On the Concentration Dependence of the Cluster Fractal Dimension in Colloidal Aggregation

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Abstract. We have undertaken the task to calculate, by means of extensive numerical simulations and by different procedures, the cluster fractal dimension (d_f) of colloidal aggregates at different initial colloid concentrations. Our first approach consists in obtaining d_f from the slope of the log-log plots of the radius of gyration versus size of all the clusters formed during the aggregation time. In this way, for diffusion-limited colloidal aggregation, we have found a square root type of increase of the fractal dimension with concentration, from its zero-concentration value: $d_f = d_f^0 + a\phi^\beta$, with $d_f^0 = 1.80 \pm 0.01$, $a = 0.91 \pm 0.03$ and $\beta = 0.51 \pm 0.02$, and where ϕ is the volume fraction of the colloidal particles. In our second procedure, we get the d_f via the particle-particle correlation function $g_{\text{cluster}}(r)$ and the structure function $S_{\text{cluster}}(q)$ of individual clusters. We first show that the stretched exponential law $g_{\text{cluster}}(r) = Ar^{d_f-3}e^{-(r/\xi)^a}$ gives an excellent fit to the cutoff of the $g(r)$. Here, A, a and ξ are parameters characteristic of each of the clusters. From the corresponding fits we then obtain the cluster fractal dimension. In the case of the structure function $S_{\text{cluster}}(q)$, using its Fourier transform relation with $g_{\text{cluster}}(r)$ and introducing the stretched exponential law, it is exhibited that at high q values it presents a length scale for which it is linear in a log-log plot versus q, and the value of the d_f extracted from this plot coincides with the d_f of the stretched exponential law. The concentration dependence of this new estimate of d_f, using the correlation functions for individual clusters, agrees perfectly well with that from the radius of gyration versus size. It is however shown that the structure factor $S(q)$ of the whole system (related to the normalized scattering intensity) is not the correct function to use when trying to obtain a cluster fractal dimension in concentrated suspensions. The log-log plot of $S(q)$ vs. q proportions a value higher than the true value. Nevertheless, it is also shown that the true value can be obtained from the initial slope of the particle-particle correlation function $g(r)$, of the whole system. A recipe is given on how to obtain approximately this $g(r)$ from a knowledge of the $S(q)$, up to a certain maximum q value.

Keywords: colloidal aggregation, fractal dimension, correlation function, structure factor

1. Introduction

Under certain conditions colloidal dispersions may aggregate [1], starting with the appearance of tight bonds between colliding particles, which leads to the formation of clusters of different sizes. The strong bonds prevent the particles to rearrange within the clusters, which results in very open and spread structures that

exhibit fractal behavior [2]. Numerous studies have been conducted in the past 15 years on these aggregating systems, motivated to a large extent by the discovery of the fractal structure [3, 4]. Among the various existing theoretical models, the diffusion limited colloidal aggregation (DLCA) [5, 6] has been shown to be adequate to describe the non-equilibrium aggregation processes of a wide variety of colloidal systems. In this model the colloidal particles and the formed clusters diffuse randomly and stick between them when they are in contact. Among the shortcomings of the model is its neglect of the hydrodynamic interactions that exist between the clusters. It also neglects the relaxation and/or conformational changes of the growing aggregates due to external parameters such as aging and shaking. Despite these deficiencies, the DLCA model has proven to be valid for a good range of colloidal systems with different mechanisms for sticking, like gold, silica and polystyrene [7]. Accepting the DLCA model as such, one might also question the existence of one unique parameter to define the fractal behavior of the aggregates. For example, in a related model, the diffusion limited aggregation, multifractality has been confirmed and thus a family of scaling parameters is needed to describe the overall "shell" structure of the aggregates [8]. Recently [9] we have demonstrated that for DLCA aggregates only one parameter is needed to describe the self-similarity, and that the fractal behavior is then different from DLA, with no evidence of a drift of the aggregates density as the surface of the poroses is approached [8].

Most of the experimental studies on colloidal aggregation were performed in a very low concentration regime, for which there are well defined limiting values of the structural and dynamical quantities. Furthermore, in many cases researchers extrapolate these results thinking that they apply to high concentrations as well. After some reasoning, it is however not possible to get away from a concentration dependence of the cluster fractal dimension: in a very concentrated regime, the small clusters are already interpenetrated before sticking and when they stick, they do so, not at the tips of their longer arms, but also in the middle. This in turn should increase the compactness of the clusters and hence the fractal dimension.

Few systematic studies [10–15] have been done before our work to try to obtain the concentration dependence of the fractal dimension in colloidal aggregation. In the experimental work of Carpineti et al. [10], the cluster fractal dimension is obtained via the intensity $S(q)$ scattered by the system in a low-angle light scattering experiment. They assumed that the behavior of $S(q)$ for large q was in the form of a power law: $S(q) \sim q^{-d_f}$ with d_f equal to the cluster fractal dimension. We will however show here that, *for concentrated systems, the behavior of $S(q)$ is not in the form of such law*. Nevertheless, the authors in Ref. [10] were working in a very low concentration regime, ranging from 1.15×10^{-6} to 5.75×10^{-5} in volume fraction ϕ, for which the above law is presumably correct. They found a decrease of d_f as a function of concentration, starting from the DLCA [5, 6] value of 1.8 for the very low concentrations studied to a value of around 1.6 for higher concentrations. The departure from the DLCA value was attributed by the authors to a deviation from the DLCA mechanism, due to the polarization of the clusters induced by the counterion screening, when the salt was added to initiate the aggregation [10]. In their simulational work, van Garderen et al. [11, 12] study the fractal properties of a gelled network made by moving randomly and simultaneously all the off-lattice particles and clusters in the reaction box, by the *same* step length, which would effectively give the same diffusivity to a monomer or to a big cluster. The method used by the authors to obtain the fractal dimension in two dimensions [11] and one of the methods used in three dimensions [12] is from the decay of the scattering function $S(q)$ for the whole system, which would only give them the fractal character of the "blobs" [15, 16] composing the "infinite" gelled network and not the fractal dimension d_f of the clusters in the flocculation regime (before the gel is formed) as we try to obtain here. Perhaps the only result from their work meaningful to ours would be the fractal dimension (called by them D_f^{Gyr} [12]), coming from the log-log plots of the radius of gyration vs. mass of all the clusters formed during the aggregation. This D_f^{Gyr} clearly shows an increase as a function of concentration, starting at around 1.8 at low concentrations and increasing up to 2.5 for $\phi = 0.3$. Even this D_f^{Gyr} should be taken with caution because their calculation suffers from the incorrect diffusivity already mentioned, which affects both the dynamical quantities and the structural quantities like the fractal dimension. Ref. [13] is a lattice DLCA simulation in two dimensions in which the diffusivity scales, more or less correctly, as the inverse of the square root of the number of particles constituting the cluster. The authors obtain a cluster fractal dimension from a classical box-counting algorithm that increases with concentration, starting at

around 1.5 for low concentrations and going up to about 2 for very high concentrations. Their data is however very scattered and no discussion on the statistics of their calculation was published, making it difficult to assess the significance of their results. In the work of Hasmy and Jullien [14], they perform an off-lattice extension of the original cluster-cluster aggregation model [5, 6], where a sufficiently large initial concentration has been considered in order to obtain a gelled network of connected clusters at the end of the aggregation process. Among other things, they calculate the particle-particle correlation function of the whole system $g(r, t)$ and the scattering function $S(q, t)$, by means of a Fourier transformation of the $g(r, t)$. For the final time (when there is one single connected cluster spanning the box) they extract the fractal dimension D of the "blobs" composing the gel, from the relations $g(r, t_{\text{final}}) \sim r^{D-3}$ and $S(q, t_{\text{final}}) \sim q^{-D}$. The fits to the $g(r, t_{\text{final}})$ were done from the smallest r values up to the position of the minimum of the function, defining the intercluster depletion region [14–18]. These authors obtain an increasing fractal dimension D as a function of concentration through the $g(r, t_{\text{final}})$ fitting, starting at around 1.8 for the smallest concentration and reaching very rapidly values close to 3, for a moderate volume fraction of 0.06. The increase of D with concentration is approximately linear although it bends down a little for the higher concentrations. They however find a decreasing fractal dimension from the $S(q, t_{\text{final}})$ procedure, starting at about 1.8 for the lower concentrations, down to 1.5 for the higher volume fraction of 0.06. González and Ramírez-Santiago [15] follow a similar approach as the one of Hasmy and Jullien for the $S(q, t)$. They consider a lattice aggregation model for which they calculate the particle-particle correlation function $g(r, t)$ and, from this, the scattering function $S(q, t)$. From the log-log plots of the scattering function, they also find a decreasing fractal dimension as a function of volume fraction ϕ. Their low concentration estimate is however somewhat larger than the one by Hasmy and Jullien, starting at around 1.95 for the lower concentrations down to 1.5 for $\phi = 0.06$.

In view of the disparity of those results and considering that several of the above works tried to find the fractal dimension of the blobs that form the gelled network and not the cluster fractal dimension in the flocculation regime, the present authors initiated a computational effort to try to elucidate the intriguing questions that popped up from all those works. In this paper, we give an account of the methods and procedures that allowed

us to obtain the concentration dependence of the cluster fractal dimension, in the flocculation regime. We will see that the cluster fractal dimension d_f increases indeed, as our reasoning indicated, when the concentration is raised. Moreover, this increase is found to be of a square root-type as a function of concentration. We will circumscribe ourselves to the DLCA model on a cubic lattice due to its proven computational speed, given the large number of simulations and calculations that we need to perform in order to have a reasonable statistical sample. Although the lattice may seem at first sight to restrict our results, previous works [19] have shown that the DLCA model on a lattice proportions results that are indistinguishable, up to the statistical uncertainty, from the DLCA results in the continuum. Section 2 describes how our first estimate of d_f was obtained, for a range in concentrations spanning two and a half decades. This was accomplished from the log-log plots of the radius of gyration vs. size of all the clusters formed during the aggregation time. In Section 3 a particle-particle correlation function for individual clusters is obtained (called $g_{\text{cluster}}(r)$) and, by means of a Fourier transformation, a cluster structure function $S_{\text{cluster}}(q)$ was produced. From both of these functions, another estimate of d_f is obtained, which is in full agreement with the estimate in Section 2. Furthermore, we note in passing that the decay of $g_{\text{cluster}}(r)$ can be fitted much better to a stretched exponential law rather than to a Fisher-Burford (simple exponential) decay [20], as was assumed in previous works [21–23]. Section 4 contains our results for the particle-particle correlation function for the whole system (called $g(r)$) which, by a Fourier transformation, produces the structure factor $S(q)$. This $S(q)$ is the one that coincides with the normalized scattered intensity of a scattering experiment. We will see that we can still get a correct cluster fractal dimension d_f from $g(r)$, by restricting the fit to small r values. This is to prevent that other clusters present in the system interfere in the evaluation of $g(r)$. Due to the fact that the $S(q)$ has contributions not only from the short range part of $g(r)$ but from everywhere, including the region around the minimum, we have found that for concentrated systems it does not have to behave as $S(q) \sim q^{-d_f}$, with d_f equal to the fractal dimension obtained from the analysis of $g(r)$. Thus, we have identified one possible source of error: trying to use the scattering function to obtain d_f in concentrated systems. All sensible estimates of d_f for DLCA lead us, therefore, to a function increasing with concentration as a square-root type law. The

last Section 5 contains a discussion of our results and presents a formula to approximately obtain the $g(r)$ if $S(q)$ is known up to a maximum q value. In a scattering experiment one precisely measures the $S(q)$ up to a certain maximum q.

2.   The Fractal Dimension from the Radius of Gyration vs. Size

The algorithm used to perform the simulations has been described before in several places [9, 16, 24, 25]. It suffices to say here that the following 14 volume fractions were used: 0.001, 0.003, 0.0055, 0.01, 0.03, 0.072, 0.1, 0.139, 0.2, 0.24, 0.3, 0.4, 0.469, and 0.5. Each simulation contained on the order of 30,000 initial monomers. For each concentration up to 0.01, a total of 40 runs were performed, whereas for each of the remaining 10 concentrations, we carried out 100 runs of our algorithm. For each of the simulation runs at each concentration, we plotted on a log-log scale the radius of gyration vs. size of all the clusters formed during the whole aggregation time, just before gelation. The inverse of the slope gave us the estimate of the fractal dimension for the corresponding run [25]. Very small clusters were neglected in this analysis, such as to cover the asymptotic regime of large clusters (greater than 50 monomers). In Fig. 1, each of the points represents the average over the 40 or 100
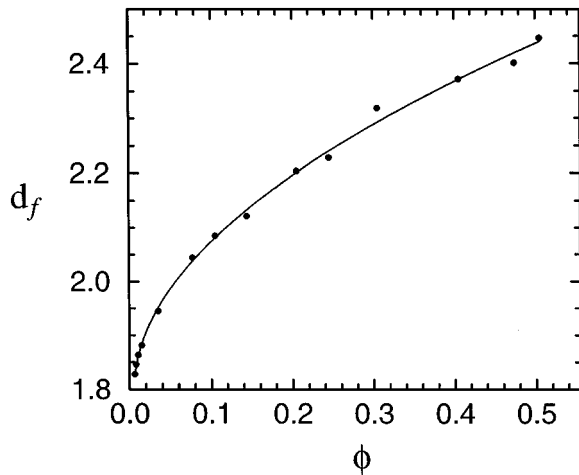

Figure 1. The fractal dimension as a function of volume fraction, obtained from the log-log plots of the radius of gyration vs. size of all the clusters formed before gelation. The points represent the average over 40 or 100 simulations (upon the case) and the curve is a best fit to the points.

simulations (upon the case) for each concentration. The best functional fit (shown as the solid line in Fig. 1) yielded a square root-type of increase of the fractal dimension from its zero concentration value [25]: $d_f = d_f^0 + a\phi^\beta$, where $d_f^0 = 1.797 \pm 0.011$, $a = 0.913 \pm 0.025$, $\beta = 0.507 \pm 0.022$. Note how we get for d_f^0 the accepted value of the DLCA fractal dimension in the dilute limit: $d_f \approx 1.8$.

3.   The Fractal Dimension from the Single Cluster Correlation Functions

In this case seven different concentrations were considered: $\phi = 0.0065, 0.008, 0.01, 0.03, 0.05, 0.065$, and 0.08, whereas the number of particles per simulation was on the order of 100,000. We performed 50 simulations at each concentration. Four different physical times along the aggregation were selected, the last one being very close to the gelation time. At each of those times, the larger clusters from all the 50 simulations were catalogued in different size sets, according to their number of particles. Seven size sets were considered for the last time: clusters containing 2001–2500, 2501–3000, . . . , 5001–5500 particles. The pair correlation function of each cluster is defined as

$$g_{\text{cluster}}(r, t) = \frac{\textit{density of pairs in } (r, r + \delta r)}{\textit{density of pairs in } (1, 1 + \delta r)}, \quad (1)$$

where the denominator corresponds to the local density of pairs within distances of one lattice spacing, which is taken equal to one. This gives the same limiting behavior at short and long distances for all clusters (1 and 0, respectively). As the $g_{\text{cluster}}(r, t)$ decayed to zero in a length scale consistent with the size of the cluster, we performed an average of this $g_{\text{cluster}}(r, t)$ over all clusters in a given set. The Fourier transform of the averaged $g_{\text{cluster}}(r, t)$ proportioned us the $S_{\text{cluster}}(q, t)$, as follows:

$$S_{\text{cluster}}(q, t) = \frac{4\pi\rho}{q} \int_0^\infty r \sin(qr) g_{\text{cluster}}(r, t) \, dr, \quad (2)$$

where ρ stands for the particle number density of the initial aggregation bath. The decay of the $g_{\text{cluster}}(r)$ is frequently expressed as the product of the algebraic decay $r^{d_f - 3}$ times a scaling cutoff function $f(r/\xi)$:

$$g_{\text{cluster}}(r) \sim r^{d_f - 3} f(r/\xi). \quad (3)$$

A function frequently used [21–23] for the $g_{\text{cluster}}(r)$ is the so called Fisher-Burford expression:

$$g_{\text{cluster}}(r) = A^0 r^{d_f^0 - 3} e^{-r/\xi^0}, \qquad (4)$$

which was initially considered by Fisher and Burford [20] in the context of the Ising model. Here A^0, d_f^0 and ξ^0 are parameters characteristic of each cluster. As we are about to see, a much better representation for the decay of $g_{\text{cluster}}(r)$ is given by the stretched exponential form:

$$g_{\text{cluster}}(r) = A r^{d_f - 3} e^{-(r/\xi)^a}, \qquad (5)$$

with $a > 1$.

In Fig. 2(a), the points represent a typical averaged $\langle g_{\text{cluster}}(r) \rangle$ for $\phi = 0.01$ and size set 3001–3500, whereas the solid line comes from a multiparameter fit of Eq. (5). As we can see, the fit is excellent. The parameters obtained for this particular case are: $d_f = 1.865$, $a = 2.626$, $A = 1.512$ and $\xi = 49.50$. In Fig. 2(b) we are showing the same points as in Fig. 2(a), except that the solid line now comes from Eq. (4). Clearly, now the fit is not as good as that from Fig. 2(a). The obtained Fisher-Burford parameters are now $d_f^0 = 1.865$, $A^0 = 1.606$, and $\xi^0 = 87.89$. In Table 1 we present the d_f values for the size sets greater than 3000 and for all the concentrations studied. On the second row, we show the d_f values coming from the formula obtained in Section 2. As we can see, the fractal dimension is independent of the cluster size we are considering (within the statistical uncertainty). Moreover, also within the statistical uncertainty, results are fully consistent with the first method described for obtaining d_f (from the log-log plots of the radius of gyration vs. number of particles of the clusters formed). For small clusters there are many particles on the cluster surface that contribute strongly to the cutoff part and not to the algebraic decay of $g_{\text{cluster}}(r)$. The $r^{d_f - 3}$ behavior is therefore buried inside the scaled decaying region, making the analysis of extracting a correct fractal dimension complicated or impossible. This is the reason why we selected large clusters and late times during the aggregation.

It can be shown [9] that the cluster structure function $S_{\text{cluster}}(q)$, obtained by means of Eq. (2) from the fitted $g_{\text{cluster}}(r)$, becomes linear on a log-log plot vs. q, for q values larger than a certain q_{min}. In Fig. 3 we show the $S_{\text{cluster}}(q)$ corresponding to the $g_{\text{cluster}}(r)$ in Fig. 2,
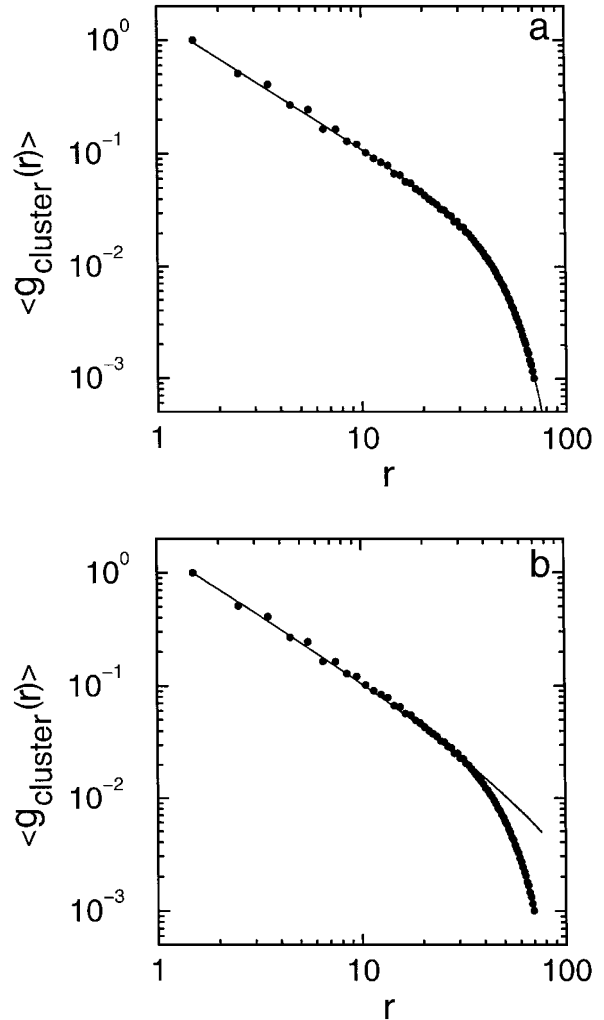

Figure 2. (a) The points represent $\langle g_{\text{cluster}}(r) \rangle$, where the average is over all the clusters existing in the 50 simulations in the size range of 3001–3500, at the last time and for $\phi = 0.01$. The curve is a best multiparameter fit of the stretched exponential law (Eq. (5)). (b) The same points as in (a), except that now the fit was done to Eq. (4).

obtained through Eqs. (2) and (5). This $S_{\text{cluster}}(q)$ displays the following structure: (a) a plateau for small q values, (b) a shoulder in the middle, coming from the stretched exponential, and (c) the linear behavior at large q values. It can also be shown [9] that the slope of the linear part coincides precisely with the d_f in Eq. (5). Therefore, the fractal dimension obtained from the relation $S_{\text{cluster}}(q) \sim q^{-d_f}$ for large q values coincides with the one extracted from the $g_{\text{cluster}}(r)$ procedure. Hence, we recover the values presented in Table 1 with this new method.

Table 1. Estimates of the cluster fractal dimension d_f at different initial concentrations, from the procedure described in Section 2 (2nd row), and from the procedure outlined in Section 3, for the bin sizes indicated.

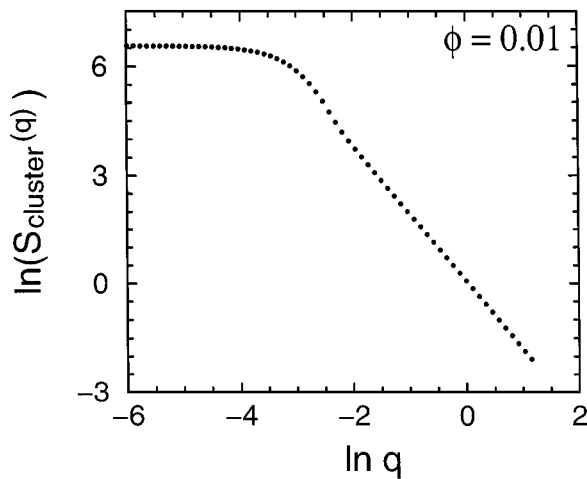| ϕ	0.0065	0.008	0.01	0.03	0.05	0.065	0.08
d_f from Section 2	1.868	1.876	1.885	1.951	1.997	2.025	2.051
d_f from bin3000	1.858	1.864	1.865	1.932	1.983	2.042	2.092
d_f from bin3500	1.867	1.861	1.873	1.932	1.981	2.054	2.087
d_f from bin4000	1.876	1.850	1.879	1.930	1.984	2.046	2.101
d_f from bin4500	1.868	1.858	1.869	1.940	1.998	2.050	2.096
d_f from bin5000	1.874	1.856	1.873	1.918	2.029	2.038	2.093

Figure 3. A typical $S_{\text{cluster}}(q)$ vs. q (on a log-log plot), coming from Eqs. (2) and (5). The curve presents the plateau, the shoulder and the q^{-d_f} decay explained in the text.

Figure 4. A log-log plot of the whole system $g(r)$ vs. r. The points come from one of the five simulations at the last time for $\phi = 0.01$, while the straight line is a fit to the first five points.

4. The Fractal Dimension from the Whole System Correlation Functions

The calculation of a $g(r)$ for the whole system of colloidal particles is a computer intensive procedure, because it involves calculating the distances between all pairs of particles. We performed this new calculation in only five simulations, for each of the concentrations used in the last section and at the same four physical times. The particle-particle correlation function for the entire reaction bath is calculated in the following way:

$$g(r, t) = \frac{\text{density of pairs in } (r, r + \delta r)}{\text{average density of pairs}}. \quad (6)$$

The structure of $g(r)$ for concentrated systems has already been reported before [14–16, 18]. We will only mention here that it decays from a high value, crosses
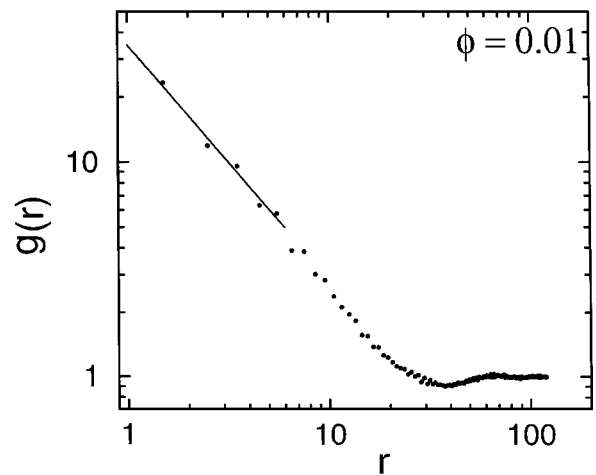
to values below one, reaches a minimum, and then increases to reach the value of one for large distances. For very short distances, $g(r)$ mainly includes intracluster particle pairs. For moderate and longer distances, the inter-cluster particle pairs are responsible for the minimum and the further increase of the $g(r)$. Therefore, if we want to have a procedure for measuring the cluster fractal dimension from $g(r)$, we need to restrict ourselves to very short distances, when the interference from the other clusters has not become appreciable. For the earlier times considered, the number of small clusters in the reaction box is large. In this case, an analysis through the pair correlation function $g(r)$ to obtain the fractal dimension is not adequate, as mentioned in the last section. Figure 4 shows the log-log plot of the $g(r)$ for one of the simulations at the volume fraction 0.01 and at the final time. The straight line comprising the first five points (which lie nicely

on the line) is a fit done to obtain the fractal dimension, using the decay $g(r) \sim r^{d_f - 3}$. The value of d_f produced in this case is 1.914, which is not far from the corresponding value of 1.885 coming from Section 2. It is important to notice that if we had taken all the points up or close to the minimum of the function, a different result would have been produced, giving rise to a larger difference with the results of Section 2. For concentrations higher than $\phi = 0.05$, when the final "blob" size is very small [15, 16], we have found that the short-range region of $g(r)$ shrinks to fewer than four points lying on a straight line. In this case, our simulational method for obtaining the d_f from the $g(r)$ is not adequate, and a more expensive simulation in the continuum could proportion the required fractal dimension. Nonetheless, it has to be mentioned here that we cannot consider the $g(r)$ only for r values arbitrarily closed to one because this would give us lattice effects or, in the case of a experimental system or of a simulation in the continuum, because we wouldn't be in the asymptotic region to obtain a reliable d_f. Table 2 contains the fractal dimension by this method, averaged over the five simulations for each volume fraction up to $\phi = 0.05$. We see that the estimates obtained from this method are again close to those from Section 2, putting on firm grounds the formula obtained there.

For the whole reaction box, the structure factor—that coincides with the normalized scattered intensity of a scattering experiment—is given by the following formula [15, 16, 26]:

$$S(q, t) = 1 + \frac{4\pi\rho}{q} \int_0^\infty r \sin(qr)(g(r, t) - 1)\, dr. \quad (7)$$

By means of this formula, we have calculated the $S(q, t)$ for each of the five simulations at each of the four different times for each concentration. The shape of this $S(q, t)$ has also been discussed before [14–18, 27]. It starts from a value of zero at $q = 0$, increases to a peak at a certain q_m, and then decreases again presumably following the law: $S(q, t) \sim q^{-D}$, with D being some characteristic fractal dimension of the system. The height of the peak increases and the value of q_m decreases as the aggregation proceeds. The distance $r_m = 2\pi/q_m$ was shown [15, 16] to coincide with the average distance between nearest neighbor clusters in the flocculation regime (before gelation) and to a characteristic "blob" size after the gel is formed. Here we have found that indeed, at some distance after the peak, there is a short region on a log-log plot of $S(q, t)$ vs. q for which the plot is approximately linear. This behavior occurs mainly at late times during the aggregation (close to gelation and afterwards) and for not very high concentrations. For earlier times and, in general, for the higher concentrations, the linear slope is not well develped or not developed at all. Nevertheless, in the range of concentrations we are working, we have found that whenever the slope is well developed it does not coincide with the value of the cluster fractal dimension obtained by the other sensible methods already mentioned. In Fig. 5 we show the $S(q)$ corresponding to the $g(r)$ of Fig. 4. As we can see, in the short region between the points A and B there is a linear behavior whose slope ($= 2.089$) is different from the d_f obtained in Fig. 4 ($= 1.914$). In fact, the slope does not have to be equal to d_f because the $S(q)$ contains contributions from $g(r)$, not only from
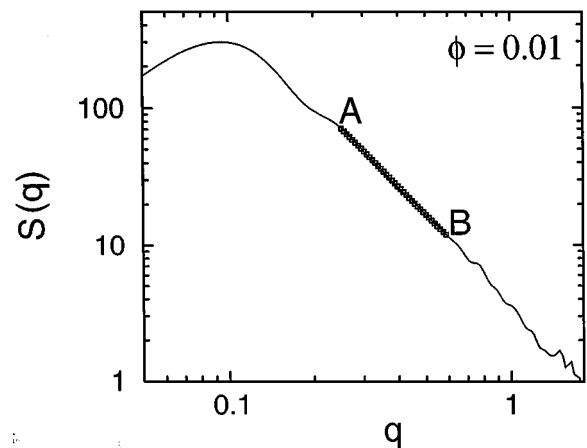
Table 2. Estimates of the fractal dimension d_f from the initial slope of the $g(r)$ of the whole system (2nd column) and estimates of the slope of $S(q)$ of the whole system (3rd column), for those concentrations for which it was possible to obtain them.

ϕ	d_f from $g(r)$	Slope from $S(q)$
0.0065	1.913	1.996
0.008	1.902	2.030
0.01	1.914	2.051
0.03	1.950	2.064
0.05	2.034	—
0.065	—	—
0.08	—	—

Figure 5. A log-log plot of the whole system $S(q)$ vs. q, for the same simulation as in Fig. 4. There is a linear part between A and B.

the very short region behaving as r^{d_f-3} but also from the minimum and the further increase of the function. It is, however, conceivable that at much lower concentrations, when well separated big clusters are present, the slope of the linear region coincides with the fractal dimension of the clusters. The slope of the linear region for the concentrations we are working appears to be more like an average fractal dimension of some "blobs" that include perhaps a big cluster and several smaller clusters rather than a cluster fractal dimension. In the gel phase and, with all the more reason, in the single gelled network state, that fractal dimension should be the one for the "blobs" that compose the "infinite" network. The third column of Table 2 contains the average over the five simulations of the linear slope at the last time, for those concentrations for which it was possible to find a linear behavior in the log-log plots of $S(q)$ vs. q. As we can see, there are serious discrepancies between the values on the two columns.

5. Discussion

We have seen how all sensible estimates of the concentration dependence of the cluster fractal dimension lead us to the formula obtained in Section 2, namely, $d_f = d_f^0 + a\phi^\beta$, with $d_f^0 = 1.80 \pm 0.01$, $a = 0.91 \pm 0.03$ and $\beta = 0.51 \pm 0.02$. However, we would like to know the range of validity of such formula. Before trying to apply this result to experimental systems, it should be mentioned that in our case, the volume fraction is defined as the fraction of cells of the lattice occupied by colloidal particles. In an experimental system, the volume fraction is defined as the volume occupied by the colloidal particles divided by the volume of the system. It does not appear obvious how to relate both volume fractions. The belief is that they are proportional to each other. If this were the case, only minor changes in the constant that multiplies the volume fraction in the above formula (the parameter a) need to be introduced. When the colloidal concentration is very high, the aggregation occurs very rapidly. Only a few movements of the particles and clusters lead to a highly aggregated state and even to gelation. In this case it is apparent that the cluster formation should be very dependent on the shape and initial distribution of the colloidal particles. Therefore, we wouldn't like to push the above expression beyond the site percolation threshold of any 3-dimensional regular lattice.

   We have also seen that the way of obtaining the cluster fractal dimension from the log-log plots of $S(q)$

leads to errors and ambiguities, for not very dilute systems. Unfortunately, the primarily used experimental technique for obtaining the d_f is precisely through the normalized scattered intensity, which coincides with the $S(q)$. One possibility to circumvent the problem is to extract the d_f from the limit of the particle-particle correlation function of the whole system, for short enough distances such that the law $g(r) \sim r^{d_f-3}$ is valid. In order to get the $g(r)$, one needs to invert Eq. (7) to solve for $g(r)$, which requires an integration of $S(q)$ from zero to infinity. The problem that arises now is that the experimentalists do not obtain the $S(q)$ up to infinity but up to a maximum q_{max} defined by the scattering apparatus. Nevertheless, it is possible to approximately invert Eq. (7) and to obtain some approximations for $g(r)$ at a discrete set of points, sparing us the integration up to infinity [9]. Let a_0 be the particle diameter and let $\Delta_n = a_0/n$ ($n = 1, 2, 3, \ldots$) be the size of the bin at whose center we want an approximation for $g(r)$ (the smaller the bin, that is the bigger the n, the better the approximation). Then, it is not difficult to show [9] that, for a given bin size, the approximations for $g(r)$ at each of the bin centers r_i ($i = \frac{2i-1}{2n}a_0$ ($i = 1, 2, 3, \ldots$)) are given by

$$g_i = 1 + \frac{1}{2\pi^2 \rho r_i} \int_0^{n\pi/a_0} q \sin(qr_i)(S_{total}(q) - 1)\, dq.$$
(8)

Given that the scattering vector q is related to the scattering angle and the wavelength by $q = \frac{4\pi}{\lambda}\sin(\theta/2)$, and assuming that the maximum scattering angle that can be measured is π (backward scattering), then we should have the following restriction $n\lambda < 4a_0$. Therefore, the better the approximation we want for $g(r)$, the bigger the particles that should be considered in the scattering experiment. Note that it is not impossible to accomplish this and still have a diffusing (non-sedimenting) DLCA system, if the solvent is picked with a density that closely matches the density of the colloidal particles (as in a mixture of water and heavy water at the correct proportions).

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