Colloid aggregation with short-step diffusion: A more realistic model in the reaction limit

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A computer model of reaction-limited colloid aggregation with diverse step lengths, allowing us to reach steps as short as one-twentieth of the diameter, together with very low sticking probabilities (0.001), is studied. In this paper a description is made of the algorithm, its importance, and the results obtained from it.

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In recent years an increasing interest has evolved in the growth and formation of random structures under nonequilibrium conditions. Among these problems, aggregation phenomena have attracted considerable interest because of the possibility of substantial practical benefits and their impact on different areas of science, such as aerosol formation, droplet formation in clouds, polymerization processes, and colloid aggregation. Computer simulations have played an important role in the development of this area. In fact, much of what we know about nonequilibrium growth processes has come from computer simulations. They are invaluable tools that can be used to test ideas concerning the behavior of experimental systems.

Shortly after the seminal work on diffusion-limited aggregation by Witten and Sander [1], in which the growing cluster was fixed in space, Meakin [2] and Kolb, Botet, and Jullien [3] introduced the more realistic clustering of clusters model for colloid aggregation, in which the clusters as well as the particles were allowed to diffuse. Later on, researchers identified two limiting regimes of the irreversible aggregation process: rapid, diffusion-limited colloid aggregation (DLCA), for which any collision between the colloidal particles results in the formation of a bond, and slow, reaction-limited colloid aggregation (RLCA), for which there is only a small probability for the particles to form a bond. Although for DLCA there is a clear correspondence [4] between experimental results and computer simulations, for RLCA there have been serious difficulties in trying to match the two sets of results. The fractal dimension is perhaps the only quantity for which the agreement between experiments and simulations is good, being around 2.1. Besides morphology, the other set of interesting results lies in the kinetics of the aggregation process. The basic concerned quantities are the cluster size distribution $N_s(t)$, the weight-average cluster size $S(t)$, and the number of clusters $N_c(t)$ [related to the number-average cluster size $S_n(t)$ by $S_n(t)=N_0/N_c(t)$, where N_0 is the number of initial colloidal particles].

Experimentally, after some transient time the cluster size distribution function decreases algebraically with the exponent τ: $N_s(t)\sim s^{-\tau}g(s/S(t))$, where g is a cutoff function that decays rapidly to zero for values of the argument greater than 1, while it takes the value of 1 for arguments smaller than 1. Most researchers [5–10] find values for τ near 1.5 in a wide variety of systems, although some others [11–13] have found values closer to 2 in some other systems, supposedly undergoing RLCA. As for the average cluster size, most investigations [7–10,14] agree on an exponential growth with time, at least for the initial stages of the aggregation, crossing over to an algebraic growth at later times [10,15]. At this point we feel it is important to mention the theory by Ball *et al.* [16] that indicates an exponent $\tau=1.5$ and an exponential growth.

On the opposite side, the computer simulations in three dimensions [17–19] have produced a whole variety of exponents τ but seldom a value of 1.5, and in many of the cases the exponents were varying with time. Meakin and Family [18], for example, report varying values of τ closer to 2 or to 1 than to 1.5, while the author [19] obtains a diminishing exponent τ for a lattice simulation with step lengths equal to the lattice spacing (i.e., the particle size). It should be mentioned, however, that the authors of Ref. [18] mainly use two algorithms [20,21] that are related to RLCA, but that have not been shown to coincide exactly with the original RLCA algorithm, that is, the DLCA algorithm plus a small sticking probability at encounters between colloidal particles.

A careful analysis of previous simulations of DLCA and RLCA reveals that two important ingredients are missing from the computer simulations, namely, (i) the true step length of a diffusing Brownian particle or cluster and (ii) the rotational diffusion of the clusters. Although for DLCA these factors should not matter because there is bonding at first contact, in RLCA there are many encounters between two colloidal particles belonging to two clusters before they go away, coming from the very short steps of the Brownian movement [22] and from the very small angles of the rotational diffusion. This rapid hitting of the two colloidal particles may change the results of the simulations and hopefully would lead us to the universal experimental results. That is why it is important to consider newer simulations in which these factors are taken into account, and to discriminate between them and even discard them if they are unimportant.

In the present paper I would like to reconsider the RLCA algorithm, now with an emphasis in reducing the step length, which in general should be much shorter than the diameter [22]. An off-lattice model needs to be used in this case, if we want to vary the step length continuously. In all these colloid aggregation algorithms in the continuum, one tests for overlapping whenever a cluster moves; it is therefore seen that a huge amount of computing time would be spent in this testing, when using very short steps. To increase the speed of the computation it was necessary to divide the clusters into two categories: (1) those which have one or more nearby neighboring clusters (with a suitable definition for this vicinity) and (2) those which have not. These last clusters can be moved with steps of a diameter or longer in size, even if the fundamental basic step is very short, by invoking a central limit theorem. So, we consider a three-dimensional cubic box of side L, with periodic boundary conditions, where at some intermediate time a collection of clusters made of barely touching spheres diffuses randomly. The step length of clusters 2 is the diameter D of the particles and that of clusters 1 is D/F, with F greater than 1. A record was kept, at all times, of the sum of the diffusion coefficients for the two cluster categories (Σ_1 and Σ_2), where the diffusion coefficient for a cluster of size s varies as $D(s) \sim s^{-1/d_f}$, where $d_f = 2.1$ is the accepted value for the fractal dimension of RLCA clusters. This last result states that the hydrodynamic radius of a cluster is proportional to its radius of gyration, which was demonstrated experimentally by Wiltzius [23]. A cluster category is picked first; category 1 with probability $P_1 = \Sigma_1 F^2/(\Sigma_1 F^2 + \Sigma_2)$ and category 2 with probability $P_2 = 1 - P_1$. If category 2 was selected, a cluster 2 is picked at random and moved by one step of a diameter in size, only if a random number X uniformly distributed in the range $0 < X < 1$ satisfied the condition $X < D(s)/D_{\max}$, where s is the size of the selected cluster and $D_{\max}$ is the maximum diffusion coefficient for any cluster in the system. After each cluster has been selected the time is incremented by $1/(D_{\max} N_c)$, whether or not the cluster is actually moved. If, on the contrary, category 1 was selected, a similar thing happens except that now the time increment is given by $1/(D_{\max} N_c F^2)$. If some spheres of the moving cluster 1 attempt to overlap spheres of another cluster, the cluster either sticks (and is merged) to the other with probability P_0—taking care to pull it back along the same line, such that only two spheres belonging to the two clusters barely touch—or it is put back to its original position with probability $1 - P_0$.

In each simulation described here, 8000 initial particles of diameter $D = \sqrt{3}$ were used in a cube of size $L = 200$.

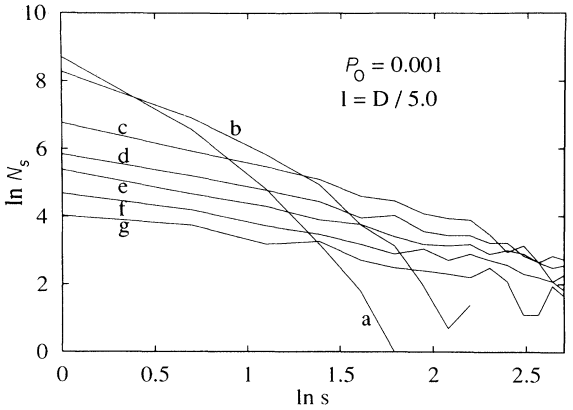

FIG. 1. A log-log plot of the number of clusters of size s, N_s, vs s for the times (curve a) 1808, (b) 4915, (c) 22 026, (d) 36 316, (e) 46 630, (f) 59 874, and (g) 76 880. The initial slope (curve c) is -1.2, while those for curves d–g are (d) $-1.16(0.09)$, (e) $-1.05(0.07)$, (f) $-0.96(0.09)$, and (g) $-0.85(0.15)$.

The sticking probability was always put at the value 0.001, because previous work [19] has shown that with such P_0 we are well inside the RLCA regime. Three step lengths were employed: $D/1.4$, $D/5.0$, and $D/20.0$. Five simulations were performed for each of the 1.4 and 5.0 cases, but only two simulations were done for the 20.0 case. The simulations were stopped when a cluster reached a maximum size of 800, and no signs of gelation were shown at that time in any of the cases. A record was kept of (a) the radius of gyration as a function of size for all the clusters formed, (b) the number of clusters in the system as a function of time, (c) the weight-average cluster size as a function of time, and (d) the number of clusters of size s as a function of s for different times. Each 1.4, 5.0, and 20.0 simulation took about 21, 43, and 144 h of a Cray Y-MP computer processor, respectively.

In Table I are shown the values of the fractal dimension for each of the 12 simulations reported here, obtained from the inverse of the slopes of the log-log plots of the radius of gyration versus size. All the errors (in parentheses) shown in this paper correspond to twice the standard deviation. We see that the average fractal dimension for the $D/1.4$ case falls within 3% of the accepted value of 2.1. However, we also notice that the average fractal dimension $\bar{d}_f$ decreases a little when we decrease the step length, although it is not possible to state this conclusively due to the high dispersion of the data, which is a consequence of not having used many particles.

In Fig. 1 we see a log-log plot of $N_s(t)$ vs s at different times, for one of the $D/5.0$ simulations. This graph is

TABLE I. The fractal dimension d_f and its average $\bar{d}_f$ for the different runs with step length l.

	d_f					
l	run 1	run 2	run 3	run 4	run 5	$\bar{d}_f$
$D/1.4$	2.23(0.09)	1.86(0.07)	2.11(0.06)	1.99(0.08)	2.01(0.09)	2.04
$D/5.0$	2.04(0.08)	1.94(0.08)	2.02(0.07)	1.96(0.07)	2.15(0.08)	2.02
$D/20.0$	1.87(0.07)	2.13(0.08)				2.00

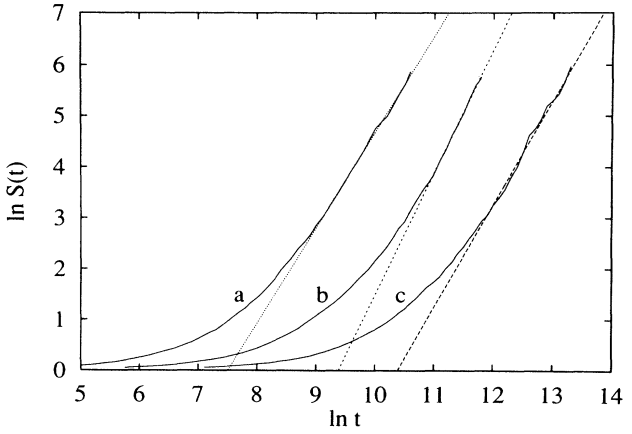

FIG. 2. A log-log plot of $S(t)$ vs t for three different runs, with step lengths of (curve a) $D/20.0$, (b) $D/5.0$, and (c) $D/1.4$.

typical of all the simulations performed and shows the following features: after some transient time for which there is a clear curvature (curves a and b), the cluster size distribution function starts to develop a straight line (curve c). Unfortunately, the slope of this line does not maintain but keeps decreasing during the whole aggregation process. This is contrary to most experimental results, for which the slope is maintained at the value 1.5.

An interesting effect coming from the different step lengths is observed in Fig. 2, where log-log plots of the weight-average cluster size versus time for the three different step lengths are shown. We see that $S(t)$ appears to grow exponentially with t at the beginning, crossing over to an algebraic growth at later times [$S(t) \sim t^z$]. However, the effect of decreasing the step length translates into a decrease of the whole aggregation time, similar to what was happening in previous simulations [19] when an increase of the sticking probability was made. In fact, by comparing the curves in Ref. [19] with those in Fig. 2, we see that the decrease in step length from $D/1.4$ all the way to $D/20.0$ corresponds to an increase of more than 10 times the sticking probability. This indeed corroborates that, when the step length is much shorter than the diameter, two nearby colloidal particles perform many encounters before they go away. It is reasonable, therefore, to expect also a decrease in the fractal dimension.

TABLE II. The limiting slopes of the log-log plots of $S(t)$ (exponent z) and $N_c(t)$ vs t, for the different runs with step length l.

	Exponent z					
l	Run 1	Run 2	Run 3	Run 4	Run 5	Average
$D/1.4$	2.0		2.4	2.0		2.13
$D/5.0$	2.4		1.9	2.0	2.1	2.10
$D/20.0$	1.9	2.2				2.05
	Limiting slope of $N_c(t)$					
l	Run 1	Run 2	Run 3	Run 4	Run 5	Average
$D/1.4$	−2.0	−1.9	−1.9		−2.0	−1.95
$D/5.0$	−2.1	−1.9	−1.8	−1.9	−1.8	−1.90
$D/20.0$	−1.8	−1.8				−1.80

The log-log plots of the number of clusters versus time, displayed in Fig. 3, show the same effect in time as in Fig. 2. From Figs. 2 and 3 it is possible to see that the final slopes for the $N_c(t)$ curves are roughly the negatives of those for the $S(t)$ curves. This indicates that, at the end of the aggregation, $S(t) \sim S_n(t)$. Due to not having used a very large number of particles, the final slopes for the $S(t)$ and $N_c(t)$ curves are not well defined in some simulations. In Table II are shown these limiting slopes, for those cases in which it was possible to define a straight line. From the average values, we see that the exponent z lies around 2.1.

Finally, in Fig. 4 are shown the semilogarithmic plots of $S(t)$ and $N_c(t)$ as a function of t, for one of the simulations with a step length of $D/5.0$. They were plotted in order to check that the weight-average cluster size really starts to increase exponentially. This graph is also typical of all the simulations performed, for all the step lengths, in that the exponential growth occurs only for a very short fraction of the aggregation time. The only major difference, already mentioned, between similar graphs

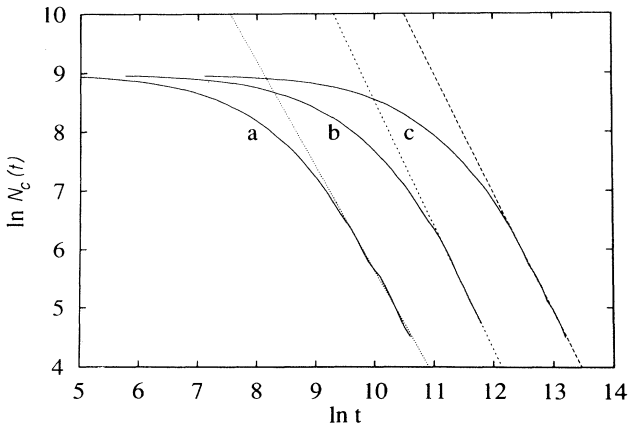

FIG. 3. A log-log plot of $N_c(t)$ vs t for the same three runs of Fig. 2.

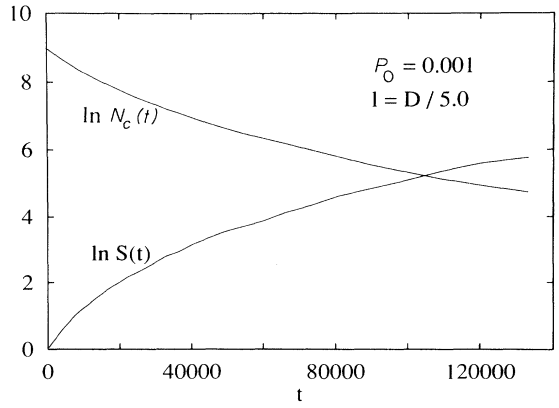

FIG. 4. A semilogarithmic plot of $S(t)$ and $N_c(t)$ vs t, for one of the runs with $l = D/5.0$.

with different step lengths lies in the size of the aggregation time. Nonetheless, it is possible to see that the initial slope for $S(t)$ is roughly twice as big as the negative of the initial slope for $N_c(t)$, and this was checked in all the 12 simulations performed. This now indicates that, at the beginning of the aggregation, $S(t) \sim [S_n(t)]^2$.

In conclusion, it appears that the sole inclusion of short steps is not enough to produce a constant exponent τ, with the value of 1.5. We also need an exponential growth of the mean cluster size, if not for the whole aggregation time at least for a good part of it [10,15]. A moment of reflection shows that, in order to have a constant exponent τ and not a decreasing one, we need a mechanism that would increase the speed of the aggregation of medium-sized and big clusters. This mechanism would also make the mean cluster size grow faster, perhaps exponentially fast for a longer range of time. When two big clusters get close, they do so not only at a single pair of approaching particles but at several pairs. However, it seems that for rigid clusters one of these pairs is favored for encounters, while at the same time hinders the collisions at the other pairs, if only translational diffusion is allowed. It then appears that the mechanism we need could be the small-angle rotational diffusion which, together with the short-step translational diffusion, would make all those pairs fully accessible for encounters. The development of such an (efficient) algorithm looks complicated, but would be of interest.

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[1] T. A. Witten and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).
[2] P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983).
[3] M. Kolb, R. Botet, and R. Jullien, Phys. Rev. Lett. **51**, 1123 (1983).
[4] T. Vicsek, *Fractal Growth Phenomena* (World Scientific, Singapore, 1989).
[5] G. K. von Schultess, G. B. Benedek, and R. W. de Blois, Macromolecules **13**, 939 (1980).
[6] M. S. Bowen, M. L. Broide, and R. J. Cohen, in *Kinetics of Aggregation and Gelation,* edited by F. Family and D. P. Landau (Elsevier, Amsterdam, 1984), p. 185.
[7] D. A. Weitz, J. S. Huang, M. Y. Lin, and J. Sung, Phys. Rev. Lett. **54**, 1416 (1985).
[8] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, Nature (London) **339**, 360 (1989).
[9] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, Phys. Rev. A **41**, 2005 (1990).
[10] M. L. Broide and R. J. Cohen, Phys. Rev. Lett. **64**, 2026 (1990).
[11] J. E. Martin, Phys. Rev. A **36**, 3415 (1987).
[12] J. G. Rarity, Faraday Discuss. Chem. Soc. **83**, 234 (1987).
[13] J. G. Rarity, R. N. Seabrook, and R. J. G. Carr, Proc. R. Soc. London, Ser. A **423**, 89 (1989).
[14] J. E. Martin, J. P. Wilcoxon, D. Schaefer, and J. Odinek, Phys. Rev. A **41**, 4379 (1990).
[15] D. A. Weitz (private communication).
[16] R. C. Ball, D. A. Weitz, T. A. Witten, and F. Leyvraz, Phys. Rev. Lett. **58**, 274 (1987).
[17] F. Family, P. Meakin, and T. Vicsek, J. Chem. Phys. **83**, 4144 (1985).
[18] P. Meakin and F. Family, Phys. Rev. A **36**, 5498 (1987); **38**, 2110 (1988).
[19] A. E. González, Phys. Lett. A **171**, 293 (1992).
[20] W. D. Brown and R. C. Ball, J. Phys. A **18**, L517 (1985).
[21] F. Leyvraz (unpublished).
[22] See for example A. Einstein, in *Investigations on the Theory of the Brownian Movement,* edited by R. Fürth (Dover, New York, 1956).
[23] P. Wiltzius, Phys. Rev. Lett. **58**, 710 (1987).