SCALING OF THE STRUCTURE FACTOR IN FRACTAL AGGREGATION OF COLLOIDS: COMPUTER SIMULATIONS

Agustín E. González and Guillermo Ramírez-Santiago

Instituto de Física, Universidad Nacional Autónoma de México,
Apdo. Postal 20-364, 01000 México, D.F., MEXICO

Abstract

In the volume fraction range (0.005,0.08), we have obtained the temporal evolution of the structure factor $S(q)$, in extensive numerical simulations of both diffusion-limited and reaction-limited colloid aggregation in three dimensions. We report the observation of scaling of this structure function in the diffusion-limited case, analogous to a spinodal decomposition type of scaling. By comparing $S(q)$ with the pair correlation function between particles, we were able to identify the peak in the structure factor as arising from the correlations between particles belonging to nearest-neighbor clusters. The exponents $a'$ and $a''$ that relate the position and the height of the maximum in $S(q)$ vs. time, respectively, were also obtained and shown to differ somewhat from the spinodal decomposition exponents. We also found a terminal shape for $S(q)$ that corresponds to a close packing of the clusters after gelation. Moreover, this picture was shown to be valid in a concentration range larger than the one suggested in recent experiments. Although the $S(q)$ for reaction-limited colloid aggregation does not show a pronounced peak for the earlier times, eventually the peak stretches and becomes higher than in the diffusion-limited case. The $S(q)$ curves, however, do not present the scaling
shown for diffusion-limited aggregation.

81.10.Dn, 02.70.-c, 05.40.+j, 64.60.Qb
1. INTRODUCTION

It is well known that colloidal dispersions may aggregate under certain conditions (1), starting with the appearance of tight bonds between colliding particles, which leads to the formation of clusters of different sizes. The fact that for a wide range of experimental systems the bonds are very strong, prevents the rearrangements of the particles within the clusters and, this in turn, makes the clusters formed to have fractal (2) structure and to possess spatial scaling behavior. The discovery (3-7) of the fractal structure stimulated a great deal of work on colloid aggregation during the last years. Among other results it was found that the dynamics of the aggregation also exhibited scaling behavior (8-12).

It is currently believed that there are two limiting regimes of colloid aggregation [13–16]. Rapid, diffusion-limited colloid aggregation (DLCA) occurs when the aggregation is limited by the time taken for the clusters to encounter each other by diffusion. In this case each collision between diffusing clusters results in the formation of a bond. Slow, reaction-limited colloid aggregation (RLCA) occurs when there is a substantial potential barrier between the particles. In this other case only a small fraction of collisions between clusters results in the formation of a bond. For DLCA the value of the fractal dimension is about 1.8, while the cluster size distribution function $n_s(t)$ takes the shape of a bell as a function of $s$, after a transient. In addition, the average cluster size grows linearly with time. In the other case of RLCA the fractal dimension takes a value around 2.1, while there is an algebraic decay of $n_s(t)$, again after a transient, defined by the exponent $\tau(= 1.5)$: $n_s(t) \sim s^{-\tau}$. Moreover, there is now an exponential growth of the mean cluster size, at least for the earlier stages of the aggregation. The data for the cluster size distribution function shows the following scaling in both cases: $n_s(t) \sim S(t)^{-2}f(s/S(t))$, where $S(t)$ is equal to the number-average cluster size for DLCA and to the weight-average cluster size for RLCA. Finally, the scaling function $f$ is bell shaped for DLCA while decays as the power law $f(x) \sim x^{-\tau}g(x)$ for
RLCA, with \( g(x) \) (a cutoff function) decaying rapidly to zero for \( x > x_c > 1 \). All these facts have been confirmed extensively, both experimentally \([10,11,14–25]\) and with computer simulations \([1,5,27,28,29–31]\).

Recent light scattering studies \([32–34]\) in dense systems have shown that the aggregation in the DLCA limit produces some kind of ordering between the clusters. It was noticed that the distribution of the scattered intensity \( S(q) \) displays a pronounced peak at a finite \( q \) vector. The position \( q_m \) of the peak shifts to smaller values while the peak intensity increases as the time goes on. This behavior is strongly reminiscent to that of some other processes, notably the spinodal decomposition process \([35]\) and some cases of crystal growth \([36,37]\). It was also found \([32]\), as in the spinodal decomposition case, that the \( S(q,t) \) curves for the later stages of the aggregation show the following scaling behavior

\[
S(q, t) = q_m^{-d} F(q/q_m(t)), \tag{1}
\]

where \( F \) is a universal function. While \( d \) was equal to 3 (the spatial dimension) in the spinodal decomposition and crystal growth processes, in our case of DLCA it takes the value \([32]\) of \( d_f = 1.8 \), the fractal dimension of the formed clusters. It is worth mentioning here that two-dimensional aggregating colloids \([38]\) in the diffusion limit also show a finite-\( q \) peak in their structure factor. In a similar way, the peak position moves to smaller values while its height increases as the aggregation proceeds. The same type of scaling for the later times was found in this case, with the only minor difference being the value of the fractal dimension of the aggregating colloids in two-dimensions \( (d_f \approx 1.4) \). To understand the similar behavior of the \( S(q,t) \) curves in all these processes, one notices quite generally that in all of them there is a domain growth or coarsening of certain structures. The appearance of a peak in \( S(q,t) \) for a certain \( q_m(t) \) simply indicates that the structures, on average, have reached a size defined by \( 2\pi/q_m \). If above that size the system is more less homogenous, it should not scatter too much at \( q \)'s smaller than \( q_m \) \([39,40]\); \( S(q,t) \) therefore should go to zero when \( q \) goes to zero. On the other hand, for \( q \)'s larger than \( q_m \), the \( S(q,t) \) curve
decays in a way that reflects the internal arrangements of those structures; for example, as $q^{-d_f}$ for fractal clusters. For the particular case of DLCA, a more detailed explanation of this behavior is based on the smaller diffusion coefficient of the bigger clusters compared to that of the smaller ones. This in turn makes the larger clusters to grow at the expense of the smaller ones by absorbing them, creating therefore depletion zones around themselves. At the same time the cluster size distribution becomes fairly monodisperse, due to the rapid removal of the small clusters; in fact it is bell shaped, as mention above. One therefore has in the system a superposition of large clusters plus depletion regions, leading to a density modulation with a wavelength of the order of the nearest-neighbor cluster distance. As is well known, a wave in real space translates into a peak in Fourier space, the less well defined the wave is the broader the peak becomes. We should therefore expect a peak for $S(q,t)$ since this quantity is just the Fourier transform of the particle-particle correlation function. This last argument, in addition, gives a value for the peak position: it should correspond in real space to the nearest-neighbor cluster distance.

It was also noticed in the aforesaid experiments that the $S(q,t)$ in the terminal stages shows a saturation effect, in the sense that the curves show little sign of change after a saturation time but before the terminal time (see below). The peak position and height remain locked close to the terminal values over a very substantial amount of time. Although it is tempting at first sight to ascribe such time to the onset of gelation or formation of an “infinite” network in the system, it will be shown below that when this occurs, the $S(q,t)$ curves are still changing in time. The saturation time should correspond more precisely to the time at which the clusters pervade the whole space in a close packed way, such that there is no more available space for an individual finite cluster to grow bigger — which would imply that the position $q_m$ of the peak becomes smaller — unless it joins the infinite network. Notwithstanding this difference, we will see that both times are of the same order of magnitude.

Another important issue raised in these systems was the presence or absence of peaks for RLCA processes. It has been suggested that the presence of peaks in the scattering intensity
is unique to gelation by a DLCA process \cite{33}, and some experiments apparently failed to see a peak at a finite \( q_m \) in RLCA \cite{41,43}. Although it is true that the RLCA cluster size distribution is highly polydisperse, we know that at any time during the aggregation there is a maximum size cluster (the cutoff size at which this distribution decays faster than any power law). The existence of a maximum size indicates that the sample should look homogeneous when viewed at distances much greater than this size. According to the general discussion above, the system should not scatter too much for very small \( q' \)'s and \( S(q, t) \) should go to zero when \( q \) goes to zero. In two dimensions, the authors of Ref. \cite{38} have in fact observed peaks for the RLCA regime. Moreover, in a more recent publication \cite{44} the authors of Ref. \cite{41} may agree on the possible existence of peaks that, however, occur for very small scattering angles, well outside the experimental accessible range. Nevertheless, the issue of peaks for RLCA is still a matter of controversy and a subject for further investigations.

In the present article we would like to report our results of extensive numerical simulations of colloid aggregation, made to enquire about a number of unresolved issues. For the first thing, we would like to identify in \( S(q) \) the position of the points that in real space define the size of the denser core, the depletion region and the nearest-neighbor cluster distance, and to compare these points with the peak position \( q_m \). Another question will be to check if the gelation time coincides with the onset of the saturation effect or if it indeed occurs before. Furthermore, it would be interesting to examine the \( S(q, t) \) curves for the RLCA case and see if there is any peak on them. The remaining of this article is organized as follows: in the next section we describe the algorithm used to do the simulations and the method from which we were able to get the pair correlation functions \( g(r, t) \) and the scattering functions \( S(q, t) \). A brief comment about the number of simulations and the concentrations used is also made. In the section that follows we will start describing the DLCA results for the \( S(q, t) \) curves and the scaling that is obtained. We continue, in the same section, presenting pairs of \( g(r, t) - S(q, t) \) curves that will make evident the position of the denser core, the depletion region and the nearest-neighbor cluster distance in the \( S(q, t) \) curves. Some other curves relating the \( q_m(t) \) vs. \( S(q_m, t) \) will be shown to proportion an estimate of the frac-
tal dimension of the clusters. Although these first three points have already been studied previously (42,45), here we present a very useful summary of an extensive set of numerical simulations of the DLCA process which, when combined with new details, provide a more complete picture. Furthermore, we present some plots of the $q_m$ vs. $t$ and $S(q_m)$ vs. $t$, from which we are able to extract the exponents $a'$ and $a''$ that are defined in the spinodal decomposition studies [46], and some arguments are presented for their values. In addition, the gelation and saturation times will be obtained, and a comparison will be made to see if they coincide. We finish the section by obtaining an analytical estimate of the terminal $q_m$, using the close packing condition; we will see that this allows us to obtain another estimate of the fractal dimension (39,40). In the following section, the RLCA results for the $S(q,t)$ curves and for the pairs of $g(r,t) - S(q,t)$ curves will be presented. We will see that although there are peaks on the $S(q,t)$ curves, particularly for the later times, there is no spinodal decomposition type of scaling. We will finish the article with a discussion section, where some final remarks about our results will be made.

II. THE MODEL AND THE METHOD

The algorithms used to study the structure factor and pair correlation functions in DLCA and RLCA, have been already applied with success to demonstrate dynamic scaling in the simulations of colloid aggregation [30,31]. Although models in the continuum can be developed [47], the algorithm used here is built on a lattice, with the convenience of its execution speed, particularly when using very large number of particles. In our model, we consider a three-dimensional cubic lattice with periodic boundary conditions, where some of the cells can be occupied (by a colloidal particle) or empty (solvent). Initially all the colloidal particles are randomly distributed and unaggregated, though some of them may touch each other at some points. As the aggregation proceeds, we deal with a collection of clusters made of nearest-neighbor lattice cells that are diffusing randomly. One of the clusters is picked at random and moved by one lattice unit in a random direction, only if
a random number $X$ uniformly distributed in the range $0 < X < 1$ satisfies the condition $X < D(s)/D_{\text{max}}$, where $D(s) \sim s^{-1/d_f}$ is the diffusion coefficient for the selected cluster of size $s$ and $D_{\text{max}}$ is the maximum diffusion coefficient for any cluster in the system. Here $d_f$ is the accepted value of the fractal dimension of the clusters, which was taken as 1.8 for DLCA and 2.1 for RLCA. Once a cluster is selected the time is incremented by $1/(N_cD_{\text{max}})$, where $N_c$ is the number of clusters in the system at that time, independently that the cluster is actually moved or not. An encounter is defined by an attempt of our moving cluster to overlap the lattice cells occupied by another. In this case the move is not permitted and the moving cluster either sticks (and is merged) to the other with probability $P_0$ or remains side by side to the other with probability $1 - P_0$. The values used for $P_0$ were one for the DLCA case, and 0.0005 and 0.0002 for RLCA. The aggregation process was continued beyond the gelation point, defined as the first time for which a cluster spans the box regardless of the direction at which such spanning occurs. We freeze any cluster that spans the lattice and consider it as part of the infinite network. However, the non-spanning clusters keep moving around and eventually stick to the infinite network. The simulation was terminated when no more moving clusters were found in the system.

We determine the particle-particle correlation function $g(r, t)$ first and, by a Fourier transformation, the structure factor. To evaluate $g(r, t)$ one momentarily stops the aggregation process at predetermined times and obtains a histogram, giving the number of pairs of particles that are found within the spherical shells of radii $r$ and $r + \delta r$, irrespective that the particles belong to the same cluster or to different ones. The pair correlation function was calculated from this histogram with the formula:

$$g(r) = \frac{\text{density of pairs in } (r, r + \delta r)}{\text{average density of pairs}}.$$  \[2\]

The scattered intensity, $S(q)$, of a macroscopic system containing identical particles with number density $\rho$, assuming single scattering, is [48, 49]
\[ S(q) = 1 + \frac{4\pi \rho}{q} \int_0^\infty r \sin(qr) \left( g(r) - 1 \right) dr. \]  

The presence of \( g(r) - 1 \) means that one has subtracted the intensity scattered by a homogeneous object having the same boundaries as the macroscopic system considered. As a consequence, with equation 3, \( S(q) \to 0 \) when \( q \to 0 \). Quantitatively, this \( q = 0 \) limit results from the following sum rules [39]:

\[ \rho \int_0^\infty g(r) 4\pi r^2 dr = N_0 - 1 \] [4]

and

\[ \rho \int_0^\infty 4\pi r^2 dr = N_0, \] [5]

where \( N_0 \) is the total number of particles contained in the macroscopic volume.

We have performed DLCA simulations for 10 different concentrations, to be able to test the picture of close packed clusters or “blobs” for the terminal system. The volume fractions studied were \( \phi = 0.005, 0.0065, 0.008, 0.01, 0.013, 0.02, 0.03, 0.04, 0.06 \) and 0.08. We also made 2 RLCA simulations with \( P_0 = 0.0005 \) and \( \phi = 0.0065 \) and 0.013, and another with \( P_0 = 0.0002 \) and \( \phi = 0.05 \), to elucidate the presence or absence of peaks in this case. In all the simulations we took on the order of \( N_0 \approx 100,000 \) initial particles, a number sufficiently large to have enough statistics for the evaluation of \( g(r) \). We even performed one DLCA simulation for \( \phi = 0.02 \) with 300,000 particles to verify the last assertion. The results were similar and consistent to those for 100,000 particles.

**III. DLCA RESULTS**

In Figs. 1-3 we present \( S(q, t) \) curves for DLCA simulations with volume fractions \( \phi = 0.008, 0.013 \) and 0.03, respectively. On top of the figures are shown the different curves corresponding to different times during the aggregation. In all three we see that the curves
start developing a peak after a certain time, in agreement with the experimental results 
[32,33]. As in the experiments, the peak position decreases while its height increases as time 
goes on. In the inset of those figures we show the same curves on a log-log plot, where it 
is made evident the $q^{-d_f}$ decay for high $q$’s, where $d_f$ is one estimate of the clusters fractal 
dimension. For comparison, some lines with the estimated slopes -1.97, -1.90 and -1.79, 
respectively, were drawn as an aid to the eye. In table 1 we show these estimates for all 
values of $\phi$ on the first column, hereafter called $d_f$. On the bottom of the figures we plotted 
the function $F \equiv q_{nl}^d(t) S(q, t)$ vs. $x \equiv q/q_{nl}(t)$ for the latest 5, 6 and 6 times, respectively. 
For all the concentrations studied we saw the curves to try to collapse into a single one, 
although in some of the cases this scaling was not as good as desired (for example, for the 
$\phi = 0.013$ case shown). This can be attributed to fluctuations from the average behavior, 
due to the finiteness of the system. On those plots, $d_f$ was taken as an adjustable parameter 
used to get the best collapse of the curves, giving us another independent estimate of the 
fractal dimension. For the scaled curves as shown in Figs. 1, 2 and 3 the values of $d_f$ were 
1.98, 1.70 and 1.68, respectively. In table 1 second column we show these new estimates, 
hereafter called $d_f'$. A variation of $d_f'$ from those values by more than 10% resulted in a 
noticeable degradation of this data collapse. We finally have to mention here that the $S(q)$ 
curves for the earlier times did not collapse on the master curve, similar to the experimental 
situation.

In Figs. 4 and 5 we show pairs of graphs $S(q)$ (top) and $g(r)$ (bottom) for $\phi = 0.01$ 
and 0.06, respectively, where the time was picked arbitrarily in each case. The $r$ scale of 
the $g(r)$ plots is given in units of the lattice spacing. For small $r$, we can see that the $g(r)$ 
curves take a high value, due to correlations of the particles belonging to the same cluster. 
For a larger value of $r$, the $g(r)$ goes into a minimum that locates the depletion zone around 
the clusters, while for even longer $r'$s the $g(r)$ increases close to one, when we reach the 
nearest-neighbor cluster distance. In all the curves we show 3 points (a, b and c). Points 
a and b are defined in the $g(r)$ plots as the size of the denser core (defined here as the size 
for which $g(r)$ crosses one) and the position of the depletion zone, respectively. Point c is
defined in the $S(q)$ plot, as the peak position $q_m$. We then divide $2\pi$ by the defined point, to get its location on the reciprocal plot. In this way, it was striking to note that for all times considered, the peak position corresponds to the nearest-neighbor cluster distance, in accord with the picture suggested in the introduction [33,38,41,42].

From Eq. [1] we can have the following relation between the peak position and its height:

$$\ln S(q_m(t)) = -d_f \ln q_m(t),$$  \[6\]

from which we can have another estimate, hereafter called $d_f''$, of the fractal dimension. For this purpose we plotted, for each concentration, the $\ln S(q_m(t))$ vs. the $\ln q_m(t)$ and fitted a straight line to the last points (remembering that scaling occurs only for the later times).

On top of Fig. 6 we show this plot for $\phi = 0.01$, obtaining a value $d_f'' = 1.79 \pm 0.03$, while on the bottom we obtain $d_f'' = 1.52 \pm 0.13$ for a much higher concentration ($\phi = 0.06$). Here the error bars correspond to twice the standard deviation. In table 2 we show the values of $d_f''$ and the corresponding error bars, for all the volume fractions studied. A comparison of $d_f'$ and $d_f''$ from tables 1 and 2 deserves a comment. Although both estimates come from the same scaling equation 1, it should not be surprising to obtain sometimes different values, like for $\phi = 0.0065$ and 0.013. In order to obtain $d_f'$ we tried to collapse the whole $S(q,t)$ curves and not only the peaks. By doing so, sometimes the peaks did not coincide very well, as in Fig. 2. If, on the other hand, we had tried to collapse the peaks, both estimates should more or less agree on the same value. Another comment is concerned with the general decrease of the fractal dimension when increasing the concentration. This behavior usually occurs when the estimate is obtained from $S(q)$, that is, in the reciprocal space [43]. However, if the estimate is obtained in real space, say from $g(r)$ [43] or directly from a log-log plot of the radius of gyration vs. size of the formed clusters [50], there is an opposite trend of increasing the fractal dimension with concentration.

As already mentioned, in the spinodal decomposition problem [46] researchers define 2 exponents $a'$ and $a''$ that describe the decay of $q_m(t)$ vs. $t$ and the increase of $S(q_m(t),t)$ vs.
To take into account many cases for which the log-log plots do not produce a straight line, perhaps due to some transient times, an additive constant to the time is introduced as follows:

\[ q_m(t) \approx A_m (t + B_m)^{-a'} \]  \[ 7 \]

and

\[ S(q_m(t), t) \approx A_s (t + B_s)^{-a''}. \]  \[ 8 \]

For the spinodal decomposition problem, one expects $a' = 1/3$ at intermediate times, arising from a diffusion and coalescence of droplets mechanism, followed by a crossover to $a' \approx 1$ for late times, due to hydrodynamic percolation effects. One also expects the scaling relation $a'' = d \, a'$ for later times, coming from Eq. [1]; that is, $a'' = 3$ at the end. For our case of DLCA, we also would expect the modified scaling relation $a'' = d_f \, a'$ at the end. However, in our case it is difficult to obtain these exponents, due to the saturation effect already mentioned (see Figs. 7 and 8). In fact, it is possible that these exponents are ill defined at the end of the aggregation. That is why we decided to do such calculation only for intermediate times. We present in Fig. 7 the plots of $q_m(t)$ for three values of the concentration, where the squares come from our simulation and the broken curves are a best fit from Eq. [7] to some of the points, eliminating mostly the final ones. In table 3 are shown the values of $A_m, B_m$ and $a'$ for all the considered values of the concentration. A similar thing was done for $S(q_m(t), t)$ and Eq. [8]. Some of the results are plotted in Fig. 8 while all the values of $A_s, B_s$ and $a''$ are presented in table 4. From table 3 we see that the exponent $a'$ oscillates around 0.4. It is indeed expected to have an exponent greater than the spinodal decomposition value, because in that case there is diffusion and coalescence of compact objects, while in our case the aggregation after diffusion builds more open fractal objects. The average cluster radius and nearest neighbor distance should then grow faster for DLCA. We finally note the increase in the value of the exponent for higher
concentrations. An inspection of table 4 shows that the apparent limit of the initial $a''$ for low concentrations is one. This is the value that one would obtain if $S(q_m(t), t)$ were proportional to the average number of particles per cluster [14,45], because this average grows linearly with time in DLCA [15,16]. We, however, find a definite decrease of $a''$ for not too high concentrations, which may suggest that this coincidence of exponents may be fortuitous. Besides, to have $S(q_m(t), t)$ proportional to the average number of particles per cluster would indicate that the scaling given by Eq. [2] is valid also for the initial times, because $q_m^{-1}$ is proportional to the average linear size of a cluster.

As already mentioned, the gelation time was defined as the first time for which a cluster spans the lattice, whether on the x, y or z direction. As for the saturation time, defined here as the time for which the $S(q, t)$ curves do not change significantly, it can only be roughly guessed. We determined exactly the gelation times and gave an estimation of the saturation times for all our DLCA simulations, within $0.005 \leq \phi \leq 0.06$. In table 5 are shown these times, where we can check the consistently smaller values for those corresponding to gelation, indicating that, at the gelation threshold, \textit{we have an infinite network made of blobs or terminal clusters, plus some holes}, where a number of finite clusters reside that have not reached the size of a terminal cluster. After gelation, we therefore need to wait for those finite clusters to grow to the size of a blob, in order to reach the saturation time.

We now proceed to obtain an analytical estimate of the terminal $q_m$ [33,41–43], which takes roughly the same value as that for saturation. As mentioned before, at saturation we have a close packed collection of $n$ fairly monodisperse blobs of linear size $R$ inside the volume $V$ of the system. The cluster volume fraction $\phi_c$ can be calculated as $(n 4\pi R^3/3)/V$. As $n = N_0/N$, where $N$ is the average number of particles per blob, and as $N \sim R^{d_f}$, we can calculate $\phi_c$ as

$$\phi_c \sim \phi R^{3-d_f}. \quad [9]$$

The close packing condition implies that $\phi_c \approx 1$ and, as $q_m \sim 1/R$ after saturation, we find
the following formula for the final $q_m(\infty)$:

$$q_m(\infty) \sim \phi^{1/(3-d_f)}$$  \[10\]

For the $S(q,t = \infty)$ curve we have evaluated the peak position for every concentration studied. In Fig. 9 we show a log-log plot of $q_m(\infty)$ vs. $\phi$, where the points correspond to the ten volume fractions considered in DLCA. The broken straight line is a best fit to the data. From the slope of the straight line and equation [10] we can extract the fractal dimension, obtaining in this case the estimate $d_f = 1.70 \pm 0.10$. A similar plot was made in Refs. [33,41] and it is instructive to compare their results with ours. In Ref. [41] the authors also obtain a straight line, working in a concentration range from about 0.0003 up to 0.003 of volume fraction, while in Ref. [33] the range of $\phi$ considered is closer to the one we study. Although our points lie closely on a straight line for volume fractions up to 0.08, in Ref. [33] it is shown a clear deviation from Eq. [10] for values of $\phi$ larger than 0.01. The volume fraction we use is the fraction of occupied lattice cells, while the experimental one is the volume occupied by the spherical particles divided by the volume of the system. Notwithstanding this difference, they should correspond nearly to each other. We believe that more experiments and simulations need to be done to corroborate this result.

Combining Eq. [1], applied to the $q = q_m$ and $t = \infty$ case, and Eq. [10] we can have the following result:

$$S(q_m, \infty) \sim \phi^{-d_f/(3-d_f)}.$$  \[11\]

A plot similar to Fig. 9 was done to corroborate Eq. [11]. In Fig. 10 we show this plot and the points correspond again to the ten volume fractions considered in DLCA. From the best fit (broken curve) and Eq. [11] we now obtain the following estimate for the fractal dimension: $d_f = 1.85 \pm 0.18$. 

14
IV. RLCA RESULTS

As already mentioned, some experiments apparently failed to see peaks for RLCA \[41,43\] and some workers think that the presence of peaks is peculiar to the DLCA process \[33\]. However, some others have seen peaks for the structure factor, although in two-dimensional reaction limited aggregation \[38\]. Due to this incertitude we decided to run some simulations with a sticking probability of 0.0005, which has already been shown to provide RLCA results that are compatible with the experiment \[31\]. The volume fractions used were $\phi = 0.0065$ and 0.013. Trying to reduce even more the sticking probability, we ran a third simulation with $\phi = 0.05$ and 0.0002 of sticking probability. We were surprised to find the development of a finite $q$ peak in all the three simulations. In Figs. 11 and 12 we show the $S(q)$ curves for $\phi = 0.013$ and 0.05. On top of the figures are shown the plots on a linear scale where we can check the appearance of peaks — although broader than in DLCA for intermediate times (insets of the figures). However, for the final times the peaks are even higher and more pronounced than in DLCA, though moved to lower-$q$ regions. We feel necessary to mention here that it is during the intermediate times that the broad cluster size distribution $n_s(t) \approx s^{-\tau}$ \[15,16,31\] is still valid. This large polydispersity prevents the formation of a structure well defined in size, which, in turn, translates into a broader $S(q)$ peak. During the terminal times the above cluster size distribution stops being valid, due to the finite size effects inherent in the system, with not many clusters remaining in our collection. The higher peak intensity during the final times of RLCA can be understood via the following arguments: as $d_f$ for RLCA is bigger and the clusters are more compact, the terminal clusters need to grow larger to form the close packed structure of blobs, which can be corroborated with Eq. [10]. As already discussed above, whether or not $S(q_m(\infty), \infty)$ is strictly proportional to the average number of particles per blob \[10,12\] it is roughly proportional. But this number of particles per blob is proportional to $\phi$ times the cube of $q_m^{-1}(\infty)$ which, for a smaller $q_m(\infty)$, is much bigger than in the DLCA case. Notwithstanding this peak formation, we tried to scale the curves as in the spinodal decomposition problem.
and found that this was not possible. Perhaps more experiments and simulations are required to verify the above assertions. On the bottom of figures 11 and 12 we are showing the same curves as on top, except that they are plotted in a log-log scale, this with the purpose of identifying the \( q^{-d_f} \) decay for the high \( q \) region. For both concentrations we obtain an estimate of around \( d_f \approx 2.25 \).

We end this section showing 2 pairs of \( S(q) - g(r) \) curves for RLCA. In Fig. 13 we do this for \( \phi = 0.013 \) and an early time during the simulation, while in Fig. 14 we consider the \( \phi = 0.05 \) simulation for the terminal time. As a general feature, the \( S(q) \) curves for the earlier times are very broad and with a small peak, while for the later times the peak stretches, becoming very pronounced. As for the \( g(r) \) curves we still have the inner core for both times, arising from the correlations between particles belonging to the same cluster. We however lack the presence of a well defined minimum and it is only barely seen after the inner core. Beyond that, the \( g(r) \) tends to one when we reach the nearest-neighbor region. The absence of a very well defined minimum signifies that there is not depletion region for the RLCA case or that it is very suppressed. Nevertheless, we found in all cases that the peak position corresponds to the nearest-neighbor region, as for DLCA.

V. SUMMARY AND CONCLUSIONS

Among the important results for DLCA, we have seen the appearance of a peak on the \( S(q) \) curves, which grows in height and moves to the left as time goes on. We have also seen the superposition of all these curves, after a transient time, when plotted with scaled variables. All this was in complete accord with the experimental results [32–34]. As is well known [31], a scaling of \( S(q,t) \) of the type given by Eq. [1] signifies that the system looks very much the same, as time goes on, except for a change of scale. Why do we need to wait for the transient, in order for this to occur? Most probably, this is connected to the time needed for the bell-shaped cluster size distribution to develop and for this cluster distribution to rearrange in space. Let us remind here that we are starting
from a monodisperse, single particles distribution, with the particles randomly positioned in space. By identifying the peak position with the nearest-neighbor distance, we corroborated the proposed picture \[33,38,41,42\] that the peak arises due to the density modulations in real space, with a wavelength of the order of the nearest-neighbor distance. Moreover, by obtaining explicitly the \(g(r)\) we were able to actually “see” the depletion region proposed in those explanations, corresponding to the minimum of the curve. That the gelation time occurs before the saturation time widens our understanding of the process and emphasizes our view that, at saturation, we have a close packed system of “blobs” or terminal clusters. This view was used \[33,41–43\] to get an estimate of the final \(q_m\) (approximately equal to the \(q_m\) at saturation), which was shown to be valid well beyond the concentration limit proposed in recent experiments \[33\].

One important comment concerns the values of the fractal dimensions \(d_f, d'_f\) and \(d''_f\). As we can see, they are in general larger than the expected value of 1.8 for the fractal dimension of DLCA clusters. However, this last value is related to the flocculation regime that occurs before gelation. In our analysis, the \(d_f, d'_f\) and \(d''_f\) were obtained by a scaling of the \(S(q)\) curves before, during and after gelation. It is conceivable that we may be measuring something different from the fractal dimension of the finite clusters. In fact, we actually should be measuring the fractal dimension of the blobs composing the infinite cluster, from a certain length scale and below, plus the few finite clusters coexisting with it.

Another important comment has to do with the decrease of the fractal dimension as concentration increases. As we have already said, this behavior occurs when the estimated fractal dimension is obtained in reciprocal space (45). If the estimate is done in real space, it will be published somewhere else (50) that the fractal dimension increases roughly as the square root of the concentration, from its zero concentration value of 1.8. This difference in behavior in real and reciprocal spaces, we believe, deserves further study.

More surprisingly, we have seen the formation of peaks on the \(S(q,t)\) curves in RLCA, during the late stages of the aggregation process, with a height reaching values much larger than in DLCA. At the same time the final peak position \(q_m\) was smaller than in DLCA for
the same concentration, and an explanation was given for this and for the higher peaks. That the $g(r)$ curves for RLCA lack a pronounced minimum indicates that the clusters may wander around the others with almost no chance of being swallowed by them, due to the very small sticking probability. We have also seen how the very wide polydispersity in this case makes the $S(q, t)$ curves also broad, during the intermediate stages of the aggregation.

One may question the reality of the peak for RLCA and may wonder if this is not an artifice of the finite size of our system. We have already mentioned that at the late stages of the aggregation we lack the cluster size distribution typical of the aggregation process in consideration, not remaining in the system enough clusters for a good statistical analysis. In fact, at the terminal time we end up with one single spanning cluster. That the $S(q)$ for this terminal time has a peak would indicate that this spanning cluster has structure, that is, it is composed of blobs of size $q^{-1}_m(\infty)$. But this is exactly what happens in the DLCA case, in both the experiments and the computer simulations. It therefore appears that the lack of a numerous cluster collection is not an issue for obtaining or not a peak in $S(q)$. Now, as already said, among the main differences between RLCA and DLCA is a large polydispersity at intermediate times in the former case, which would imply that the final spanning cluster is composed of a very polydisperse collection of blobs. But this would contradict the presence of a very pronounced $S(q)$ peak at low $q$, as seen in Figs. 11 and 12. One nevertheless notes, in the same plots, that the $S(q)$ for larger $q$'s reamins similar to what it was at intermediate times, except perhaps for an increase in the noise. (we cannot, however, go to $q$'s much larger than one, say, without reaching spurious effects provoked by the lattice.) We therefore may advance the idea that the terminal spanning cluster consists of a fairly monodisperse collection of close packed blobs, each of them structured in a way similar to what the system was at intermediate times. Inside each blob we would have a fractal dimension of $d_f \approx 2.1$. Nonetheless, before especulating more, it is perhaps safer to wait for further work to prove or disprove the presence of peaks in $S(q, \infty)$ for RLCA, and check whether or not they are an artifice provoked by our finite lattice model.
ACKNOWLEDGEMENTS

We thank the committee at DGSCA-UNAM for granting us a generous amount of CPU time on the Cray Y-MP supercomputer. This work was partially supported by CONACYT grant No. 4906-E. GRS was also partially supported by DGAPA-UNAM grants IN-103294 and IN-100595, while AEG was partially supported by CONACYT-NSF grant E120.1381.
REFERENCES

[1] “Colloid Science” (H. R. Kruyt, Ed.), Elsevier, Amsterdam, 1952, Vol. 1.

[2] Mandelbrot, B. B., “The Fractal Geometry of Nature.” Freeman, San Francisco, 1982.

[3] Forrest, S. R., and Witten, T. A., J. Phys. A 12, L109 (1979).

[4] Meakin, P., Phys. Rev. Lett. 51, 1119 (1983).

[5] Kolb, M., Botet, R., and Jullien, R., Phys. Rev. Lett. 51, 1123 (1983).

[6] Weitz, D. A., and Oliveria, M., Phys. Rev. Lett 52, 1433 (1984).

[7] Schaefer, D. W., Martin, J. E., Wiltzius, P., and Cannell, D. S., Phys. Rev. Lett. 52, 2371 (1984); in “Kinetics of Aggregation and Gelation” (F. Family and D. P. Landau, Eds.), p. 71, Elsevier, Amsterdam, 1984.

[8] Vicsek, T., and Family, F., Phys. Rev. Lett. 52, 1669 (1984).

[9] Kolb, M., Phys. Rev. Lett. 53, 1653 (1984).

[10] Weitz, D. A., and Lin, M. Y. Phys. Rev. Lett. 57, 2037 (1986).

[11] Pefferkorn, E., Pichot, C., and Varoqui, R, J. Phys. France 49, 983 (1988).

[12] Van Dongen, P. G. J., and Ernst, M. H., J. Phys. A 18, 2779 (1985).

[13] Weitz, D. A., and Huang, J. S., in “Kinetics of Aggregation and Gelation” (F. Family and D. P. Landau, Eds.), p. 19, Elsevier, Amsterdam, 1984.

[14] Weitz, D. A., Huang, J. S., Lin, M. Y., and Sung, J., Phys. Rev. Lett. 54, 1416 (1985).

[15] Lin, M. Y., Lindsay, H. M., Weitz, D. A., Ball, R. C., Klein, R., and Meakin, P., Nature 339, 360 (1989).

[16] Broide, M. L., and Cohen, R. J., Phys. Rev. Lett. 64, 2026 (1990).

[17] Aubert, C., and Cannell, D. S., Phys. Rev. Lett. 56, 738 (1986).
[18] Bolle, G., Cametti, C., Codastefano, P., and Tartaglia, P., *Phys. Rev. A* **35**, 837 (1987).

[19] Ferri, F., Giglio, M., Paganini, E., and Perini, U., *Europhys. Lett.* **7**, 599 (1988).

[20] Lin, M. Y., Lindsay, H. M., Weitz D. A., Ball, R. C., Klein, R., and Meakin, P., *Proc. Roy. Soc. London A* **423**, 71 (1989).

[21] Lin, M. Y., Lindsay, H. M., Weitz, D. A., Klein, R., Ball, R. C., and Meakin, P., *J. Phys. Condens. Matter* **2**, 3093 (1990).

[22] Lin., M. Y., Lindsay, H. M., Weitz, D. A., Ball, R. C., Klein, R., and Meakin, P., *Phys. Rev. A* **41**, 2005 (1990).

[23] Carpineti, M., Ferri, F., Giglio, M., Paganini, E., and Perini, U., *Phys. Rev. A* **42**, 7347 (1990).

[24] Martin, J. E., Wilcoxon, J. P., Schaefer, D., and Odinek, J., *Phys. Rev. A* **41**, 4379 (1990).

[25] Broide, M. L., and Cohen, R. J., *J. Colloid Interface Sci.* **153**, 493 (1992).

[26] Vicsek, T., “Fractal Growth Phenomena.” World Sci., Singapore, 1989.

[27] Kolb, M., and Jullien, R., *J. Phys. Lett. France* **45**, L977 (1984).

[28] Jullien, R., and Botet, R., “Aggregation and Fractal Aggregates.” World Sci., Singapore, 1987.

[29] Meakin, P., Vicsek, T., and Family, F., *Phys. Rev. B* **31**, 564 (1985).

[30] González, A. E., *Physica A* **191**, 190 (1992).

[31] González, A. E., *Phys. Rev. Lett.* **71**, 2248 (1993).

[32] Carpineti, M., and Giglio, M., *Phys. Rev. Lett.* **68**, 3327 (1992).

[33] Bibette, J., Mason, T. G., Gang, H., and Weitz, D. A., *Phys. Rev. Lett.* **69**, 981 (1992).
[34] Bibette, J., Mason, T. G., Gang, H., Weitz, D. A., and Poulin, P., *Langmuir* **9**, 3352 (1993).

[35] Furukawa, H., *Adv. Phys.* **34**, 703, (1985).

[36] Schatzel, K., and Ackerson, B. J., *Phys. Rev. Lett.* **68**, 337 (1992).

[37] Banfi, G. P., Degiorgio, V., Rennie, A. R., and Barker, J. G., *Phys. Rev. Lett.* **69**, 3401 (1992).

[38] Robinson, D. J., and Earnshaw, J. C., *Phys. Rev. Lett.* **71**, 715 (1993).

[39] Hasmy, A., Anglaret, E., Foret, M., Pelous, J., and Jullien, R., *Phys. Rev. B* **50**, 6006 (1994).

[40] Hasmy, A., Foret, M., Anglaret, E., Pelous, J., Vacher, R., and Jullien, R., *J. Non-Cryst. Solids* **186**, 118 (1995).

[41] Carpineti, M., and Giglio, M., *Phys. Rev. Lett.* **70**, 3828 (1993).

[42] González, A. E., and Ramírez-Santiago, G., *Phys. Rev. Lett.* **74**, 1238 (1995).

[43] Dietler, G., Aubert, C., Cannell, D. S., and Wiltzius, P., *Phys. Rev. Lett.* **57**, 3117 (1986).

[44] Carpineti, M., Giglio, M., and Degiorgio, V., *Phys. Rev. E* **51**, 590 (1995).

[45] Hasmy, A., and Jullien, R., *J. Non-Cryst. Solids* **186**, 342 (1995).

[46] Gunton, J. D., San Miguel, M., and Sahni, P. S., in “Phase Transitions”, Vol. 8 (C. Domb and J. E. Lebowitz, Eds.) p. 267, Academic, London, 1983.

[47] González, A. E., *Phys. Rev. E* **47**, 2923 (1993).

[48] Watts, R. O., and McGee, I. J., “Liquid State Chemical Physics.” Wiley, New York, 1976.
[49] Feigin, L. A., and Svergun, P. I., “Structure Analysis by Small Angle X-rays and Neutron Scattering.” Plenum, New York, 1987.

[50] Lach-hab, M., González, A. E., and Blaisten-Barojas E., to be published.

[51] Stanley, H. E., “Introduction to Phase Transitions and Critical Phenomena.” Oxford Univ. Press, Oxford, 1987.

FIGURE CAPTIONS

Fig. 1. Top: the $S(q, t)$ curves for a DLCA simulation with $\phi = 0.008$, for the times (from bottom to top) 665, 1 339, 2 697, 5 432, 10 938, 22 026, 44 356, 89 322, 179 872 and 296 559. In the inset it is shown, in a log-log plot, the high-q behavior of these curves. Bottom: a plot of the function $F \equiv q_m^{d_f}(t) S(q, t)$ vs. $x \equiv q/q_m(t)$ for the curves corresponding to the last 5 times on top.

Fig. 2. As in Fig. 1, but now for a DLCA simulation with $\phi = 0.013$ and for the times 403, 665, 1 097, 1 808, 2 981, 4 915, 8 103, 13 360, 22 026, 36 316 and 49 021. The scaling is now tested for the last 6 times on top.

Fig. 3. As in Fig. 1, but now for a DLCA simulation with $\phi = 0.030$ and for the times 148, 245, 403, 665, 1 097, 1 808, 2 981, 4 915, 8 103 and 8 955. The scaling is considered only for the last 6 times.

Fig. 4. The $S(q)$ (top) and $g(r)$ (bottom) curves corresponding to the time $t = 2 981$, for a DLCA simulation with $\phi = 0.01$. Points a and b are defined in $g(r)$ as the size of the denser core and the minimum position, respectively, while point c is defined in $S(q)$ as the peak position.

Fig. 5. As in Fig. 4, but now for a DLCA simulation with $\phi = 0.06$, corresponding to the time $t = 403$. Note how the depletion region is not very well developed at this early time.

Fig. 6. A plot of $\ln (S(q_m))$ vs. $\ln (q_m)$ to get an estimate of the fractal dimension, from Eq. [6]. The top graph corresponds to $\phi = 0.01$ while the bottom is for $\phi = 0.06$. Note that...
the straight line is fitted to the points corresponding to the later times.

Fig. 7 A best fit of Eq. [7] to the $q_m(t)$ plots, in order to get the exponent $a'$, for three values of the concentration: $\phi = 0.005$ (top), $\phi = 0.02$ (middle) and $\phi = 0.08$ (bottom).

Note that only the initial times are fitted to the curve.

Fig. 8. A best fit of Eq. [8] to the $S(q_m(t), t)$ plots for $\phi = 0.005$ (top), $\phi = 0.013$ (middle) and $\phi = 0.06$ (bottom), with the purpose of obtaining the exponent $a''$. Also here, only the initial times are considered in the fitting.

Fig. 9. A log-log plot of $q_m(\infty)$ vs. $\phi$, for the ten volume fractions considered in DLCA. The broken straight line is a best fit to the data from Eq. [10].

Fig. 10. A log-log plot of $S(q_m(\infty), \infty)$ vs. $\phi$, again for the ten concentrations considered. Now the best fit is done from Eq. [11].

Fig. 11 Top: the $S(q)$ curves for a RLCA simulations with $\phi = 0.013$, corresponding to the times 162 755 (f), 442 413 (e), 1 202 604 (d), 3 269 017 (c), 8 886 111 (b) and 17 894 429 (a). Bottom: the same curves shown on a log-log scale. The straight line with slope -2.25 is just a guide to the eye.

Fig. 12. Same as in Fig. 11, except that the volume fraction considered is $\phi = 0.05$ and the times are now 162 755 (e), 442 413 (d), 1 202 604 (c), 3 269 017 (b) and 3 612 823 (a).

Fig. 13. The $S(q)$ (top) and $g(r)$ (bottom) curves corresponding to an early time ($t = 162 755$) of a RLCA simulation with $\phi = 0.013$. Points a, b and c are defined as in the DLCA case.

Fig. 14. Same as in Fig. 13, but now for the terminal time ($t = 3 612 823$) of a RLCA simulation with $\phi = 0.05$. 

24
| $\phi$ | $d_f$ | $d_f'$ |
|-------|------|------|
| 0.0050 | 1.90 | 2.00 |
| 0.0065 | 1.95 | 2.02 |
| 0.0080 | 1.97 | 1.98 |
| 0.0100 | 1.93 | 1.80 |
| 0.0130 | 1.90 | 1.70 |
| 0.0200 | 1.90 | 1.85 |
| 0.0300 | 1.79 | 1.68 |
| 0.0400 | 1.73 | 1.60 |
| 0.0600 | 1.50 | 1.65 |
| 0.0800 | - | 0.50 |

**TABLE I.** Two estimates of the fractal dimension in DLCA for all the volume fractions $\phi$ studied in this work. $d_f$ comes from the $q^{-d_f}$ decay of $S(q)$ at high $q$'s and $d_f'$ comes from the scaling equation 1. There was not a straight line to get $d_f$ for $\phi = 0.08$. 
TABLE II. Another estimate of the fractal dimension in DLCA, $d_f''$, coming from Eq. [6].

| $\phi$   | $d_f''$ | $\Delta d_f''$ |
|----------|---------|---------------|
| 0.0050   | 1.89    | 0.15          |
| 0.0065   | 1.76    | 0.12          |
| 0.0080   | 1.90    | 0.17          |
| 0.0100   | 1.79    | 0.30          |
| 0.0130   | 1.48    | 0.17          |
| 0.0200   | 1.93    | 0.14          |
| 0.0300   | 1.75    | 0.06          |
| 0.0400   | 1.48    | 0.22          |
| 0.0600   | 1.52    | 0.13          |
| 0.0800   | 0.49    | 0.10          |

The error bars on the third column correspond to twice the standard deviation.
| $\phi$  | $A_m$ | $B_m$  | $a'$  | $\Delta a'$ |
|-------|-------|--------|-------|-------------|
| 0.0050 | 5.79  | 463.71 | 0.41  | 0.02        |
| 0.0065 | 3.32  | -146.59| 0.36  | 0.02        |
| 0.0080 | 6.00  | 218.36 | 0.43  | 0.02        |
| 0.0100 | 4.18  | 14.08  | 0.39  | 0.02        |
| 0.0130 | 4.45  | -20.85 | 0.41  | 0.04        |
| 0.0200 | 5.00  | 56.90  | 0.43  | 0.04        |
| 0.0300 | 2.25  | -80.32 | 0.33  | 0.02        |
| 0.0400 | 3.69  | -11.66 | 0.40  | 0.02        |
| 0.0600 | 323.25| 337.24 | 1.04  | 0.08        |
| 0.0800 | 8.25  | 236.96 | 0.47  | 0.02        |

TABLE III. The values of $A_m$, $B_m$, $a'$ and its error bar $\Delta a'$, coming from the best fit of Eq. [7] to the initial points of $q_m(t)$. 
| $\phi$   | $A_s$ | $B_s$   | $a''$ | $\Delta a''$ |
|--------|-------|---------|-------|-------------|
| 0.0050 | 0.007 | -21.14  | 1.06  | 0.02        |
| 0.0065 | 0.020 | -99.33  | 0.98  | 0.03        |
| 0.0080 | 0.028 | -90.48  | 0.95  | 0.03        |
| 0.0100 | 0.042 | -95.87  | 0.92  | 0.02        |
| 0.0130 | 0.038 | -47.99  | 0.96  | 0.01        |
| 0.0200 | 0.086 | -34.18  | 0.88  | 0.03        |
| 0.0300 | 0.325 | -59.59  | 0.71  | 0.01        |
| 0.0400 | 0.134 | 2.96    | 0.85  | 0.03        |
| 0.0600 | 0.827 | -26.95  | 0.54  | 0.01        |
| 0.0800 | 0.755 | -14.11  | 0.55  | 0.01        |

TABLE IV. The values of $A_s$, $B_s$, $a''$ and its error bar $\Delta a''$, coming from the best fit of Eq. [8] to the initial points of $S(q_m(t), t)$.
| $\phi$  | $t_g$   | $t_s$   |
|--------|---------|---------|
| 0.0050 | 109 098 | 300 000 |
| 0.0065 | 80 822  | 180 000 |
| 0.0080 | 26 903  | 170 000 |
| 0.0100 | 22 026  | 100 000 |
| 0.0130 | 14 765  | 40 000  |
| 0.0200 | 6 003   | 13 000  |
| 0.0300 | 2 441   | 5 000   |
| 0.0400 | 1 212   | 3 000   |
| 0.0600 | 545     | 1 100   |

TABLE V. The gelation ($t_g$) and saturation ($t_s$) times for all concentrations studied between $0.005 \leq \phi \leq 0.06$. 