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# Structure Factors for Fractal Aggregates Built Off-Lattice with Tunable Fractal Dimension

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**Abstract.** — Structure factors for fractal aggregates with a range of fractal dimensions have been studied. To this end, a hierarchical computer algorithm is presented which is able to build, in the three-dimensional space, disordered off-lattice fractal aggregates made of identical tangent spheres, whose fractal dimension can be varied from 1 up to an upper limit of about 2.55. The correlation functions and their Fourier transforms  $S(q)$  (structure factors) are calculated for various fractal dimensions. It is shown that the  $S(q)$  curve exhibits a characteristic sigmoidal shape for  $D > 2$  and that it is necessary to include a cluster size power-law polydispersity to recover a power-law behavior of  $S(q)$  in a large range of  $q$  values, as observed in experiments.

## 1. Introduction

Small angle scattering (SAS) techniques (X-rays, neutrons or light) have been widely used to determine experimentally the fractal dimension of various fractal aggregates [1–17]. Such techniques give informations on the Fourier transform  $S(q)$  of the pair correlation function  $\rho(r)$  between particle centers within an aggregate. As a consequence of the fractal power-law behavior  $\rho(r) \sim r^{-(3-D)}$  the scattering function  $S(q)$  should behave as  $q^{-D}$ , leading to a very simple determination of  $D$  using a log-log plot of  $S(q)$  versus  $q$ . These methods are complementary of the direct analysis of digitalized micrographs [18–20] which gives informations on the fractal properties of two-dimensional projections. The SAS techniques have the great advantage to be not destructive. Moreover it is generally believed that they are not limited to fractal dimensions smaller than 2, as it is for the micrograph analysis methods (as the fractal dimension of a cluster projection cannot be larger than 2).

However, it is known [21–24] that the Fourier transform of a power law of the type  $r^{-(3-D)}$  diverges for  $D > 2$  if there is no upper cut-off to the power law. Therefore the precise shape of the surface of the aggregate, which can be described by a cut-off function in  $\rho(r)$ , enters in a non-trivial fashion the  $S(q)$  curve and can affect the experimental determination of  $D$  for  $D > 2$ . Such an effect has already been evidenced using some *ad-hoc* cut-off functions [24]. Here, we would like to study this effect on some more physical examples computer generated

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fractal aggregates with tunable fractal dimensions ranging from  $D = 1$  up to  $D = 2.55$ . These aggregates, which contain up to 8192 particles have been generated using a new aggregation model which is an off-lattice extension of the recently introduced variable- $D$  model [25]. This model can be viewed as an extension of the existing aggregation models [26] since the penetration of aggregates when sticking, which determines their fractal dimension, is now controlled. The advantage of the present off-lattice version compared to the previous on-lattice one is that it is more realistic and that the input fractal dimension is exactly, and not approximately, recovered. But, it has the same limitation as fractal dimensions larger than 2.55 cannot be reached. Therefore the purpose of this paper is two-fold: first, a new algorithm to build off-lattice cluster-cluster aggregates is presented and, second, a first application of this algorithm to the study of the structure factor of fractal aggregates is presented. In Section 2 we describe the model. In Section 3, we give the numerical results for the correlation functions and their Fourier transform. And in Section 4 we discuss our results at the light of experimental data.

## 2. The Off-Lattice Variable- $D$ Model

The model uses the previously introduced [25, 27] hierarchical procedure which starts with a collection of  $2^n$  identical spherical particles of unit diameter. At iteration  $i$ , a collection of  $N_c = 2^{n-i}$ , containing  $N_i = 2^i$  particles each, is built. To proceed with the next iteration, the aggregates are grouped into pairs and the two aggregates of a pair are stuck together according to a given rule. The procedure ends with a unique aggregate of  $N = 2^n$  particles at iteration  $n$ .

The rule for sticking two aggregates (1) and (2) of  $N$  particles is chosen in order to satisfy the relation:

$$\Gamma^2 = k^2 R_N^2 + 1 \quad (1)$$

where  $\Gamma = G_1 G_2$  is the distance between the centers of mass  $G_1$  and  $G_2$  of the aggregates when they are in their sticking position,  $R_N^2 = (R_N^2(1) + R_N^2(2))/2$  is their mean radius of gyration squared, and  $k$  is related to the input fractal dimension  $D$  by:

$$k = 2\sqrt{4^{1/D} - 1} \quad (2)$$

The corrective term  $+1$  in (1), which becomes negligible for large aggregates, is introduced to satisfy exactly  $R_N^2 = (N^2 - 1)/12$  for  $D = 1$  (linear chain of  $N$  tangent particles).

These relations implies that the effective fractal dimension  $D(N)$ , calculated by comparing the results from one iteration to the next one:

$$D(N) = \frac{\log 4}{\log(R_N^2 - \frac{1}{4}) - \log R_{N/2}^2} \quad (3)$$

is automatically equal to the input fractal dimension, for all  $N$ . The corrective term  $-1/4$  in (3), which is consistent with the extra term  $+1$  in (1), is introduced to take care of "trivial" corrections to scaling, as discussed in [28, 29].

The recipe is the following. Suppose one knows the aggregates (1) and (2), their centers of mass  $G_1$  and  $G_2$ , their radii of gyration, and consequently the parameter  $\Gamma$  given by (1). One first chooses at random one particle of cluster (1) and one particle of cluster (2). Let us call  $I_1$  and  $I_2$  their centers. Then one determines a neighboring site of  $I_1$ , say  $J_1$  (such that  $I_1 J_1 = 1$ ) as a candidate to be the position of  $I_2$  when sticking. The azimuthal direction of the vector  $I_1 J_1$  around the axis  $G_1 I_1$  is chosen at random uniformly between 0 and  $2\pi$ , but the direct angle  $\theta = (G_1 I_1, I_1 J_1)$  is chosen such that:

$$\theta = \pi \xi \sqrt{\frac{2}{D-1}} \quad (4)$$

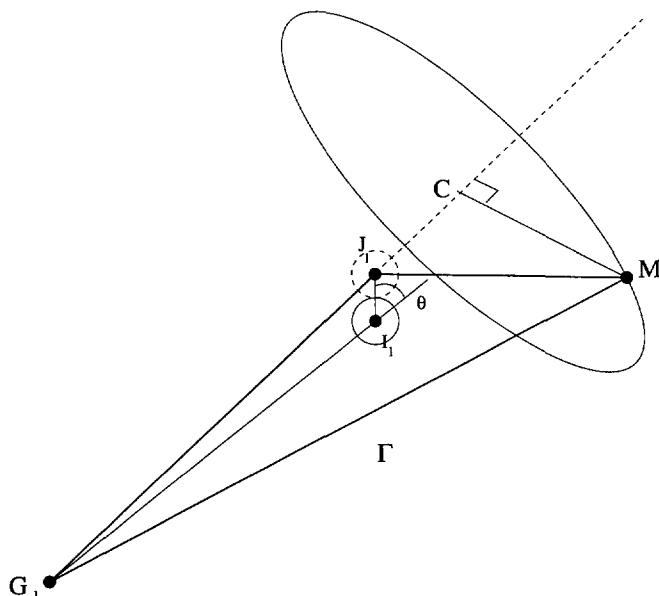


Fig. 1. — Three-dimensional sketch of the determination of the position of  $G_2$  vs.  $G_1$  (centers of mass of aggregate (2) and (1) respectively) to satisfy the conditions (6a) and (6b), as explained in text.

where  $\xi$  is a random variable uniformly distributed between 0 and 1. This insures that  $\theta$  is uniformly distributed between 0 and  $\pi$  when asking for  $D = 3$ , but reduces to  $\theta = 0$  in the limit  $D = 1$ . Such anisotropy in the choice of  $J_1$  is necessary if we want to be able to recover the linear chain for  $D = 1$ . Obviously the precise form entering formula (4) becomes irrelevant for very large clusters.

At this stage, a test is performed to verify the following triangular condition on distances:

$$G_1J_1 + G_2I_2 > \Gamma \tag{5}$$

If this condition is not satisfied, one chooses again two particles  $I_1$  and  $I_2$ . If the condition is satisfied, one determines the circle of axis  $G_1J_1$  (see Fig. 1) such that any point  $M$  of this circle satisfies the two conditions:

$$G_1M = \Gamma \tag{6a}$$

$$J_1M = G_2I_2 \tag{6b}$$

Then one chooses at random, but uniformly on the circle, a point  $M$  and we move the cluster (2) in order that  $G_2$  coincides with  $M$  and  $I_2$  with  $J_1$ . Note that there remains an indetermination for the azimuthal angle defining the position of cluster (2) around  $G_2I_2$ . This angle is chosen at random uniformly between 0 and  $2\pi$ .

Cluster (2) being positioned, one performs a test for overlaps between any particle of (1) and any particle of (2). To avoid a double loop which would be time consuming, we have built a cubic sub-lattice to label the particles of (1) and we have used it to test only the nearest neighborhood of each particle of aggregate (2). If there is an overlap, one goes back to choose again two particles  $I_1$  and  $I_2$  and so on. If there is no overlap, the ensemble of aggregate (1) and aggregate (2) is stored as an aggregate of  $2N$  particles of the next generation.

We have checked that the procedure works for any fractal dimension ranging from  $D = 1$ , where a linear chain of particles is recovered, up to an upper fractal dimension  $D_m$  which is

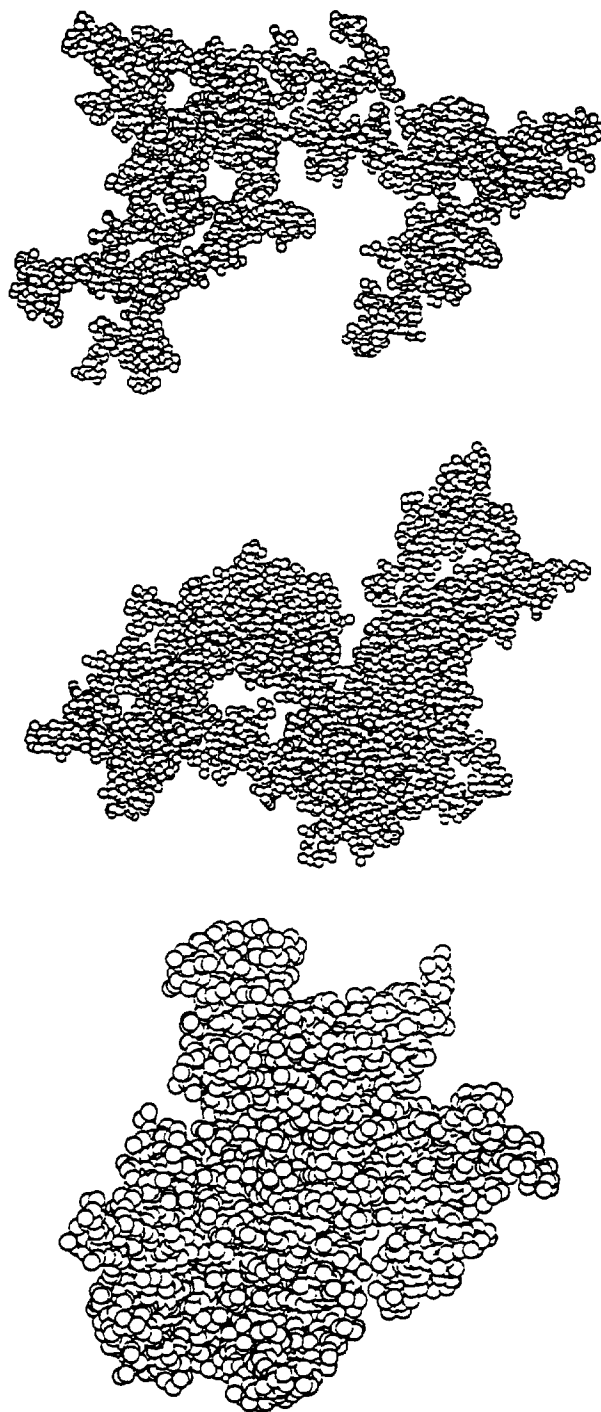
difficult to estimate with precision as the computing time diverges as  $D$  approaches  $D_m$ . This upper limit is about 2.55, in agreement with the one obtained with the lattice version of the model [25]. We recall that this limitation is due to frustration effects coming from disorder: the hierarchical method introduces some surface roughness while to reach a compact cluster (with  $D = d$ ) one needs a smooth surface.

In Figures 2a and 2b, one shows the two-dimensional projections of typical aggregates of 4096 particles with  $D = 1.2, 1.6, 2, 2.1, 2.3$  and  $2.5$ .



(a)

Fig. 2. — Two-dimensional projections of typical three-dimensional aggregates of  $N = 4096$  particles obtained for  $D = 1.2, 1.6, 2.0$  (a) and  $D = 2.1, 2.3, 2.5$  (b).



(b)

Fig. 2. — (Continued.)

### 3. Numerical Results

For an aggregate of  $N$  particles, the correlation function  $\rho(r)$  can be calculated as the distance distribution function between particle centers. With a convenient normalization, it is given by:

$$\rho(r) = \frac{dN}{4N\pi r^2 dr} \quad (7)$$

where  $dN$  is the number of distances lying between  $r$  and  $r + dr$ . Here the normalization is such that:

$$\int_0^\infty \rho(r) 4\pi r^2 dr = \frac{N-1}{2} \quad (8)$$

The numerical results for aggregates of  $N = 8192$  particles, averaged over 5 independent samples are presented as log-log plot in Figures 3a and 3b for fractal dimensions smaller than 2 and larger than 2, respectively. In each figure the expected slope  $-(3-D)$  is indicated. Even if the fractal regime is less extended for fractal dimension larger than 2, the expected slope is well recovered.

When considering a small angle scattering experiment on randomly oriented aggregates of  $N$  identical spherical particles, the scattering intensity  $I(q)$  writes:

$$I(q) = NS(q)P(q) \quad (9)$$

where  $P(q)$  is the form factor of the particles and  $S(q)$  is the structure factor, or scattering function, which the Fourier transform of  $\rho(r)$ :

$$S(q) = 1 + \frac{1}{N} \int_0^\infty \rho(r) \frac{\sin qr}{qr} 4\pi r^2 dr \quad (10)$$

We would like to emphasize that these formulae are valid even though the aggregates are intrinsically anisotropic as it is known in such a cluster-cluster process [31] (the presence of  $\sin qr/qr$  inside the integral results from the angular average of the intensity over the random orientations of the aggregate for a fixed  $\mathbf{q}$ ).

The numerical results for  $S(q)$  are given in Figures 4a and 4b. All the curves tends to 1 with damped oscillations as  $q$  tends to infinity. These oscillations are characteristic of the short range correlations between particles [32]. But here we would like to focus on the intermediate (fractal) regime. In the figures the expected slope  $-D$  is indicated. For  $D < 2$  the linear fractal regime is quite well recovered. For  $D > 2$ , one observes a characteristic sigmoidal shape corresponding to the crossover between the small- $q$  Guinier regime and the fractal regime, as already found with *ad-hoc* cut-off functions [24]. As it can be seen in Figure 5 the sigmoidal shape exists for all cluster sizes up to the largest available size and therefore can hardly be attributed to finite size effects. The location of the crossover is shifted towards large  $q$  values as  $D$  increases and therefore, a more and more extended  $q$  region exhibits a quite large apparent slope. As already noticed, this region is characteristic of the surface of the aggregate and would merge into the  $q^{-4}$  Porod regime if one would be able to reach  $D = 3$  (diffusion by an homogeneous sphere). As a consequence of this crossover, the fractal regime becomes badly defined.

The existence of a sigmoidal shape of  $S(q)$  for  $D > 2$  is, in fact, quite general and this is illustrated in Figure 6 where we compare an  $S(q)$  curve for  $N = 8192$  aggregates built with our algorithm with an input fractal dimension of  $D = 2.45$  with the one of three-dimensional off-lattice Witten-Sander aggregates [26] containing the same number of particles. The latter aggregates have been built with the standard particle-cluster aggregation process [26, 30] in

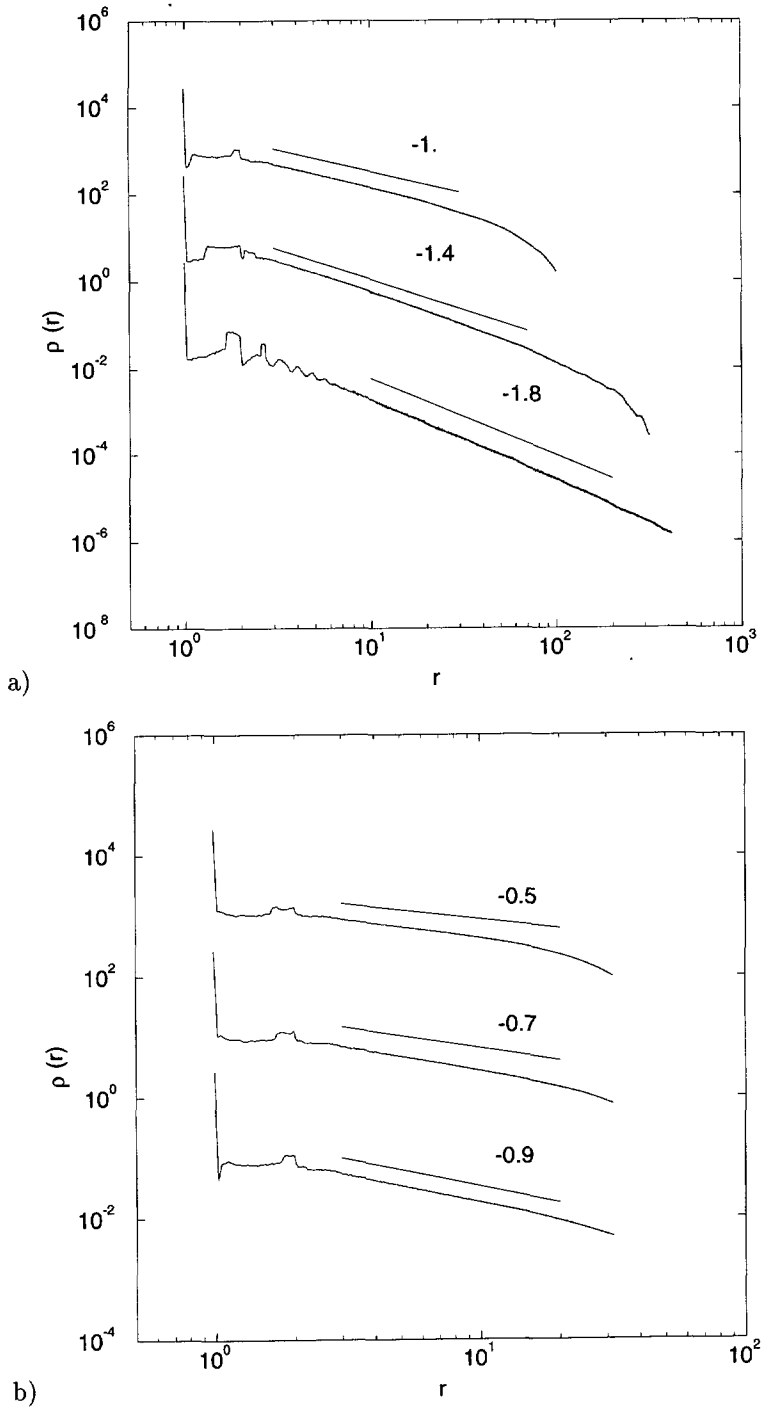


Fig. 3. — Numerical results for the distance distribution function  $\rho(r)$  averaged over 5 different samples, in the case of aggregates containing  $N = 8192$  particles, for  $D < 2$  (a) and  $D > 2$  (b). The expected slope  $-(3 - D)$  is indicated.



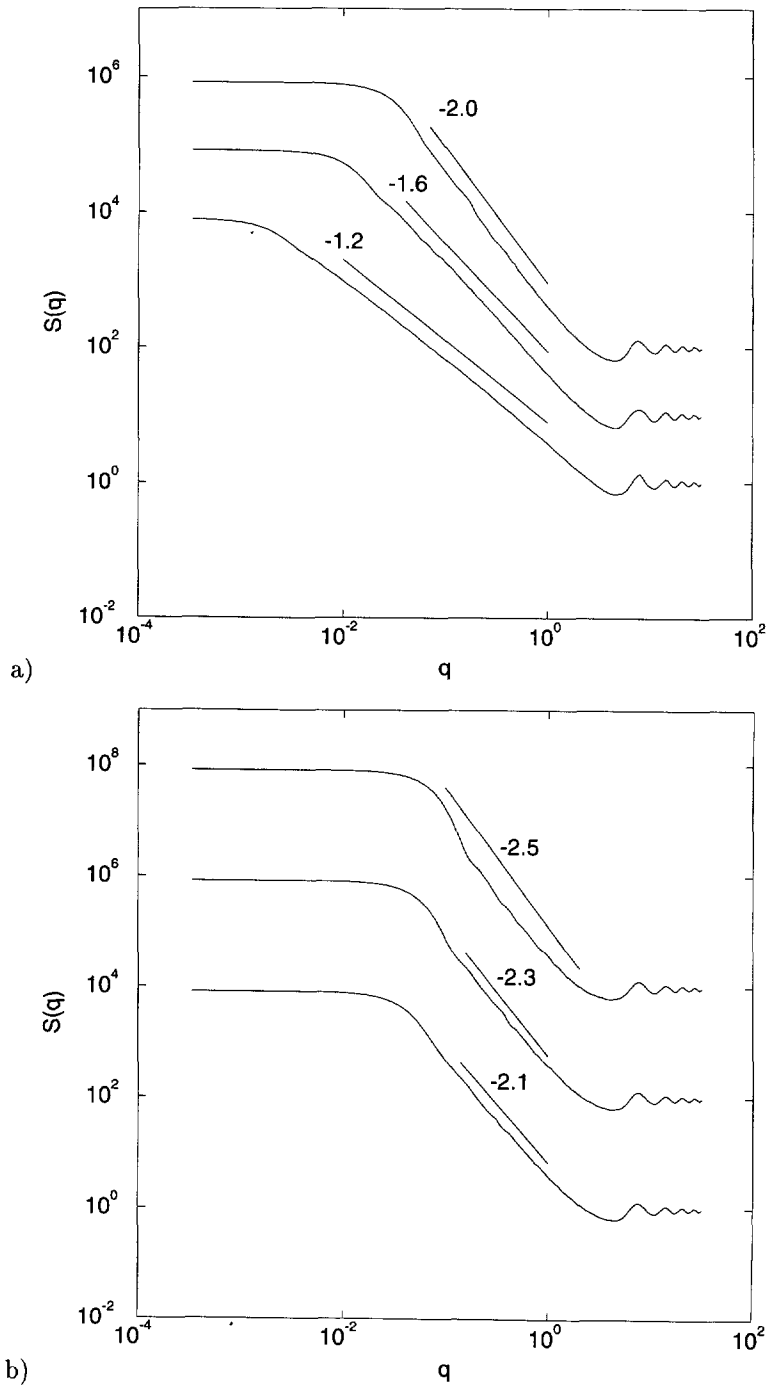


Fig. 4. — Numerical results for the scattering function  $S(q)$ , calculated for aggregates containing  $N = 8192$  particles, (averaged over 5 different samples), for  $D < 2$  (a) and  $D > 2$  (b). The expected slope  $-D$  is indicated.

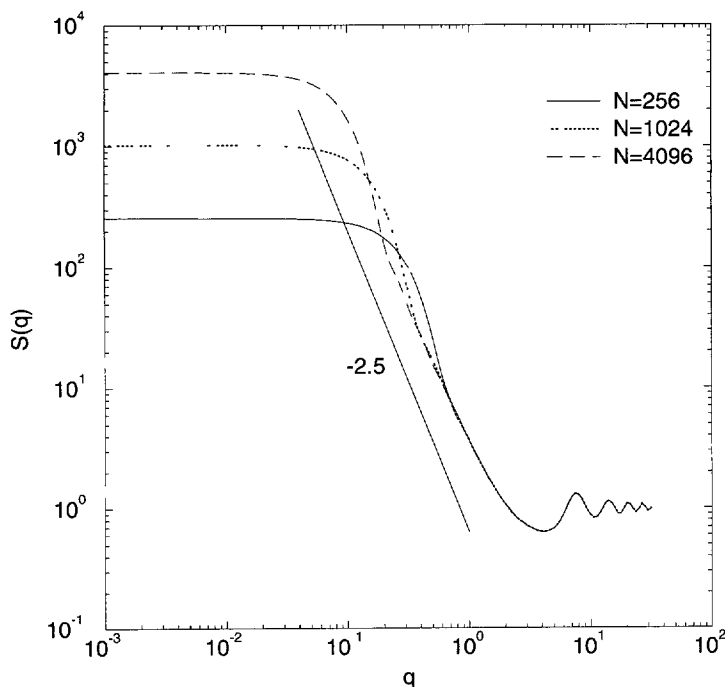


Fig. 5. — Comparison between the  $S(q)$  curves obtained with  $D = 2.5$  and different  $N$  values:  $N = 256, 1024, 4096$ .

which single particles are stuck one after one to a single cluster after a random walk in space starting from random points on a large sphere centered on a seed particle. The two curves are almost superimposed in the large- $q$  as well as intermediate- $q$  (fractal) regimes suggesting that both clusters have the same fractal dimension of  $D = 2.45$  (even if the effective slope is smaller in that region). This result is consistent with the value  $D = 2.50 \pm 0.05$  already known for 3-d Witten-Sander aggregates [26, 30]. The sigmoidal shape is observed in both cases but the inflexion in the crossover region is less pronounced in the Witten-Sander case. This can be understood by the roughness of the surface which is certainly higher for an aggregate made with particle-cluster aggregation. Therefore, although the sigmoidal shape is always seen, the precise shape of the curve in the crossover region is not universal.

#### 4. Discussion and Conclusion

To our knowledge, the sigmoidal shape of  $S(q)$ , for  $D > 2$ , has never been observed in experiments [1, 3, 6–9, 11]. In this section, we would like to stress that this is because the experiments are always dealing with a collection of polydispersed aggregates, and not with a monodisperse collection of randomly oriented aggregates of the same size. It is known that, in the “floculation” regime, described by diffusion-limited cluster-cluster processes, the cluster size distribution exhibits a well defined maximum and decreases exponentially at large sizes [26, 33]. Therefore in that case, the fractal slope of the  $S(q)$  curve for a collection of aggregates should be the same as the one for a single (randomly oriented) aggregate of the mean size. In contrast with this situation, a gelling system, in which a single “infinite” aggregate appears at a given

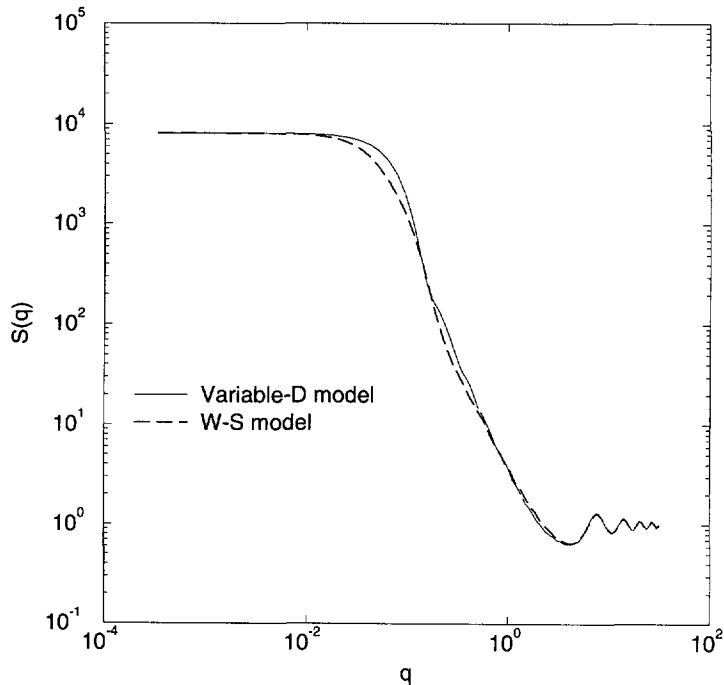


Fig. 6. — Comparison between the  $S(q)$  curve for  $N = 8192$  aggregates obtained with our model for  $D = 2.45$ , with the one of three-dimensional off-lattice Witten-Sander aggregates containing the same number of particles.

time, exhibits large size power-law polydispersity with cluster-size distribution  $f(N) \sim N^{-\tau}$  with  $\tau > 2$  [33]. It is known that, in that case, the slope of the  $S(q)$  curve is no more equal to  $D$ , but to  $D_{\text{eff}} = D(3 - \tau) < D$ , which can be interpreted as the effective fractal dimension of polydisperse clusters, rather than the fractal dimension  $D$  of an individual cluster.

In our case we can study such an effect by introducing artificially a size polydispersity  $g(p)$  out of our clusters of  $N = 2^p$  particles, with  $p$  ranging from 1 to 13. To recover  $f(N) = N^{-\tau}$ , one should use  $g(p) = f(N) \frac{dN}{dp} \propto N f(N) = N^{1-\tau}$ . Taking care that for a polydisperse system one should add the scattering intensities, which are proportional to  $NS_N(q)$  (see formula (9)), one can construct the effective scattering function for a power-law polydisperse collection using the following formula:

$$S_{\text{eff}}(q) = \frac{\sum N^{2-\tau} S_N(q)}{\sum N^{2-\tau}} \quad (11)$$

where the sum runs over  $N = 1, 2, 4, \dots, 8192$  and where  $S_N(q)$  denotes the scattering function for a single aggregate of  $N$  particles (for  $N = 1$ , one considers  $S_1(q) = 1$ ). In Figure 7, we give the  $S_{\text{eff}}$  curves calculated this way, using our clusters with  $D = 2.45$  and Witten-Sander aggregates, taking  $\tau = 2.2$  in both cases (which is the value of  $\tau$  for percolation [33]). It is striking that, in both cases, we recover a nice linear behavior with a slope of 1.85 quite close (but slightly smaller) to the expected value  $D_{\text{eff}} = (3 - \tau)D = 1.96$ .

This discussion is rising some problems with fractal dimensions larger than 2, previously reported in the literature from small angle scattering experiments. Although some authors

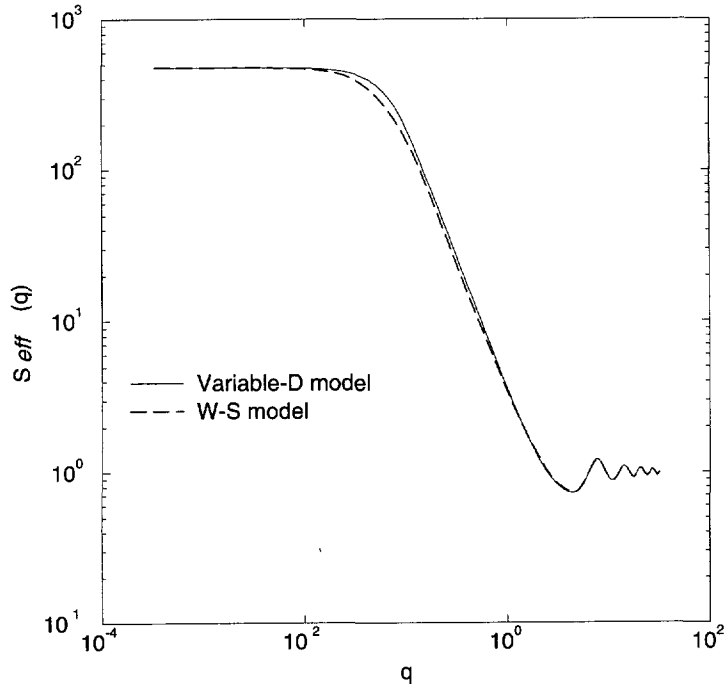


Fig. 7. — Comparison between  $S_{\text{eff}}(q)$  for a collection of polydisperse aggregates obtained with our model for  $D = 2.45$ , with a collection of three-dimensional off-lattice Witten-Sander aggregates made of aggregates of 2, 4, ..., 8192 particles with a polydispersity exponent of  $\tau = 2.2$ .

have already noticed that the slope of the scattering curve was leading to an effective fractal dimension smaller than the true fractal dimension [7, 11], some others were reporting fractal dimensions larger than 2 as being exactly the slope of their  $S(q)$  curves ([1, 3, 6, 8, 9]). In that case, the process involved is unlikely of the diffusion-limited cluster-cluster type as their curves do not exhibit the sigmoidal shape characteristic of a quite monodisperse cluster collection. If they should have taken into account power-law polydispersity the fractal dimension of their aggregates might actually be larger (unless there might be other reasons for modifying the fractal regime).

In conclusion the aim of this paper was two-fold. First we have reported on a new algorithm able to build off-lattice fractal aggregates with a tunable fractal dimension ranging from  $D = 1$  to  $D = 2.55$ . Second, we have calculated the  $S(q)$  curves for these aggregates and we have shown that, for  $D > 2$ , they exhibit a sigmoidal shape. To account for the linear fractal regime observed in the experiments, one are obliged to consider a power-law size distribution of clusters and, as a consequence, the slope of the  $I(q)$  should be smaller than the actual fractal dimension of the individual clusters. In the future, we intend to use our algorithm to study other physical properties of random fractal aggregates. The calculations of vibration spectrum is under progress.

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