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A scaling correction in cluster-cluster aggregation

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Abstract. — A general correction term in the radius of gyration scaling law is discussed. The work incorporates the finite size effect considered by Ball and Jullien (J. Phys. Lett. France 45 (1984) L1031) and is a potentially useful extension of their analysis to polydisperse systems. Numerical simulations verify these results for one particular model, and demonstrate the remarkable accuracy of the scaling law, even for clusters of very few monomers, once this relatively trivial scaling correction has been made.

It is now well established that most forms of irreversible aggregation lead to self-similar, or fractal, aggregates [1, 2]. Cluster-cluster aggregation [3, 4] is one example of such a process. The self-similar nature of the aggregates is shown in the scaling laws which link average cluster properties to the number of monomers in the aggregate. One such property is the radius of gyration $R_G$ of an aggregate. $R_G$ has the advantage of being directly obtainable from static light scattering measurements in real systems [5], and easily computed in numerical simulations of the aggregation process. Since $R_G$ reflects the overall linear size of an aggregate, it should scale with $N$ raised to a non-integral power, the reciprocal of the fractal dimension $D_F$ [6]:

$$R_G = bN^{1/D_F}$$ (1)

An explicit prefactor $b$ has been introduced into this scaling law. However this scaling law is only exact asymptotically, i.e. as $N \to \infty$, and one would anticipate corrections to the scaling law for small values of $N$. Equation (1) can therefore be generalised to

$$R_G = bN^{1/D_F}(1 + kN^{-\theta} + \ldots)$$ (2)

The leading correction term decays as $N^{-\theta}$ ($\theta > 0$). In the rest of this note I explore the consequences of such a correction coming from the radius of gyration initially assigned to the monomers.

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Scaling correction to the radius of gyration.

It is customary to assign a zero radius of gyration to the monomers. If however the radius of gyration of the monomers (assumed all identical) is changed from zero to $R_0$, then the square of the radius of gyration of the aggregate changes from $R_G^2$ to $R_G^2 + R_0^2$. This arbitrariness in $R_G$ leads to a correction term to the radius of gyration scaling law and suggests that

$$R_G^2 = b^2 N^{2/D_F} + \gamma + \text{other corrections},$$

(3)

where $\gamma$ is a constant term, independent of $N$. A constant term of this type gives rise to an exponent $\theta = 2/D_F$ in the general scaling law (2) above. One can test this prediction directly, but we will examine the accuracy of (3) in an alternative way. Let us assume, for the moment, that the other corrections in (3) are negligible. Then the scaling law should hold even at extreme values of $N$.

For monomers, inserting $N = 1$ in (3) shows that the constant term is $\gamma = R_0^2 - b^2$ since the radius of gyration of a monomer is fixed at $R_0$. This gives

$$R_G^2 = b^2 (N^{2/D_F} - 1) + R_0^2.$$  

(4)

For dimers, inserting $N = 2$ in this gives $R_G^2 = b^2 (2^{2/D_F} - 1) + R_0^2$. However the radius of gyration of a dimer is also known. Taking the monomers to be spheres of unit diameter, then for dimers $R_G^2 = \frac{1}{4} + R_0^2$. Comparing the two expressions shows that

$$b^2 (2^{2/D_F} - 1) = \frac{1}{4}.$$  

(5)

For $N > 2$ the radius of gyration of the aggregate is not simply determined. However if we know the fractal dimension $D_F$, then $b$ is predicted by (5) and the radius of gyration of an aggregate of an arbitrary aggregation number is predicted by (4). In particular for large aggregates (5) suggests that there is a connection between the scaling exponent and the prefactor in (1). Of course these remarks are dependent on the neglect of other possible corrections in (3). We can test the accuracy of this assumption numerically.

Note that the predicted scaling correction in (4) does not disappear when $R_0 = 0$. We must set $R_0 = b$ to get the correction to vanish. If $R_G$ is the radius of gyration of an aggregate made of monomers for which $R_0 = 0$, then using the scaling prefactor $b$ one can define a «corrected» radius of gyration

$$R_G^* = (R_G^2 + b^2)^{1/2}$$

(6)

for which the scaling correction discussed here should be absent.

Numerical work.

I have done numerical simulations of one particular model (off-lattice hierarchical reaction limited cluster-cluster aggregation (RLCA) [7, 8]) in several space dimensions and collected statistics on the radius of gyration of the aggregates. All simulations consisted of 102 400 particles aggregated to form 400 clusters of size 256 particles. These numerical results are collected in table I, and plotted in figure 1a. The fractal dimension $D_F$ and scaling prefactor $b$, were extracted graphically from log-log plots [9], and from least squares fits to equation (4). The results are shown in table II, together with the LHS of (5) calculated from these results.
Table I. — Simulation results for radii of gyration $R_G$ as a function of aggregation number $N$ for several values of the space dimension $d$. The algorithm used was off lattice, hierarchical, reaction limited cluster-cluster aggregation. The figure in brackets after a result indicates an estimate of the error in the final digit of that result.

<table>
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<tr>
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<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
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<td>0.8309(5)</td>
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<tr>
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<tr>
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<tr>
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<td>8.53(6)</td>
<td>6.19(4)</td>
<td>5.12(3)</td>
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</table>

Table II. — Fractal dimension $D_F$ and radius of gyration prefactor $b$ extracted from the data in table I. The final column corresponds to the LHS of (5) in the text. As before, the figure in brackets after a result indicates an estimate of the error in the final digit of that result.

<table>
<thead>
<tr>
<th>$d$</th>
<th>$D_F$</th>
<th>$b$</th>
<th>$b^2(2^{2D_F} - 1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.53(1)</td>
<td>0.415(5)</td>
<td>0.255(5)</td>
</tr>
<tr>
<td>3</td>
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<td>0.495(5)</td>
<td>0.255(5)</td>
</tr>
<tr>
<td>4</td>
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<td>0.56(1)</td>
<td>0.26(1)</td>
</tr>
<tr>
<td>5</td>
<td>2.55(5)</td>
<td>0.60(2)</td>
<td>0.26(2)</td>
</tr>
</tbody>
</table>

Finally I used the scaling prefactor to calculate the corrected radius of gyration as defined in equation (6). These results are plotted in figure 1b, and confirm that, for this data at least, by far the most significant scaling correction is the one discussed here.

Before discussing these results I will indicate the connection with the finite size effect discussed by Ball and Jullien [10].

**Connection with earlier work.**

In hierarchical aggregation, only clusters whose aggregation number is a power of two are formed. One method of extracting the fractal dimension is to plot

$$D(N) = \frac{\log 2}{\log (R_G(2N)/R_G(N))}$$  \hspace{1cm} (7)

against $N$ [7]. The function defines an effective, $N$-dependent exponent which tends to $D_F$ as $N \to \infty$; a numerical value for $D_F$ is obtained by extrapolation. Ball and Jullien [10] suggested an improvement could be made by using $D^*$ where

$$D^*(N) = \frac{\log 4}{\log ([R_G(2N)/1/4]/R_G(N))}.$$  \hspace{1cm} (8)

Fig. 1. — Log-log plots of radius of gyration $R_0$ against aggregation number $N$ for the data in table I. The radius of gyration has been scaled by $N^{1/D_\sigma}$ in order to bring out the approach to scaling more clearly (the values of $D_\sigma$ being taken from Tab. II): a) the uncorrected radius of gyration is used; b) the «corrected» radius of gyration, defined in equation (6) in the text, has been used. In both plots datum points for space dimensions $d = 2, 3, 4, 5$ are represented by squares, circles, triangles and diamonds respectively; the error associated with each data point is not greater than the size of the symbol. The full lines are the predictions of equation (4) in the text ($b$ and $D_\sigma$ being taken from Tab. II).

They proved that $D^*$ was rigorously independent of $N$ for linear aggregates $d = 1$ and ghost aggregates [11, 12] ($d > d_c$, where $d_c$ is the upper critical dimension), and showed that $D^*$ only had a very weak $N$-dependence at intermediate $d$ for hierarchical ballistic and diffusion limited aggregation models. A similar result for reaction limited aggregation was demonstrated by Jullien and Kolb [13].

This result also follows from the scaling correction discussed in the previous section. Making use of the corrected radii of gyration $R_0^*$ defined in (6), and assuming (4) to be true, it is straightforward to show that

$$D^* = \frac{\log 2}{\log (R_0^*(2N)/R_0^*(N))}$$

(9)

is the same as the $D^*$ defined in equation (8), and that both formulae are independent of $N$. The very weak $N$-dependence of $D^*$ is then a measure of the weakness of the other corrections in (3). It follows from the work of Ball and Jullien that linear aggregates and ghost aggregates obey the proposed scaling laws (4) and (5) exactly, and have no other scaling corrections. It is also possible to demonstrate this directly.

Discussion.

Extensive results on reaction limited cluster aggregation were obtained by Meakin [14]. His data for hierarchical aggregation were partially analysed using the $D^*(N)$ introduced by Ball and Jullien, and the results are more or less consistent with the results obtained in the present paper. However significant $N$-dependence starts to appear at higher spatial dimensions. This
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effect may just be seen in the slight curvature in the data obtained here for \( d = 5 \) (shown in Fig. 1b), and it also explains a small discrepancy between the value for \( D_F \) obtained here (in Tab. II) and that obtained by Meakin, for \( d = 5 \). One may conclude that corrections to \( R_0 \) other than the one discussed here are becoming more significant at higher space dimensions. In addition Meakin’s data from lattice based algorithms also show significant, but rapidly decaying, \( N \)-dependence of \( D^* \) This is consistent with scaling corrections coming from lattice effects [8, 9].

To summarise, the numerical results obtained here, together with those obtained by Meakin, show that the radius of gyration follows the proposed scaling law (4) very accurately (the best agreement being obtained for off lattice, hierarchical RLCA in low space dimensions). Moreover the very weak \( N \)-dependence of \( D^* \) observed by Ball and Jullien [10] indicates that this conclusion is also valid for hierarchical ballistic and diffusion limited cluster aggregation.

The analysis may be extended to polydisperse aggregation, and it should be noted that (4) and (5) provide an effective extension of the \( D^* \) method to these systems. The method adopted here (namely fit the data to the proposed scaling law (4), and compare \( b \) and \( D_F \) so obtained with the predicted relation (5)) could also be profitably applied to polydisperse systems.

The relationship (5) between \( b \) and \( D_F \) is unusual in that the prefactor in a scaling law is usually regarded as a model dependent parameter, whereas the exponent should have a degree of universality. The simulations show that for this particular model the relationship is accurately obeyed over a range of space dimensions: it would be interesting to test (5) for other models.

It is remarkable how accurately the scaling law holds even for clusters of very few monomers once the relatively trivial scaling correction in (6) has been made. This is illustrated in figure 1b for the aggregation model considered here, and also appears to work reasonably well for other models, as shown for example in figures 1 and 2 of the paper by Ball and Jullien [10].

Acknowledgments.

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References