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MULTISCALING IN RANDOM CLUSTER-CLUSTER AGGREGATES

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Two-point density correlation functions are studied numerically in computergenerated three-dimensional lattice cluster-cluster aggregates with the number of particles up to 20,000. The "pure" aggregation algorithm is used, where subclusters of all possible sizes are allowed to collide. We find that large cluster-cluster aggregates demonstrate pronounced multiscaling, i.e., the power-law exponents in the pair-correlation function p(r) are not constants, but depend on r and the number of particles in a cluster. In particular, the fractal dimension determined from the slope of the two-point correlation function at small distances differs from that found from the dependence of the radius of gyration on the number of monomers (1.8 and 2.0, respectively, according to our data). We also consider different functional forms of p(r) and their general properties. We find that if the fractal dimension for the cluster-cluster aggregates can be defined as a continuous function $D = D(r/R_g)$, where R_g is the radius of gyration, it must have a maximum at some value of $r/R_g = x_m$, where $D(x_m) > 2$.

1 Introduction

Computer algorithms play a very important role in understanding aggregation phenomena and physical properties of aggregates. In many instances, computer simulation is the only feasible theoretical approach to very complex stochastic aggregation processes, when traditional techniques of statistical mechanics cannot be applied due to strong fluctuations and absence of equilibrium. These algorithms have attracted much attention since Witten and Sander¹⁴, Meakin¹ and Kolb, Botet and Jullien² proposed realistic algorithms which simulate natural aggregation processes to much detail.

One of the most extensively used applications of computer-generated clusters is the study of density correlation functions. A direct experimental measurement of these functions has also been carried out (see, for example, Ref.4), but such experiments face considerable difficulties. First, it is hard to calculate inter-particle distances from a two-dimensional electron micrograph images of three-dimensional clusters ³, and, second, the process of taking the electron micrograph itself can damage the cluster structure.

Density correlation functions provide important geometrical characteristics of clusters, carrying valuable physical information. Correlation functions are especially useful in optics 3,4,5,6,7 . The two-point correlation function describes the average intensity of light scattered by an ensemble of clusters ⁴, while the four-point correlation function governs fluctuations in the scattered light ⁷.

In the present paper we study the two-point correlation function in aggregates obtained by the numerical algorithm known as the cluster-cluster aggregation (CCA) 1,2,8,9,10 . The CCA algorithm provides a very accurate simulation of aggregation processes which occur in nature, under the conditions that there is no spatially fixed center of aggregation and the concentration of aggregating material is sufficiently low. These conditions are well satisfied, for example, for formation of fractal carbone soot 4 and metallic colloids 11 .

In its most pure form, the CCA algorithm involves the following steps: First, a set of N point-like particles are randomly placed on a simple cubic lattice of the size $L \times L \times L$. The size of the lattice is chosen so that the average density of particles, N/L^3 , is much smaller than unity. Those particles which are separated by only one lattice unit are considered to be rigidly bound to each other and form a subcluster. Then a subcluster is picked randomly out of the set and moved one lattice unit in one of the six possible directions, chosen at random. If, after this move, the subcluster contacts other cluster(s) (via nearest-neighbor occupancy), these subclusters stick together to form a larger subcluster. The steps are repeated until a single cluster of N particles is left.

A great number of modifications of the algorithm exists, among which are random rotations of subclusters, prescribing "mobility" to each subcluster (which is, typically, proportional to the inverse number of particles in this subcluster), hierarchical models, off-lattice models and so on 12 . Some of these modifications, such as the hierarchical model, are intended to simplify the numerical procedure and to make it possible to generate large clusters in a feasible time; the price of these simplifications is sacrificing some essential features of real aggregation. The other modifications, such as random rotations of subclusters, are, on the contrary, intended to make the algorithm more realistic, while complicating the numerical procedure.

In the present paper we use only the pure algorithm described above and generate three-dimensional clusters with N up to 20,000. For comparison, the correlation functions in Ref.14 are studied using computer generated CCA clusters with the maximum value of N = 900. Clusters with the number of particles comparable to 20,000 have been generated earlier ^{9,10}, but with the use of the hierarchical model ⁸, which allows only subclusters of the same size to collide, and considers aggregation of only two subclusters at a time. Though this model was shown to produce clusters very similar to those obtained by the direct calculation, it evidently lacks some important features of the real aggregation process. In particular, this model may be incapable of producing the multiscaling effect (which is established for the Witten-Sander clusters ¹³).

Using the computer-generated CCA clusters with large N, we argue that the pure CCA model produces clusters possessing multiscaling. A manifestation of this effect is that the fractal dimension measured from the dependence of radius of gyration on the number of particles differs from that measured from the pair correlation function at small distances.

2 The correlation function and the fractal dimension

The CCA aggregates are known to be fractal clusters. The fractal dimension can be defined either through the gyration radius or with the use of the two-point correlation function. In the first method, we consider ensembles of clusters with different numbers of particles N (a separate ensemble for each N), and calculate the ensemble-average gyration radius R_q for each N according to

$$R_g^2 = \langle (\mathbf{r}_i - \mathbf{R}_{cm})^2 \rangle , \qquad (1)$$

where \mathbf{r}_i is the radius-vector of the *i*th particle in a cluster, \mathbf{R}_{cm} is the the radius-vector of the center of mass of the cluster, and $\langle ... \rangle$ denotes ensemble averaging. One can define the fractal dimension D_2 from the dependence of R_q on N:

$$R_q(N) = R_0 N^{1/D_2} , \quad N \gg 1 ,$$
 (2)

where R_0 is a constant of the order of the minimum separation between particles.

Another possible definition of the fractal dimension uses the pair density correlation function. In this case we consider only one ensemble of clusters containing N particles each and define the function p(r) as the probability density to find two distinct particles belonging to the same cluster separated by the distance r. Then

$$p(r) = aN^{-1}r^{D_1-1}, \quad R_0 \ll r \ll R_g,$$
(3)

where a is a constant.

If there is no multiscaling phenomena, both constants coincide: $D_2 = D_1 = D$. Then the pair correlation function can be written in the form

$$p(r) = aN^{-1}r^{D-1}f(r/R_g) . (4)$$

The function f(x) describes the cut-off of the correlation function. As follows from (3), f(x) is close to unity if $R_0/R_g \ll x \ll 1$. When $R_0 \ll R_g$, this can be expressed as f(0) = 1. For large x, f(x) must decrease fast enough to allow normalization. From normalization of p(r) and formula (2) for R_g it follows that

$$aR_0^D \int_0^\infty x^{D-1} f(x) dx = 1 .$$
 (5)

Another relation for f can be obtained by calculating the root-mean square distance between monomers, $R_{rms} = \sqrt{2}R_g$, by using $R_{rms}^2 = \int_0^\infty r^2 p(r) dr$. This relation is

$$aR_0^D \int_0^\infty x^{D+1} f(x) dx = 2 . (6)$$

Given the rules (5,6), the possible choice of the cut-off function is still very wide³. The value of aR_0^D is fixed: it does not depend on the choice of the unit of length, i.e., it is invariant with respect to any scale transformations.

Now let us turn to the case of multiscaling, when $D_2 \neq D_1$. In this case the functional form (4) for the correlation function does not provide correct normalization for an arbitrary N. Therefore, we need to use a more general functional form:

$$p(r) = aN^{-1}r^{D_1 - 1}g(r/R_g, N) , \qquad (7)$$

where R_g is still defined by (2) with a constant $D_2 \neq D_1$. The two rules for g(x, N), analogous to (5,6), are

$$aR_0^{D_1} \int_0^\infty x^{D_1 - 1} g(x, N) dx = N^{1 - D_1/D_2} , \qquad (8)$$

$$aR_0^{D_1} \int_0^\infty x^{D_1+1} g(x, N) dx = 2N^{1-D_1/D_2} .$$
(9)

As above, $aR_0^{D_1}$ is invariant with respect to any scale transformation; besides it does not depend on N by the definitions of the constants a and R_0 . Therefore, the only source of the dependence on N in the left-hand part of (8) is the function g(x, N). We note that $g(x, N) \to 1$ when $x \to 0$ for any N, and it is impossible to factorize g(x, N) as $g(x, N) = g_1(x)g_2(N)$.

Another form for p(r) in the case of multiscaling was proposed in Ref.15:

$$p(r) = aN^{-1}r^{D(r/R_g)-1}R_0^{D_1-D(r/R_g)}h(r/R_g) .$$
(10)

Here D(x) is a continuously changing fractal dimension. Since (10) must coincide with (3) when $r \ll R_g$, we require that $D(0) = D_1$ and h(0) = 1. Note that there is no general requirement that $D(\infty) = D_2$; at least it can not be deducted from the definitions of D_2 (2) and h (10). The functional dependence (10) is less general than (7). The latter is, evidently, the most general form of a function of two variables, r and N. In order for (7) and (10) to represent the same function, the following relation must hold:

$$q(x,N) = x^{D(x)-D_1} N^{[D(x)-D_1]/D_2} h(x)$$
(11)

If the representation (10) describes the correlation function correctly, then $g(x, N) \sim N^{1-D_1/D_2}$ for $x \gg 1$.

An interesting property of D(x) can be obtained by applying the normalization rules (8) to the function g(x, N) written in the form (11). Substitution of (11) to (8) yields

$$aR_0^{D_1} \int_0^\infty x^{D(x)-1} N^{D(x)/D_2 - 1} h(x) dx = 1 .$$
 (12)

By taking a derivative $\partial/\partial N$ of the equation (12), we find that the function $D(x)/D_2-1$ must change its sign, since all the other values under the integral are positively defined. In particular, if $D_2 > D_1$, the function D(x) can not be monotonously decreasing, as was theoretically predicted ¹³ for Witten-Sander clusters. We will return to this aspect of D(x) in more detail in section 5.

3 Numerical procedures

We have implemented the CCA algorithm on a simple cubic lattice with periodic boundary conditions. We have built 40 random clusters for each value of the number of particles in a cluster N, except for N=20,000, when we have built only 20 clusters. The size of the lattice L varies depending on N. The following values of L were selected: L = 200 for N = 5,000; L = 260 for N = 7,500; L = 300 for N = 10,000; L = 310 for N = 12,500; L = 340 for N = 15,000; and L = 350 for N = 20,000.

This ensured that the density of monomers was low enough $(3.7 \cdot 10^{-4} \text{ for } N = 10,000)$ and that the cluster size was smaller than the size of the lattice. For example, the root-mean square (r.m.s.) distance between two particles in clusters with N = 10,000 was 99.4, which is substantially less than the corresponding lattice size. This was true also for the largest clusters with N = 20,000 with r.m.s distance between particles equal to 141.7.

During the aggregation, each subcluster was moved with equal probability (independently of its size), and no rotations were allowed. Our simulations showed that clusters of all sizes were colliding during the aggregation. At approximately 1/2 of the full aggregation time, a main subcluster was formed, which accounted for about half of all aggregating mass, while the rest of the particles were aggregated in subclusters of widely varying size, including single non-aggregated monomers. Closer to the end of aggregation, one large subcluster and a number of small subclusters were left. This aggregation pattern suggests that the hierarchical model⁸, which allows only clusters of the same size to collide, is, in principle, different from the "pure" aggregation algorithm.

The correlation function p(r) is defined as the probability density to find a pair of distinct monomers belonging to the same cluster separated by the distance r. For finite lattice clusters it is, strictly speaking, a highly-singular function. However, if the correlation function is used for calculation of some average values $\langle F \rangle$ according to

$$\langle F \rangle = \int_0^\infty F(r)p(r)dr ,$$
 (13)

and the function F(r) changes slowly enough, we can replace the exact function p(r) by some "smoothed" function according to

$$p(r) \to \frac{1}{\delta} \int_{r-\delta/2}^{r+\delta/2} p(r') dr' .$$
(14)

Below, we will use the notation p(r) for the smoothed function.

For numerical calculation of p(r) the natural choice of the constant δ is the lattice unit. If we choose δ to be less than the lattice unit, the resultant function p(r) will fluctuate strongly at small distances, and if we choose δ to be larger than the lattice unit we will lose precision at large distances.

We have set the lattice unit and the value of δ to be equal to unity and calculated the function p(r) for integer values of r beginning with r = 1 (p(0) = 0 by definition) by enumeration of all possible pairs of particles in each cluster.

Even after smoothing, the correlation function of a lattice cluster possesses some random irregularities, which are more pronounced at small distances and may seem to be random, but are, in essence, artifacts of the lattice on which the cluster was built. The origin of these irregularities is that the density of sites of the lattice itself (measured at a certain distance from the origin and averaged over angles) has certain fluctuations, which disappear at large distances, when the discrete structure of the lattice is no more of importance. To eliminate these irregularities in the correlation function, we suggest using the following procedure: First, we define the density of lattice sites $\nu(r)$ as

$$\nu(r) = \Delta N_{latt}(r) / V(r) , \quad V(r) = \frac{4\pi}{3} [(r+1/2)^3 - (r-1/2)^3] , \qquad (15)$$

where the variable r takes the integer values beginning from r = 1, and $\Delta N_{latt}(r)$ is the number of lattice sites which lie in the spherical shell r - 1/2 < r' < r + 1/2 with the center in the origin. Evidently, this function becomes close to unity as r grows, but for small r it can significantly differ from unity ($\nu(1) \approx 1.32$). Then we define the corrected correlation function as

$$\rho(r) = p(r)/\nu(r) \tag{16}$$

Since $\nu(r)$ looks much like a statistical noise, and is unity on average, we can assume that $\int_0^\infty \rho(r)dr = \int_0^\infty p(r)dr$, which means that the normalization of p(r) is conserved.

In Fig. 1 we compare the original function p(r) and the modified function $\rho(r)$ for an ensemble of 40 clusters with N = 10,000.

4 Results of numerical calculations

The asymptotic behavior (3) of the correlation function is illustrated in Fig. 2. We plott the lattice modified correlation function $\rho(r)$ (16) multiplied by the number of particles in a cluster N for several values of N. As we can see, the asymptote (3) is very accurate, and the interval of r where it is valid grows when N (and, consequently, R_q) grows.

The coefficients for the theoretical asymptote plotted in Fig. 2 were found by linear regression. We find that $a = 3.89 \pm 0.01$ and $D_1 = 1.804 \pm 0.001$ from the data for N = 15,000 and $3 \le x \le 30$, where the uncertainties are shown at the level of one standard deviation. The use of the original correlation function p(r) gives essentially the same results, but much lower precision. Namely, we obtain from linear regression of p(r) for N = 15,000 and in the same interval of r: $a = 3.9 \pm 0.2$ and $D_1 = 1.8 \pm 0.1$. This example shows that the use of the corrected correlation function $\rho(r)$, as proposed in section 3, allows one to increase precision in calculating the regression coefficients by one order of magnitude. Finally, the values of a and D_1 were calculated using the data for other values of N. The results are very close to those for N = 15,000.

From the above data we can conclude that the value of D_1 for our clusters is close to 1.8, which is the accepted value for the fractal dimension of the CCA aggregates ¹². However, the value of D_2 , calculated from the dependence of R_g on N turns out to be much closer to 2 (see Fig. 3) ^a. We have calculated the values of R_0 and D_2 defined by (2) and find that $R_0 = 0.68 \pm 0.08$ and $D_2 = 1.99 \pm 0.05$. All errors, including the errorbars in Fig. 3, are shown at the level of one standard deviation.

^{*a*}A similar result was found for a three-dimensional off-lattice CCA model wherein subclusters aggregated via *linear* trajectories⁹. The authors generated clusters containing up to 32,000 particles and found that "...the limiting $(N \to \infty)$ dimensionality may be much closer to 2.0", concerning the dimensionality found from the slope of the radius of gyration.



Figure 1: Comparison of the original p(r) and the corrected $\rho(r)$ correlation functions for N = 10,000.

Figure 3: Radius of gyration as a function of N; $R_0 = 0.68, D_2 = 1.99.$



Figure 2: Numerically calculated functions $N\rho(r)$ for different N and the theoretical asymptote (3); $a = 3.89, D_1 = 1.804$.

Figure 4: Function g(x, N) plotted as a function of x for different N.



Figure 5: Function D(x).

In Fig. 4 we show the function g(x, N) defined by (7) as a function of x for different values of N. We have calculated g(x, N) by multiplying the modified correlation function $\rho(r)$ for clusters with different N by the factor N/ar^{D_1-1} . Note that for the calculation of $x = r/R_g$ we took not the actual $R_g(N)$ for the ensemble with the corresponding N, but the theoretical value (2) with the constants $R_0 = 0.68$ and $D_2 = 1.99$ found from the linear regression. The two values of R_g are slightly different; we believe that the use of the *theoretical* value of R_g with numerically calculated coefficients is more appropriate, since it utilizes all the ensembles of clusters, instead of one finite ensemble for each N. In other words, the experimental values of N and $R_g(N)$ in finite ensembles do not satisfy (2) exactly due to statistical errors; but the regression coefficients found from a number of experimental point N, $R_g(N)$ are expected to provide a closer fit to the theoretical curve (2) which is presumably correct for infinite ensembles. A pronounced and systematic dependence of g on N is apparent from Fig. 4. In accordance with the fact that $D_2 > D_1$ and properties (8), g(x, N) grows when N grows and x = const.

From the above data we can conclude with high precision that for CCA clusters $D_2 > D_1$ (the difference $D_2 - D_1$ is equal to four standard deviations of D_2 , while the standard deviation of D_1 is very small and can be neglected). Let us consider the case when the correlation function is correctly described by (10). As was discussed at the end of section 2, $D(0) = D_1$ and the function $D(x)/D_2 - 1$ must change sign. Together with the inequality $D_2 > D_1$, this means that for some regions of x of nonzero measure, D(x) must be greater than D_2 .

Our numerical data are insufficient for an accurate calculation of the function D(x) or even for verifying that the functional form (10) describes p(r) correctly. However, we present our results for D(x) in Fig. 5. We calculated D(x) by fixing the value r/R_g and calculating the slope of p(r) as a function of r (for clusters with different N, different values of r correspond to a fixed value of r/R_g). The number of points on this kind of graph is equal to the number of different N used. Again, we calculated R_g using formula (2) instead of taking the actual value of R_g for each N.

It should be noted, that our results for D(x) in the region x > 1.5 are not reliable since we did not have enough points on the graph to determine the slope, and a strong noise maid it difficult to determine if the power-law dependence can even be applied at all. As a result, the statistical errors of the regression coefficients are huge in this region. On the other hand, the error-bars in Fig. 5 represent only statistical errors associated with the linear regression procedure. An accurate assessment of statistical errors should involve errors of R_g , errors associated with "smoothing" of the correlation function, etc., and is a fairly complex procedure.

Nevertheless, the main trend of D(x) can be seen from Fig. 5. It experience first a slight increase, reaching a maximum at a level $D(x) > D_2$, and then decreases.

5 Discussion

The fact that $D_2 \neq D_1$ implies that the formulas (2) and (3) are correct and D_2 and D_1 do not depend on r/R_g . As discussed in section 2, this is, in general, compatible with the definition of the fractal dimension $D(r/R_g)$ as a function continuously depending on r/R_g with $D(0) = D_1$ and R_g defined by (2). We emphasize that there is no requirement that $D(\infty) = D_2$. Our numerical results confirm with good precision that the asymptote (3) is correct and D_1 is a constant for CCA clusters. However, we cannot state with enough confidence the same for D_2 . Though in our range of N we find that D_2 is a constant close to 2.0, we have a considerable statistical error of D_2 (20 times larger than that of D_1). Further, we can not rule out a possible change in D_2 if we go to larger cluster sizes.

Let us now turn to the dependence D(x). In Ref.15 the authors argued that D(x) must be a non-increasing function of x for Witten-Sander clusters (known also as diffusion-limited aggregation clusters). The authors considered the density function at the distance r from the origin, which would be equal to $Np(r)/4\pi r^2$ (with p(r) being the density correlation function studied in this paper) after placing the origin at all the monomers in the cluster and taking an average. However, the origin is fixed and coincides with the first monomer in the Witten-Sander aggregation process (the "seed"). The authors argued that due to irreversibility of the Witten-Sander aggregation process, the density function measured at the distance r must be greater in a cluster with greater number of particles (and greater radius of gyration). Applied to (10), this means that

$$r^{D(x_2)-D(x_1)}h(x_2, R_0)/h(x_1, R_0) \ge 1$$
, if $x_2 < x_1$. (17)

By fixing the values of x_1 and x_2 and taking large values of r, we can conclude from (17) that $D(x_2) > D(x_1)$. Numerically, a small bump in D(x) was found in twodimensional Witten-Sander clusters ¹³, in contrast with the theoretical predictions. The authors proposed that the asymptotic regime has not been reached (R_g was not large enough), which resulted in the above discrepancy. This means that the functional form (10) becomes correct only for very large clusters. (According to the estimates made in Ref.15, when $N \sim 10^{17}$ for two-dimensional Witten-Sander clusters; in practice this number of particles is, of course, not very realistic.) The above arguments cannot be directly applied to the correlation function studied in this paper because we have considered all possible pairs of distinct monomers for the calculation of p(r), which is equivalent to averaging the density function studied in Ref.15 over all possible positions of the origin; moreover, a unique origin or a "seed" is not defined for CCA clusters. However, it is clear from Fig. 2 that for a fixed value of r, the correlation function multiplied by N, i.e., Np(r), for an ensemble with a greater N is greater than or equal to that for an ensemble with a smaller N (the equality takes place in the asymptotic region defined in (3)). This brings about inequality (17) and the conclusion that D(x) must be a monotonously decreasing function. Still, the numerically calculated D(x) has a maximum (Fig. 5).

Apart from the reason that the asymptotic regime is not reached yet, and the maximum will disappear for clusters with larger N, we can suggest that the functional form (10) is incompatible with (2,3) with $D_2 > D_1$ for clusters which aggregate via an irreversible aggregation process. The multiscaling function g(x, N)is more general and complex in this case.

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References

- 1. P.Meakin, Phys. Rev. Lett. 51, 1123 (1983).
- 2. M.Kolb, R.Botet and R.Jullien, Phys. Rev. Lett. 51, 1123 (1983).
- 3. J.Cai, N.Lu and C.M.Sorensen, J. Colloid and Interface Sci. 171, 470 (1995).
- 4. M.V.Berry and I.C.Percival, Optica Acta 33, 577 (1986).
- 5. M.Carpineti, M.Giglio and V.Degiorgio, Nuovo Cimento 16D, 1243 (1994).
- 6. D.Asnaghi, M.Carpineti, M.Giglio and A.Vailati, Physica A 213, 148 (1995).
- 7. V.A.Markel, V.M.Shalaev, E.Y.Poliakov and T.F.George, JOSA A, in press.
- 8. R.Jullien, M.Kolb and R.Botet, J. Physique Lett. 45, L211 (1983).
- 9. P.Meakin, *Phys. Rev. A* **29**, 997 (1984).
- 10. P.Meakin, Phys. Lett. A 107, 269 (1985).
- 11. Yu.E.Danilova, A.I.Plekhanov and V.P.Safonov, Physica A 1-4, 61 (1992).
- 12. R.Botet and R.Jullien, Phase Transitions 24-26, 691 (1990).
- C.Amitrano, A.Coniglio, P.Meakin and M.Zannetti, *Phys. Rev.* B 44, 4974 (1991).
- 14. T.A.Witten and L.M.Sander, Phys. Rev. Lett. 47, 1400 (1981).