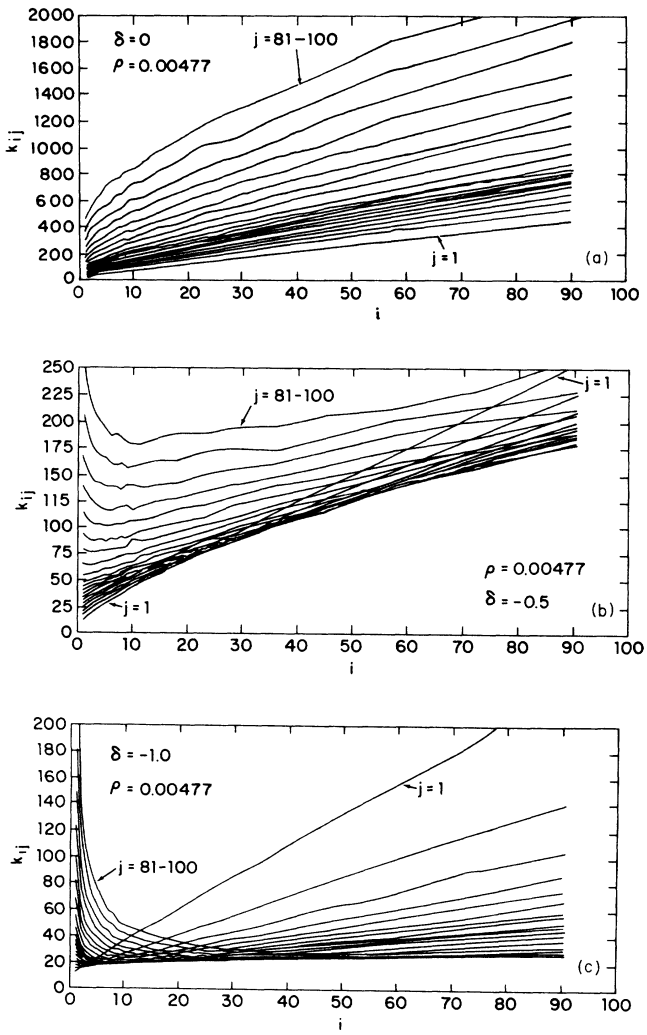

FIG. 11. Elements of the reaction kernel (K_{ij}) obtained from simulations using model II. Each curve shows K_{ij} as a function j for $i=1$, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11–12, 13–15, 16–20, 21–25, 26–31, 32–40, 41–50, 51–63, 64–80, and 81–100. (a) The results obtained from simulations carried out using 10 000 particles on 128^3 lattices with δ [Eq. (10)] set equal to 0. (b) and (c) The results obtained from similar simulations carried out with $\delta=-0.5$ and -1.0, respectively.

tial transient behavior is observed resulting from the establishment of a "depletion zone" around each cluster.[31,32] In the reaction-limited case this effect does not occur since diffusion is much faster than cluster addition.

Since the reaction kernel elements $K_{ij}(t)$ are (almost) time-independent quantities, they can be averaged over the whole simulation to reduce the statistical uncertainties. Figure 11 shows the results obtained in this way for $\delta=0$, -0.5, and -1.0. The scaling properties of the reaction kernel[33,34] can be used to obtain important information about reaction kinetics, even if the full Smoluchowski[35] equation cannot be solved analytically. Consequently, it is important to determine these scaling properties since they can be used to help understand the observed kinetics.

Reference 30, which contains a preliminary account of this work, shows the dependence of $\ln(K_{ii})$ on $\ln(i)$ and the dependence of $\ln(K_{1j})$ on $\ln(j)$ obtained from the simulations carried out with $\delta=0$ (RLCCA). The results shown in Ref. 30 indicate that $K_{ii}\sim i^{\lambda}$ ($\lambda\sim 1.15$) and $K_{1j}\sim j^{\mu}$ ($\mu\sim 0.89$) under the conditions of our simulations. In the asymptotic limit ($j>0$) we would expect the exponent μ to have a value of 1.0. Consequently, the value obtained for μ should be regarded as an effective exponent. Similarly, the value of 1.16 obtained for λ should also be regarded as an effective exponent and the limiting ($\rho\to 0$, $i\to\infty$) value may be substantially different. In particular, we cannot rule out an asymptotic value of 1.0 for λ on the basis of these results.

In Fig. 12 we display the quantities $1/2(i^{\delta'}+j^{\delta'})K_{ij}^0$ for $\delta'=-0.5$ and -1.0 for values of i and j in the range 1–100. Here K_{ij}^0 is the element of the reaction kernel (K_{ij}) for $\delta=0$. A comparison of Figs. 12(a) and 12(b) with 11(b) and 11(c), respectively, indicates that

$$K_{ij}^{\delta}\sim\tfrac{1}{2}(i^{\delta}+j^{\delta})K_{ij}^0 \ . \tag{12}$$

Here K_{ij}^{δ} is the rate constant for addition of clusters of size i to clusters of size j for model II in which $G(s)\sim s^{\delta}$. Equation (12) could be expected if cluster structure did not depend on δ. In fact,[30] the effective fractal dimension does change with δ, but this effect is relatively small for negative values of δ. Consequently, Eq. (12) provides a reasonably good approximation to the reaction kernel for $\delta<0$.

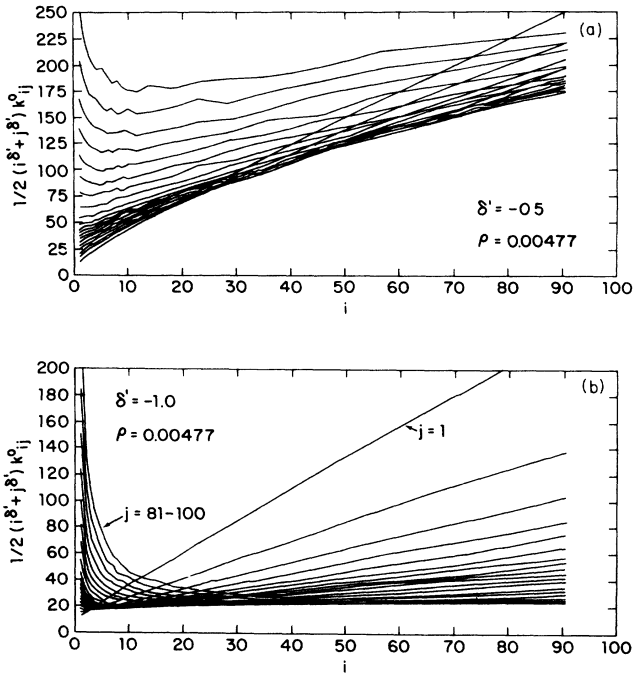

FIG. 12. Dependence of $[(i^{\delta'}+j^{\delta'}]/2)K_{ij}^0$ on i and j. Here K_{ij} is the ij deviant of the reaction kernel obtained using model II with $\delta=0$. (a) The results obtained with $\delta'=-\frac{1}{2}$ and (b) the results obtained with $\delta'=-1$. The results shown in (a) and (b) should be compared to those shown in Figs. 11(b) and 11(c), respectively.

C. Model III

Model III simulates RLCCA in the zero density limit. In this model we start with a list of particles (in most of our simulations 200 000 particles were used); pairs of particles are selected at random from the list and brought into contact with each other. If both particles are isolated particles (not part of a cluster) they are joined and returned to the list as a binary cluster. As the simulation proceeds many of the randomly selected particles, which have other particles associated with them, will be part of a cluster. If the two particles belong to the same cluster, another selection is made. If they belong to different clusters, the two clusters are rotated to random orientations (for the off-lattice model only) and the two particles are placed into contact with each other. If no overlap occurs between any pair of particles in either of the two clusters, the two clusters are combined in this configuration and returned to the list. This process is continued until the largest cluster size exceeds a predetermined value ($s_{\max}$) or until only a single cluster remains. This model can be made time dependent by incrementing the time by a constant amount each time a pair of particles is selected from the list (whether or not their associated clusters are combined). Simulations were carried out using both a cubic lattice and off-lattice version of this model.

Figure 13 shows the dependence on $\ln(R_g/s^{1/2})$ obtained from both the lattice and off-lattice versions of model III. The lattice model results were obtained using 200 000 particles in each simulation and the simulations were stopped where the maximum cluster size exceeded 300 or 10 000 particles. For $s_{\max}=300$ the results from 1000 simulations were averaged and for $s_{\max}=10\,000$ the results from seven simulations were averaged. The effective exponent β [Eq. (11)] was found to depend slightly on $s_{\max}$ and values of 0.458 and 0.453 ($D_\beta=2.18$ and 2.21, respectively) were found for $s_{\max}=300$ and 10 000. Results obtained from the off-lattice model with $s_{\max}=300$ and 3000 are shown in Fig. 13(b). For the case $s_{\max}=3000$ a value of about 0.478 was found for β ($D_\beta\sim2.09$). The development of a higher fractal dimensionality for larger values of $s_{\max}$ is related to the evolution of a broader cluster-size distribution as the aggregation process proceeds.

The time dependence of the mean cluster size $[S(t)]$ obtained from 22 off-lattice simulations, each using 200 000 particles, is shown in Fig. 14. In these simulations the maximum cluster size ($s_{\max}$) was 3000. These simulations are less subject to finite-size effects than those carried out using models I or II. Although the results are consistent with a power-law growth in the mean cluster size [$S(t)\sim t^z$ with $z\sim4.2$; Fig. 14(a)] the dependence of $S(t)$ on t can be fit by an exponential growth form over a longer time range [Fig. 14(b)]. Similar results obtained from the lattice model are shown in Fig. 15.

Both the lattice and off-lattice versions of model III have been used to obtain time-dependent cluster-size distributions $N_s(t)$. Some of the results from the off-lattice model have been presented earlier[30] and are consistent with a power-law cluster-size distribution [Eq. (8)] characterized by an exponent τ with a value of about 1.7. Figure 16 shows similar results obtained from the lattice model. In this case our results indicate that $N_s(t)\sim s^{-\tau}$ with τ having a value of about 1.9. The results obtained from both the lattice and off-lattice versions of model III are quite similar to those obtained from model I (Fig. 2) with $\gamma=-\frac{1}{2}$ and from model II [Fig. 7(b)] with $\delta=0$.

An important quantity in understanding the aggregation kinetics associated with model III is the probability (P_{ij}) that two particles in clusters of size i and j, respectively, can be brought together without overlap between any pair of particles in the two clusters. Figure 17 shows some of the results obtained from both the lattice and off-lattice versions of model III for pairs of clusters in the size range $1\le i\le100$ and $1\le j\le100$. These simulations indicated that $P_{ii}\sim i^{-0.88}$ for the off-lattice model and $P_{ii}\sim i^{-0.84}$ for the lattice model. These results would correspond to values for the exponent λ describing the dependence of the diagonal elements of the reaction kernel ($K_{ii}\sim i^{\lambda}$) of 1.12 and 1.16, respectively, in good agreement with the results obtained from model II ($\lambda=1.16$, Ref. 30). For the off-lattice model the dependence of $\ln(P_{ii})$ on $\ln(i)$ was linear for all cluster sizes (i) in the range $1\le i\le100$. For the lattice model, the effective value of λ decreases (increased in magnitude) with increasing cluster size.

Because of the possibility that the asymptotic value of

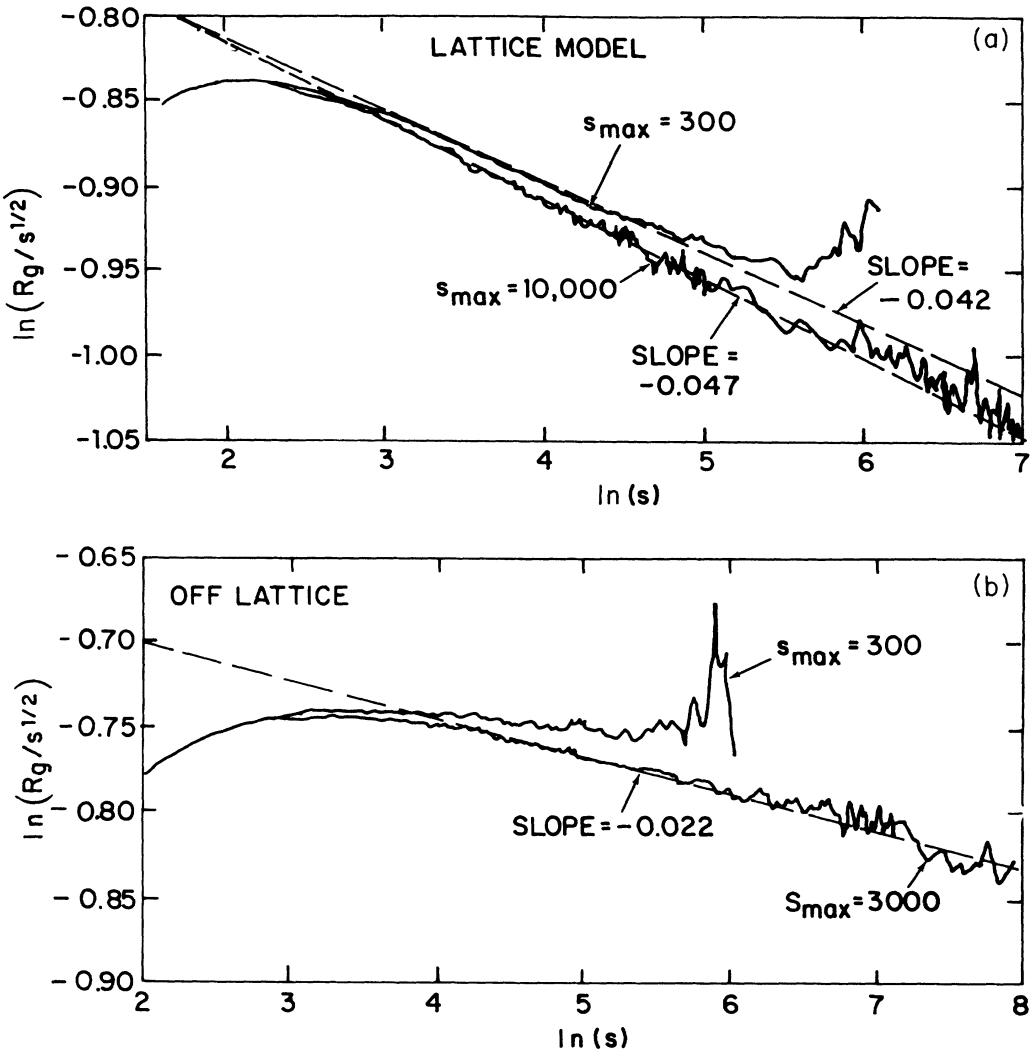

FIG. 13. Dependence of $\ln(R_g/s^{1/2})$ on $\ln(s)$ obtained from the lattice version (a) and the off-lattice version (b) of model III with the exponent ε set to a value of 0. The simulations carried out to obtain these results were started out with 200 000 particles and were terminated when the largest cluster exceeded a size of s_{max}. In these figures R_g is the cluster radius of gyration and s is its size (number of particles or occupied lattice sites).

λ might be 1.0[23] a considerable effort was made to extend these results to larger cluster sizes. For the lattice version of model III, 377 simulations were carried out, each using 200 000 particles with a value of 3000 for s_{max}. For the off-lattice model 123 simulations each using 200 000 with a value of 3000 for s_{max} were carried out. The results from these simulations, which were presented in Ref. 30, indicate that $P_{ii} \sim i^{-0.88}$ for the off-lattice model for clusters in the size range $1 \leq i \leq 1000$ particles. From the lattice-model simulations we found that $P_{ii} \sim i^{-0.95}$ for clusters in the size range $100 \leq i \leq 1000$ lattice sites. This result is consistent with the idea that the asymptotic value for λ might be 1.0. However, it is apparent that if this is the correct asymptotic value the approach to this limiting ($i \rightarrow \infty$) behavior is quite slow. For both the lattice and off-lattice versions of model III our results are consistent with the idea that P_{1i} approaches a constant value with increasing i.

It is possible that in real cluster-cluster aggregation (at least for reasonably small cluster sizes where translation is more important than internal modes) the rate at which two clusters join may depend on the frequency with which they "collide" as well as on the amount of time they spend together. It is also reasonable to suppose that the collision frequency for clusters i and j will be given by $v(i,j)=\mathcal{D}_i+\mathcal{D}_j$ when $\mathcal{D}_i$ and $\mathcal{D}_j$ are the cluster diffusion coefficients. Consequently, versions of model III have been developed in which pairs of particles (i and j) are selected at random with probabilities $(s_i^{\varepsilon}+s_j^{\varepsilon})$ where s_i and s_j are the sizes of the clusters containing particles i and j, respectively. Figures 18 and 19 show some of the results obtained from simulations carried out with $\varepsilon=-\frac{1}{2}$ (approximately $-1/D$). Figure 18 shows the dependence of $\ln(R_g/s^{1/2})$ on $\ln(s)$ for both the lattice and off-lattice models. As expected,[20,32] the effective fractal dimensionality ($D_\beta=1/\beta$) is slightly smaller for

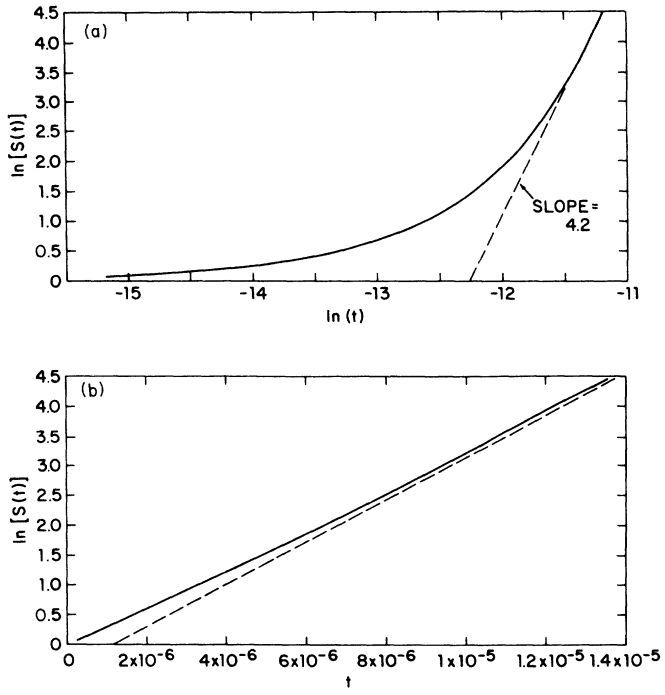

FIG. 14. Time dependence of the mean cluster size $[S(t)]$ obtained using the off-lattice version of model III with $\varepsilon=0$.

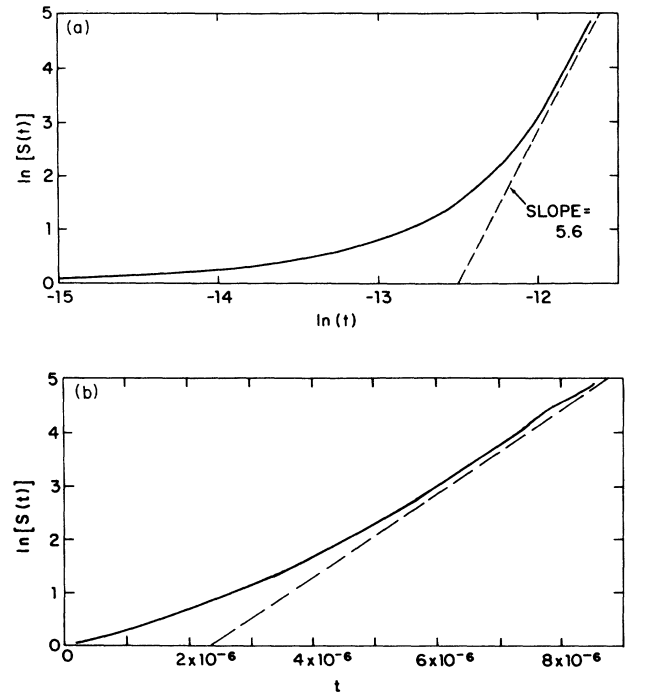

FIG. 15. Time dependence of the mean cluster size $[S(t)]$ obtained from the lattice version of model III with $\varepsilon=0$. These results were obtained from 20 simulations each using 200 000 occupied lattice sites to represent particles.

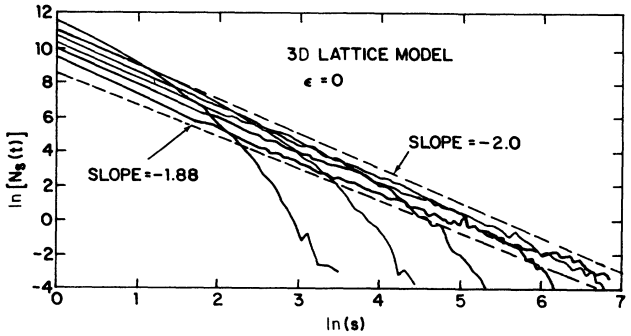

FIG. 16. Cluster-size distributions $N_s(t)$ obtained from the on-lattice version of model III with $\varepsilon=0$. Each curve shows the cluster-size distribution at the stage where the total number of clusters has been reduced from $N_0=200\,000$ to $N_0/2^n$, with $n=1-6$.

$\varepsilon=\frac{1}{2}$ and than it is for $\varepsilon=0$. Figure 19 shows the time-dependent cluster-size distributions $N_s(t)$ obtained from both the lattice and off-lattice models. These cluster-size distributions (at intermediate times) have an approximately power-law form with an effective exponent τ of close to 1.0. These cluster-size distributions should be compared with those shown in Fig. 9 (model II with $\delta=-\frac{1}{2}$), which also give an effective value of about 1.0 for τ.

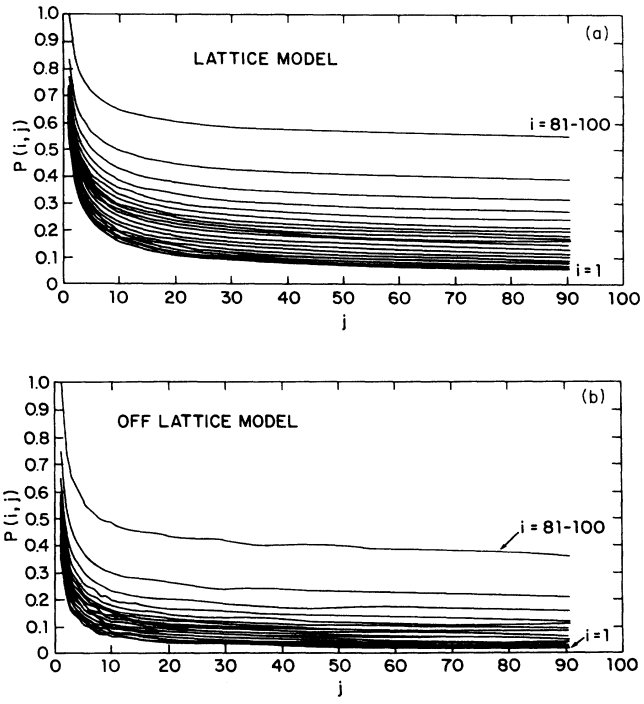

FIG. 17. Dependence of the probabilities P_{ij} that two clusters of size i and j can be joined by bringing two randomly selected particles (one from each cluster) into contact without overlap of the two randomly oriented clusters. (a) The results obtained from the lattice version of model III with $\varepsilon=0$, (b) the results obtained with the off-lattice model (also with $\varepsilon=0$).

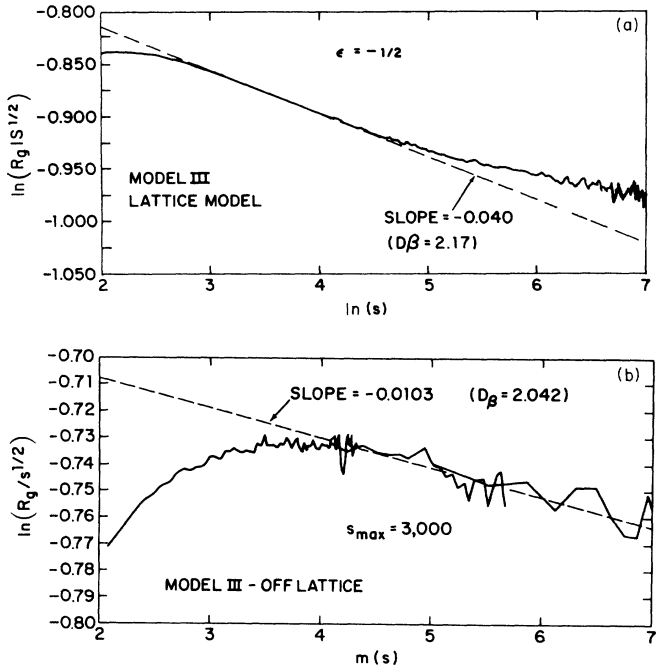

FIG. 18. Dependence of $\ln(R_g/s^{1/2})$ on $\ln(s)$ for clusters generated using model III with $\varepsilon=-\frac{1}{2}$. (a) The results obtained from the lattice model, and (b) results obtained using the off-lattice model. In each case s_{max} was 3000 and the results were obtained by averaging a number of simulations starting with 200 000 particles.

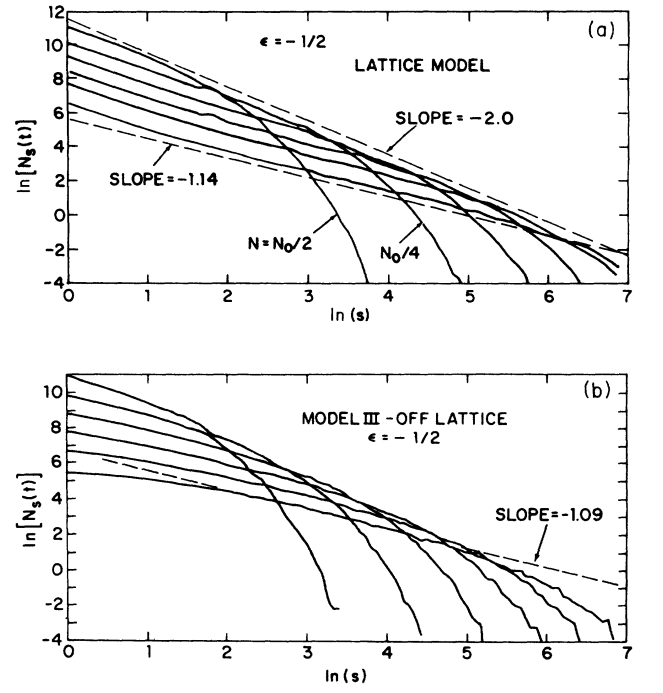

FIG. 19. Time-dependent cluster-size distributions obtained from the lattice version (a) and off-lattice version (b) of model III with $\varepsilon=-\frac{1}{2}$. In each case the curves correspond to cluster-size distributions obtained at the stage where the number of clusters had been reduced from an initial value of $N_0=200\,000$ particles to $N_0/2, N_0/4, \ldots, N_0/64$ ($N_0/2^n$, $n=1-6$).

The conditions represented by model II with $\delta=-\frac{1}{2}$ and model III with $\varepsilon=-\frac{1}{2}$ can also be approached with a modified version of model I. In this model we use a value of $-\frac{1}{2}$ for the exponent γ and the probability that two adjacent clusters will combine before one of them is randomly selected and move is now given by $p=\sigma$ instead of Eqs. (5) or (6). Some results from this model (model Ia) are shown in Fig. 20. The dependence of $\ln[S(t)]$ on $\ln(t)$ suggests that $S(t)\sim t^z$, with a value of about 2.3 for the exponent z. Simulations carried out using the off-lattice version of model III with a value of $-\frac{1}{2}$ for ε give similar results and the effective value of z obtained from these simulations is about 2.25 (Fig. 21).

III. DISCUSSION

We have investigated three models for reaction-limited aggregation. All three models give results which are in good qualitative agreement with each other. Because of finite-size effects, statistical uncertainties, and in some cases finite concentration effects, the qualitative results are not in perfect agreement. Under conditions in which the probability that two clusters will combine is proportional to the amount of time that they spend in contact with each other, our results indicate that the mean clus-

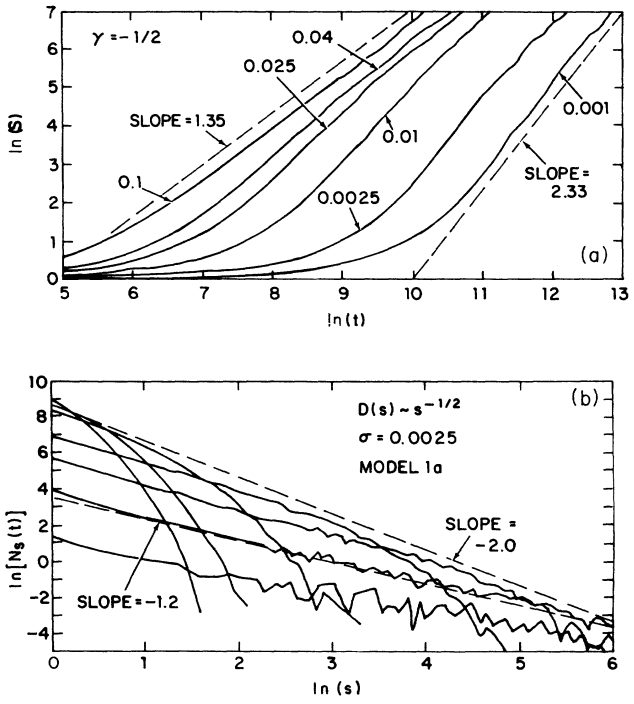

FIG. 20. Dependence of the mean cluster size $[S(t)]$ (a) and cluster-size distributions $[N_s(t)]$ (b) on time obtained from 3D simulations carried out using model I with γ set to a value of $-\frac{1}{2}$ (approximately $-1/D$). (a) Results for several different values of the reactivity parameter σ [Eq. (6)]. (b) The time-dependent cluster-size distribution for a small value of σ (10^{-3}) at the times 555.9, 2019, 7335, 26 650, 50 780, 76 790 and 184 500.

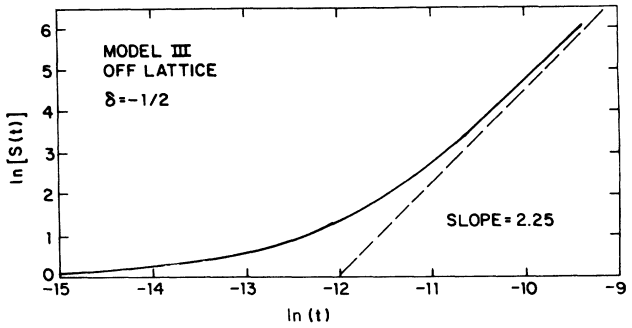

FIG. 21. Dependence of the mean cluster size $[S(t)]$ on time obtained from the off-lattice version of model III with $\delta=-\frac{1}{2}$. These results were obtained from 20 simulations each using 200 000 particles.

ter size $S(t)$ grows exponentially with time, $S(t)\sim e^{at}$ for large t. We cannot, on the basis of our simulation results rule out power-law growth, $S(t)\sim t^z$, or gelation, $S(t)\sim(t_g-t)^{-\gamma}$. Exponential growth is in agreement with the theoretical results of Ball *et al.*[23] and a variety of experiments under slow aggregation conditions.[15,16] However, it is as difficult to distinguish between power-law growth with a large-z exponent, exponential growth, and gelation experimentally as it is in our computer simulations. If the probability that two clusters combine is proportional to the number of times that they collide with each other, then we find power-law growth $[S(t)\sim t^z$ with z in the range 2.0–2.5] for the mean cluster size if the clusters are rigid.

In all cases the cluster-size distribution at intermediate times can be described in terms of a power law $N_s(t)\sim s^{-\tau}$, at least to a good approximation. If the probability that two clusters will join depends only on the time that two clusters remain in contact with each other, then our simulation leads to a value for the exponent τ which is close to 1.75. On the other hand, if the probability that two clusters will combine is proportional to the number of times which they collide with each other, then we find a value for τ which is close to 1.0.

Weitz *et al.*[15] have determined the exponent τ under slow aggregation conditions. They find an exponent τ close to 1.5 for the aggregation of colloidal gold particles. Schaefer *et al.*[16] found a similar value for τ for aggregation of silica colloids. Similar results have been found in other systems. For example, von Schulthess *et al.*[36] have found a value of 1.40 ± 0.15 for τ associated with the antibody aggregation of antigen-coated polystyrene latex particles. However, the structure of these aggregates is less well characterized than that of the gold particle aggregates[15] and the clusters observed are relatively small. Similarly, Martin[37] and Rarity and Pusey[38] have found values for τ close to 2 in other systems undergoing what is believed to be reaction-limited aggregation.

The aggregation of large floppy clusters might be expected to depend only on the time that two clusters spend in contact with each other since the number of contacts between the two clusters would then be controlled by local internal motions which would be independent of the cluster size. Under these conditions our results would indicate that the exponent τ should have a value of about 1.75. The aggregation of rigid clusters should depend only on the number of times that their Brownian trajectories bring them into contact with each other. Consequently, we might expect a value for τ which is close to 1.0 for the aggregation of rigid clusters. In practice, we might expect an effective value for τ in the range $1.0<\tau<2.0$ with smaller values of τ for more rigid (or smaller) clusters. Consequently, the smaller values for τ obtained for the slow aggregation of colloidal gold than for the slow aggregation of colloidal silica might be a result of the higher rigidity and/or smaller size of the colloidal gold aggregates. For model I we have carried out simulations using values of the parameter σ [Eq. (6)] or σ' [Eq. (5)] in the range $10^{-3}\leq\sigma'\leq1$.

This has allowed us to investigate the crossover from diffusion-limited to reaction-limited aggregation. For real systems the effective value of σ or σ' might be much lower than 10^{-3}. In fact, values as low as or lower than 10^{-3} are quite reasonable. Nevertheless, for systems of the size used in our simulations a value of 10^{-3} for σ' or σ is sufficient to closely approach the reaction-limited regime, and for values of σ or σ' close to 10^{-3} results very similar to those generated by model II or model III were obtained. For large systems smaller values of σ would be required. In principle, diffusion-limited aggregation will always be seen in infinite systems which are sufficiently dilute at long enough times. However, such conditions may be difficult to attain in practice and other effects such as settling under gravity, convection, mechanical instability of large clusters, etc., may prevent the diffusion-limited regime from being attained.

Of the models discussed here only model I takes into account the fact that all possible bonding configurations might not be geometrically accessible. However, this model overestimates these effects since no cluster rotations are allowed, thus restricting the ability of two clusters to interpenetrate. Similarly, model II does not allow clusters to rotate but the "zero-dimensional" trajectories allow pairs of clusters to find bonding configurations which would be inaccessible in model I. In model III all possible configurations can be found, though some of them might be geometrically inaccessible. The magnitude of these effects is difficult to assess. However, the similarities between the results obtained from these models suggest that they are not large. We would expect that the effects of geometric inaccessibility would be larger in two-dimensional systems and smaller in higher-dimensional systems. It would be possible to develop an off-lattice model in which only accessible bonding configurations were selected. However, such a model would be cumbersome and it would not be possible to obtain results from simulations carried out on the scale presented here. Consequently, it would probably not be possible to reduce finite-size effects and statistical uncertainties to a satisfactory level in order to make meaningful comparisons with models I, II, and III of this work.

ACKNOWLEDGMENTS

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