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On the self-similarity of fractal colloidal aggregates in two dimensions

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Abstract

It is argued that colloidal fractals are self-similar because all computed fractal dimensions of a given fractal have the same value. However, in a mathematical sense the self-similar character of a set implies not only that all fractal dimensions agree in value but also the existence of a set of similarities that generates the fractal. In this paper we report some results from two-dimensional aggregation experiments at the air–liquid interface and show that, with the appropriate selection for the similarities, the colloidal fractal aggregates can be considered as self-similar in a more mathematically rigorous form.

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1. Introduction

The mathematical formulation of fractals is based on the measure theory dating from the beginning of the 20th century and based mainly on the works of Hausdorff [1] and Besicovitch [2]. However, the term 'fractal' was coined by Mandelbrot [3]. In his most famous book (*The Fractal Geometry of Nature*), he showed that nearly all processes in nature have a fractal behaviour, at least in the sense of the original Latin term 'fractus'. Beyond this general fractal character of nature this behaviour is limited to some scale range and thus the mathematical limit is not really approached.

Mathematical fractals are characterized by their Hausdorff dimension (HD). The HD definition, which follows directly from the generalization of the concept of measure by Hausdorff, is the main parameter forming the mathematical basis of fractal theory [4, 5]. However, in practice HD is difficult to calculate so we need to use some alternative fractal dimensions whose definitions are far from rigorous [6].

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The fractal behaviour of colloidal aggregates in two dimensions formed in different experimental regimes has been reported elsewhere [7]. This behaviour is limited experimentally to a scale range that usually goes from the size of the smallest particles composing the system to the size of the biggest aggregate. This fact is a challenge when calculating the fractal dimension of these systems.

2. The computation of the fractal dimension

Different methods have been used to estimate the fractal dimension of colloidal aggregates. Most of them use all aggregates contained in the system, so its application assumes some kind of statistical similarity between the different aggregates. This assumption does not imply the self-similar character of each aggregate individually but a scale between different aggregates.

The main methods used to compute the fractal dimension of colloidal aggregates are: radius of gyration (RG), nested squares or balls method (NS) and the density correlation function (DCF) method.

The RG method uses the relation that exists between the aggregate Hausdorff measure, the mass (M), the radius of gyration (R_g) and the fractal dimension D:

$$M \propto R_g^D. \tag{1}$$

This dependence is used to compute the fractal dimension, so to apply the RG method it is usual to average the mass of the aggregates using bins of the same width in the log scale for RG.

The NS method uses the proportionality relation between the measure of the fractal contained into a ball of radius r, M_r, centred in a point of the aggregate, usually its mass centre, its radius and the fractal dimension of the fractal aggregate:

$$M_t \propto r^D. \tag{2}$$

The correlation function, $C(r)$, gives us the probability that two points separated a distance r belong to the fractal set. The DCF method makes use of the proportionality relation between $C(r)$ and r:

$$C(r) \propto r^{D-d} \tag{3}$$

where D is the fractal dimension and d is the embedding space dimension. In this expression it is assumed that the fractal is isotropic, so there is no dependence on the spatial direction, only with distance. As for the NS method an average for all aggregates is usually taken.

It must be noted that, while theoretically all these values for the fractal dimension have the same value, in the experimental case we must consider the above quoted limitation of fractal behaviour and also experimental errors that can occur. We must also take into account that these methods, when used to calculate the fractal dimension, do not assume that the fractal aggregates are self-similar but that a similarity between big and small aggregates exists.

3. Two-dimensional aggregation results

In this paper we apply the above fractal characterization to analyse the fractal behaviour of a two-dimensional aggregating system formed by polymer colloids with a 600 nm diameter. After the beginning of the aggregation process different images were obtained of the system time evolution. A typical picture of the aggregating system is shown in figure 1. The picture was taken from an aggregation made at the air–liquid interface, where the subphase has a pH of 1.50 and an ionic strength equal to 2.0 M of KBr. A diffusion limited cluster aggregation (DLCA) regime is expected under these experimental conditions.

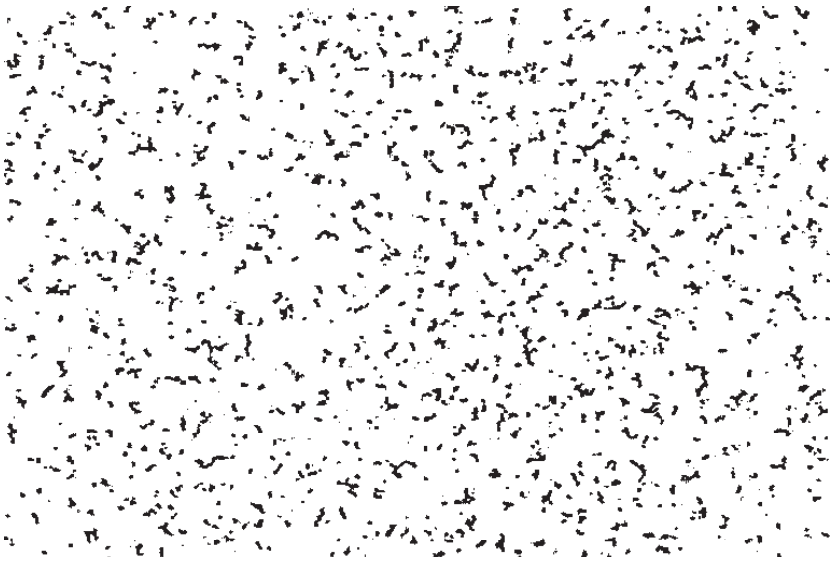

Figure 1. Typical picture of an aggregating system at the air–liquid interface. This digital image is already processed to separate the aggregates from the background. The digital image processing (DIP) is the most important step of data processing because all the following results are dependent on the DIP quality.

Table 1. Experimental values obtained when the RG, NS and DCF methods are applied to calculate the fractal dimension of the colloidal aggregates contained in figure 1. These are typical values that are widely obtained in experimental systems aggregating in two dimensions. The F_{exp} column corresponds to the value of the Fisher–Snedecor F distribution obtained from the fitting to experimental data. All values are greater than the theoretical one that is near 5.0, reflecting the goodness of the fitting. The mean value of these three values is 1.41 ± 0.03, close to the value from simulation and experimental data [7].

Method	Fractal dimension	F_{exp}
RG	1.387 ± 0.021	4238.0
NS	1.44 ± 0.04	1687.4
DCF	1.41 ± 0.03	309.9

First, we calculate the fractal dimension for the aggregates contained in the picture 1 using the three methods mentioned above. As an example of the worth of the results we show in figure 2 the corresponding fitting for the RG method. The results for the three methods are shown in table 1. It can be easily verified that the three values agree within experimental error. This result reflects the correctness of the scaling between small and big aggregates implicitly assumed when applying them. Also, the average experimental value (1.41 ± 0.03) is very close to the value obtained from simulation in the DLCA regime (1.44 ± 0.04).

4. The self-similarity problem

To show the self-similar character of the colloidal aggregates formed in the two-dimensional aggregation process we must find the similarities that generate them. These similarities must verify the open set condition: *a set of similarities* $\{\phi_1, \ldots, \phi_n\}$ *verifies the open set condition if there is a bounded open set* $V \subset R^n$ *that* $\phi_i(V) \cap \phi_j(V) = \emptyset$ *for* $i \neq j$ *and that* $\cup_i^n \phi_i(V) \subset V$.

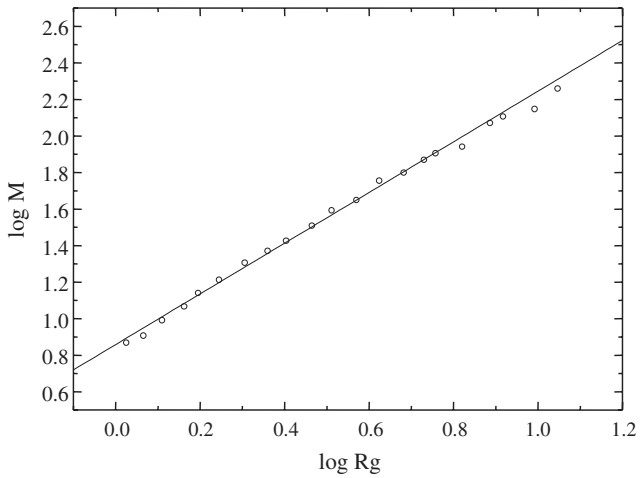

Figure 2. Application of the RG method to compute the fractal dimension for the aggregates contained in the picture in figure 1. The worth of the fitting of the log M versus log R_g dependence is evident.

It is clear that the set of similarities is not unique, since if we have a set of similarities $\{\phi_1, \ldots, \phi_n\}$ that generates the fractal then the set $\{\phi_1\phi_1, \ldots, \phi_1\phi_n, \phi_2\phi_1, \ldots, \phi_n\phi_n\}$ also generates the fractal set. When generating a self-similar set from their similarities we apply these similarities to the initial set V determined by the open-set condition and obtain a reduced copy of it for each similarity. This process is continued iteratively, applying the similarities again to obtain, in the limit, the fractal set.

These fractal sets, which are defined with an iterative way using a set of similarities verifying the open set condition, have a fractal dimension value that is easy to calculate. The main expression giving this fractal dimension value is

$$\sum_{i}^{N} r_i^D = 1 \tag{4}$$

where r_i are the ratios of the similarities, N is the number of similarities and D is the solution of this equation, which corresponds to the Hausdorff fractal dimension of the set. In this case we talk about the similarity dimension. For mathematical fractals all definitions of the fractal dimension must have the same value [8]. However, only when the fractal is self-similar does it make sense to talk about the similarity dimension.

This construction method suggested to us to consider as a first approximation that each particle of an aggregate could be considered as corresponding to a similarity with a contraction ratio equal to the ratio of their size to the aggregate radius. This selection gives us a set of N (the number of particles of the aggregate) similarities with the same contraction ratio verifying the open-set condition, as is illustrated in figure 3. The application of this approximation gives as a fractal dimension

$$D = \frac{\log N}{\log |A|} \tag{5}$$

where $|A|$ is the radius of the aggregate and N is the aggregate particle number. With this approximation we consider that the radius of single particles is 1 and the contraction ratio is $1/|A|$.

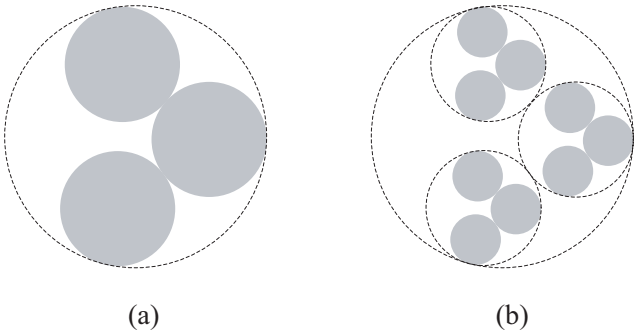

Figure 3. To find the similarities that allow us to consider a fractal aggregate as a self-similar set is a difficult task. In this picture we show that a possibility for the selection of these similarities can be to consider each particle as a similarity, which means each particle can be considered as equivalent to the whole aggregate. Picture A represents an aggregate formed by three particles. (*a*) shows the aggregate being transformed by the transformations corresponding to each particle of the aggregate. This selection verifies the open-set condition: the outer circle defines an open set V and each similarity is defined by the application of this open set to one of the particles, represented by a grey background.

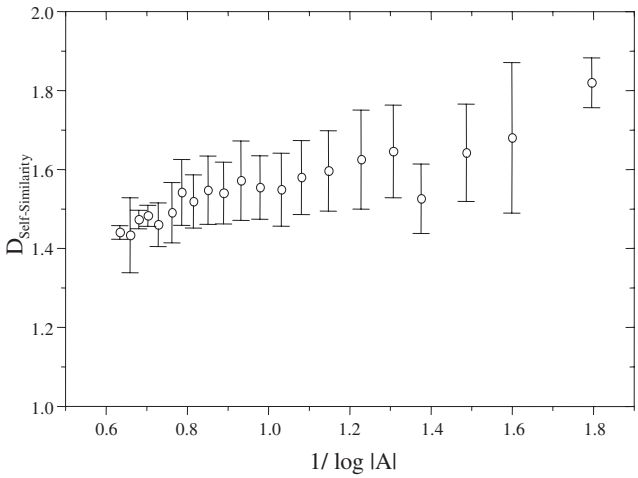

Figure 4. Similarity dimension versus the inverse of the decadic log of the fractal diameter. The values of the fractal dimension were obtained by averaging at bins with a fixed width at the log scale for the aggregate size.

However, this construction is not unique and we can select a different set of similarities using different covers, without intersection to prevent that the open-set condition is verified, of the whole aggregate. Each cover element defines a similarity whose contraction ratio can be determined by the quotient of the diameter of its intersection with the aggregate and the aggregate diameter. After this determination is completed the fractal dimension can be computed numerically from equation (4). In this paper we have used covers of sizes 1, 2 and 3, and as is indicated below our results show that the fractal dimension for the two-dimensional aggregates is independent of the size of the boxes used to cover the fractal aggregates.

Using this method to compute the fractal dimension we obtain a different value for each aggregate being convenient to average the obtained values. This average can be made in

different forms. We can average either over the whole population or in different aggregate sizes. As the last method does not assume a scaling relation between small and big aggregates, we believe it is better than others. The result of this average for all the aggregates in figure 1 is shown in figure 4. In this figure we can see that the fractal dimension of the aggregates is size dependent. This fact is not revealed by the RG, NC and DCF methods as they use all the aggregates contained in the system to made a global computation of the fractal dimension. The average value corresponding to the first five points, i.e. the biggest aggregates, is 1.458 ± 0.021, very close to the fractal dimension obtained with the NS method. This value, common for cover sizes 1, 2 and 3, reflects the self-similar character of the fractal aggregates that are formed in two-dimensional aggregation of polymer colloids.

5. Conclusions

We have suggested a method to compute the similarity fractal dimension for colloidal aggregates that gives values that, within experimental error, agree with values computed using other methods. Our results are also similar to that of Earnshaw and Robinson [7] for the DLCA studied case.

The main conclusion of this paper is that, within experimental errors, we can consider that colloidal aggregates at the air–liquid interface are self-similar. However, we can affirm nothing about three-dimensional aggregates [9] but we hope that similar results could be found.

Acknowledgments

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