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Cluster–cluster aggregation and calculated SAXS patterns: application to concentration dependence of fractal parameters

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Abstract. Two new computer simulation programs are presented, GRASP and DALAI. GRASP is an off-lattice implementation of the cluster–cluster aggregation model, including diffusion- and reaction-limited aggregation as well as aggregate reorganization. The aggregate systems produced by GRASP are characterized by DALAI, which calculates the x-ray scattering pattern using a CPU-efficient simplified version of the Debye formula. We describe the scope and potential of the two programs and we show how they can be used together to follow the time evolution of aggregation processes in large systems. We also present results of DLCA calculations for representative 2D and a series of 3D systems in the volume concentration range 0.25–30.0% with the purpose of investigating the influence of concentration on fractal parameters.

1. Introduction

The description of experimental aggregation processes with computer models started with pioneering simulations by Sutherland [1] in 1967. The introduction of the diffusion-limited aggregation (DLA) model by Witten and Sander [2], where a ‘seed’ aggregate grows by addition of monomers, is the first example of the use of the concept of fractal in simulations.

The DLA model and its successors, which included, for instance, reaction limitations (RLA) and linear instead of Brownian trajectories, have now become part of the particle-cluster aggregation (PCA) family of models. The PCA models have been successful in describing several cases of experimentally observed fractal behaviour [3, 4], but they have failed to describe experimental situations where larger aggregates are formed from a polydisperse collection of smaller aggregates.

Meakin [5] and Kolb [6] subsequently developed the cluster–cluster aggregation (box CCA) model, which simulates aggregation processes in a two- (2D) or three-dimensional (3D) box, where a polydisperse distribution of aggregates carrying out Brownian movements and obeying sticking rules forms larger aggregates until a final single aggregate is formed.

The PCA and CCA model families have been extended and adapted to model different experimental observations. Diffusion-limited (DLA, DLCA), reaction-limited (RLA, RlCA) and

§ In this paper chemical or physical experiments will be referred to as ‘experimental’. The computer models will be referred to as ‘simulated’ or ‘model’.
ballistic versions [7] have been extensively employed in the interpretation of experimental data [8].

The major obstacle in performing box simulations of large systems has been the severe demands such algorithms make on processing power. Furthermore, the theoretically predicted fractal properties and scaling behaviour are observed only in the zero-concentration limit [7]. For these reasons, simplified non-box CCA models (hierarchical and polydisperse) that are much less demanding in processing power have been introduced and large-scale simulations (> $10^6$ monomers) have been reported [7].

These non-box CCA models work implicitly in the zero-concentration limit and are very well suited to studying many statistical properties of CCA [9, 10]. The DLCA aggregation processes are adequately described by the non-box CCA models, however, it has now become clear that they cannot describe properly the cluster size scaling behaviour of RLCA whereas box models do this quite well [11]. Furthermore, box models are better suited to studying the influence of parameters that represent chemical and physical properties of actual experimental systems.

In our case, we are particularly interested in studying the role of aggregation parameters that affect the time evolution of the system such as diffusion coefficient concentration, association and dissociation probabilities and in measuring system properties such as fractality, connectivity, gelation time and percolation threshold. We are also interested in simulating reorganization processes because of the insight these could give in understanding experimentally observed changes in the fractal behaviour of silica gels [12, 13] following changes in experimental conditions.

Since the introduction of the CCA models in 1983 computers have become much faster. This has enabled us to implement the off-lattice, box CCA model with advanced aggregation algorithms and to include all the main methods of analysis of the properties of the system without having to limit the computations to very small systems. We present here the program GRASP† which simulates the aggregation process in a hyper-cubic box of Euclidean dimension $d = 2, 3, 4, \ldots$. The monomer coordinates are passed to the program DALAI [14], which calculates the corresponding small-angle x-ray scattering (SAXS) pattern.

The power-law relation between length and scattering mass (e.g. monomers) in the fractal region of aggregates allows us to extract the fractal dimension $D_f$ very easily from the slope of the straight section in the log $l$ versus log $q$ plot of the SAXS pattern as shown schematically in figure 1. The $q$ vector is related to the Euclidean space vector $r$ as

$$q = \frac{2\pi}{r}.$$ (1)

With the GRASP–DALAI combination we are able to compare directly the simulated and experimental results, and have an easy and accurate method to retrieve fractal parameters ($D_f$ and its limits) from the simulated data. In the following sections we first introduce the methods used to obtain the scaling behaviour of aggregates in simulations and experiments. We then briefly describe the DALAI algorithm and proceed to outline the main features of the GRASP program with examples to demonstrate its scope and potential. Finally, we present calculations for DLCA systems covering a wider range of concentrations than has been reported in the literature to date.

† GRASP stands for gelation, reactivity and aging simulation program.
Cluster–cluster aggregation and SAXS patterns

Figure 1. Schematic representation of the scattering pattern of a fractal system. At $q$ values above that for the primary scattering monomer the slope of the curve is $-4.0$ (Porod region). The inflection point is used to experimentally determine the size of the primary scatterer. The flattening out of the curve beyond the size of the largest aggregate in the system is rarely observed experimentally. The region with fractal properties lies between $q_{\text{low}}$ and $q_{\text{high}}$.

2. Methods for studying scaling behaviour

The approaches that have been used to determine $D_f$ since the introduction of modelling of random aggregation processes are reviewed in detail in Vicsek's broad survey [15]. They may be grouped into two types. The first type are based on counting numbers of monomers and are characterized by the fact that they provide only a limited number of data points per simulation run (or experiment) so that many runs have to be performed to enable a reasonable determination of $D_f$. The second type are based on pair distances or a scaling relation for which data are collected during the (simulated) aggregation process. Determination of $D_f$ from the scattering pattern falls in the same category, since it is based on pair-distance correlations. We briefly describe four of the most widely used methods. Methods (1) and (2) are of the first type, methods (3) and (4) of the second.

(1) Mass scaling with length: $D_f$ is obtained by counting the mass $M$ within a radius $r$ from the center of mass of the system. For a fractal system of monomers we can write

$$M(r) \sim r^{D_f}$$

from which

$$D_f = \frac{\log M}{\log r}.$$  \hspace{1cm} (3)

It is a simple matter to compute this expression from the mass distribution of a simulated system. The method can be used on experimental data as well, e.g. electron micrographs or STXM (scanning transmission x-ray microscopy) [16] if appropriate thresholds are used to eliminate the contribution of noise.

(2) Box counting: the simulation space is divided into successively smaller sub-spaces (boxes). Each subspace is checked for whether it contains mass. The $\log$–$\log$ plot of the number of filled boxes versus the size of the box results in a straight line, the slope of
which gives $D_f$. This method is also of use in characterizing experimental systems [17] and in principle can be used for 3D data, e.g. confocal microscope 3D images.

(3) Mass correlation function: this uses all mass–mass correlations present in the simulated system of $N$ monomers by calculating the density–density correlation function

$$C(r) = \frac{1}{N} \sum_{r'} \rho(r + r') \rho(r').$$  \hfill (4)

Since fractal objects have a correlation function that scales homogeneously under rescaling of lengths we can write

$$\langle \rho(r + r') \rho(r') \rangle \propto r^{-\alpha}$$ \hfill (5)

where $\alpha$ is related to $D_f$ as $D_f = d - \alpha$. The function often shows a 'bumpy' course, making reliable determination of the fractal dimension very difficult.

(4) Radius of gyration measurements: $D_f$ is obtained from the expected scaling of $R_g$ with aggregate mass $M$. For all aggregates formed during the aggregation process, $M$ and $R_g$ are recorded. For centered aggregates $R_g$ is defined as

$$R_g^2 = \frac{1}{N} \sum_{i=1}^{N} R_i^2$$ \hfill (6)

where $R_i$ is the distance of each monomer in the aggregate from the center of mass. $D_f$ can then be found from the relation

$$R_g \sim M^{1/D_f}.$$ \hfill (7)

The GRASP–DALAI combination offers an alternative method. For fractal systems, a power-law relation between length and mass must exist by definition. Therefore, a good method of determining the behaviour of a model random system should not make any \textit{a priori} assumptions concerning its fractal nature. In addition, a given characterization method is more valuable if it enables direct comparison with experimental data. The method we introduce next does, indeed, make no \textit{a priori} assumptions about the fractal nature of the system and can be used to directly compare simulations with experimental data, at any stage of the aggregation process (the latter being the main motivation for its use), regardless of whether or not the system is fractal and whether a $D_f$ value can be measured unambiguously.

3. SAXS calculations using the program DALAI

Experimentally, fractal scaling behaviour in 3D is determined mainly from SAXS, SANS (small-angle neutron scattering) or light-scattering data [8]. For monodisperse systems, the scattered intensity $I(q)$ is the product of the structure factor $S(q)$ of the system and the square of the form factor $F(q)$. The scattered intensity $I(q)$ can be expressed by the relationship [18]

$$I(q) = S(q)P(q)$$ \hfill (8)

and $P(q)$ is related to the form factor $F(q)$ by

$$P(q) = F^2(q).$$ \hfill (9)

A power-law dependence for $S(q)$ is expected expressed by the relationship

$$S(q) \sim q^{-D_f}.$$ \hfill (10)

In situations where the radius $R_0$ of the primary scatterers is small compared to the length scale at which the scattering is measured, the influence of the shape of the form
factor can be neglected (taken as constant) and $D_f$ values can be measured directly from the linear part of the log $S$ versus log $q$ plot. The calculated SAXS patterns that follow in later sections in this paper are given as structure-factor patterns. By omitting the (multiplicative) contribution of the form factor of the monomer the $D_f$ values are determined in accordance with formula (10).

A frequently used approach to simulating SAXS patterns of large molecules, particularly protein molecules and super-molecular assemblies, is to build models of $N$ closely packed spheres and then use Debye's formula [19-21]

$$I(q) = \sum_{i=1}^{N} I_i(q) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} F_i(q) F_j(q) \frac{\sin q r_{ij}}{q r_{ij}}$$

(11)

to calculate $I(q)$ for each value of the scattering vector modulus, $q$. $F(q)$, the form factor for each (different) sphere, is given by

$$F(q) = V \rho \left[ 3 \frac{\sin q R_0 - q R_0 \cos q R_0}{(q R_0)^3} \right]$$

(12)

where $V$, $\rho$ and $R_0$ are the sphere volume, density and radius. $I_i$ is the intensity scattered by each sphere, $r_{ij}$ is the distance between pairs of spheres. The first sum in (11) gives the scattered intensity from all spheres in isolation, while the double sum gives the contributions from density-density correlations. Equation (11) can be very easily implemented into a computer program, the only problem being that the computation of the terms $\sin(q r_{ij})/q r_{ij}$ is very costly in CPU time when the number of spheres exceeds a few hundred. For monodisperse systems the formula can be further simplified to

$$I(q) = N I_s(q) + 2 F_s^2(q) \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\sin q r_{ij}}{q r_{ij}}$$

(13)

since $F_i = F_j$ and $\sum I_i(q) = N I_s(q)$. This improves execution speed considerably because its implementation is handled more efficiently by vector processors. A further, more drastic simplification can be brought about at the expense of analytical precision. Pair distances are discretized in a histogram of bin size commensurate with the required spatial resolution in the pattern. This effectively 'fuzzes out' the positions of the spheres by an amount that would not be detected in the resolution range of the calculation. The pair distance matrix of $r_{ij}$ values now becomes a one-dimensional array of distances weighted by the number of distances occurring within an interval of bin size, the bin population. The terms $\sin(q r_{ij})/q r_{ij}$ can be precalculated now in array $\sin(q r_{ij})$. The scattering formula becomes

$$I(q) = N I_s(q) + 2 F_s^2(q) \sum_{i=1}^{n_{\text{bins}}} M(r_i) \sin(q r_i)$$

(14)

where $M(r_i)$ is the bin population at pair distance $r_i$ and $n_{\text{bins}}$ is the number of terms in the sum, the number of populated distance bins. For $F^2(q) = 1.0$, i.e., point monomers, this expression gives the 'structure factor' of the system. The error introduced by using the distance-histogram approximation can be evaluated by varying the number of distance bins used for the histogram. In general the histogram bin size should be much smaller than the size of the primary scatterers $R_0$ ($\sim R_0/50$).

This method has been used very effectively to interpret changes in the SAXS data of the iron carrying protein transferrin [22] and in interpreting the scattering profiles of different types of the microtubule organelle [23]. Models of thousands of spheres can be treated in a few seconds or minutes of CPU time on modern workstations. A parallel implementation
of the algorithm on the Intel iPSC/860 hypercube has been described by Pantos and Bordas [14].

To demonstrate the validity of the DALAI approach on fractal systems we applied it to the 2D and 3D deterministic fractals first presented by Vicsek [15], constructed by an iteration procedure (figure 2). The total number \( N \) of monomers and the size \( r \) are functions of the iteration number. The \( D_f \) of this deterministic fractal can be calculated easily by counting \( N \) within a radius \( r \) from the center of mass. In figures 3 and 4 we compare graphically the results obtained with the correlation function method and with DALAI on Vicsek's fractals, with \( 5^8 \) (390,625) and \( 9^6 \) (531,441) monomers in 2D and 3D, respectively. It is obvious from comparison of figures 3 and 4 that the DALAI results are superior to the correlation functions. The DALAI curves show perfect regular patterns in the fractal region whereas the correlation function shows an irregular 'bumpy' line, which makes the determination of \( D_f \) very difficult.

![Figure 2. Four iterations of Vicsek's 2D deterministic fractal. The starting structure contains only five monomers. In the next iteration we see five copies while the overall structure size has increased by a factor of three. \( D_f \) is computed from \( \log(5)/\log(3) \approx 1.465 \) in 2D and \( \log(9)/\log(3) = 2.0 \) in 3D.](image)

4. DLCA and RLCA simulation with GRASP

The basic building block is a spherical monomer with maximum functionality (maximum connectivity) of \( n_{\text{bonds}} \). In the examples we shall describe in this paper only non-directional bonds are formed. The code also provides the option for monomers to form bonds with specific bond angles or within a bond-angle range, to enable the study of short range interaction effects.

At startup, all monomers are placed on a lattice to avoid initial overlap. The spacing is determined by the concentration of the system. In the first step all monomers are moved in a random direction by a distance defined in a variety of ways. Overlap is detected by searching for monomer-monomer distances smaller than two monomer radii and is subsequently removed by displacing (bouncing off) monomers to the closest non-overlapping position. Sticking rules, described below, determine the formation of new bonds. Newly
bonded pairs of monomers continue their diffusive random walk as aggregates of mass two, together with the remaining free monomers. In subsequent steps all monomers and new aggregates are moved in the same way and any collisions are checked with the same rules for monomers and aggregates, resulting in a mixture of aggregates with various sizes.

Aggregates diffuse within the simulation box with either periodic-boundary or reflecting-wall conditions. The maximum step size $\mu$ is set by the function

$$
\mu = \mu_{\text{max}} M^Y
$$

where $\mu_{\text{max}}$ defines the mean step for a variety of diffusion length functions and $M$ is the
mass of the aggregate. The exponent $\gamma$ should be $-0.5$ if the diffusion length is to be inversely proportional to aggregate mass or zero for a diffusion length independent of mass. Continuation of this process (see figure 5 for 2D examples) leads to the formation of a polydisperse mass distribution of aggregates since both monomers and aggregates can form new bonds. Finally only one aggregate is left in the box and the calculation stops.

Rotation of aggregates during the aggregation process is known to have a profound effect on morphology and fractality of the aggregates [24]. GRASP is capable of handling these rotation effects generally by allowing for internal flexibility of the aggregates (see figure 7). We consider aggregate rotation as a kind of reorganization or aging process and therefore rotation effects will be ignored in the simulations presented.

GRASP uses the cell-grid-neighbor-table method [25, 26], which we have generalized to use hypercubic cell grids. A neighbor list is constructed for each cell by calculating all distance vectors between monomers that do not belong to the same aggregate in that cell and its neighboring cells. This way any monomer overlap is detected and subsequently removed by slight adjustment of the monomer–monomer distances. Sticking-pair candidates are now handled according to the sticking rules. Since the grid method has a CPU dependence that is linear with the number of monomers we believe that implementation of the program on a faster, maybe parallel, computer will enable us to perform aggregation experiments with $> 10^6$ monomers. On the other hand, Lopez-Quintela et al [27] have shown that fractal behaviour is already present at modest aggregate sizes so it is no serious drawback that the number of monomers has to be limited in the box model because of computational constraints. To date, we have used GRASP to perform simulations in 2D and 3D for up to 90,000 and 125,000 monomers respectively (unpublished results), and are able to confirm Lopez-Quintela’s observations for DLCA. Execution times depend not only on number of monomers but also on the value of step size and the sticking probabilities and on whether reorganization of the aggregates is applied, either by bond breaking and subsequent sticking elsewhere or by branch movements. CPU figures for some typical situations are summarized in table 1.

Although the total number $N$ of monomers is constant during the aggregation process, the aggregate-size distribution $n_s$ changes because of sticking events. In order to provide greater flexibility in the selection of aggregation conditions we have included the gelation parameters as introduced recently by Kallala et al [28]. They use a kinetic aggregation kernel to select bonding events. The sticking probability $f$ is a function of the individual monomer connectivity $q_i$,

$$f(q_i) = \omega^{q_i} \quad (\text{with } i = 0, \ldots, n_{\text{bonds}})$$ (16)

When $\omega = 1.0$, all $f(q_i)$ are 1.0 and the model reduces to the standard DLCA model where all monomers have a sticking probability of 1.0. For values of $\omega$ smaller than 1.0

Figure 5. (Opposite.) 2500 monomer inset of different stages of a 2D DLCA simulation at 10.0% volume concentration and step size 0.25Rg. (a) After 128 moves from start, the starting lattice distance correlations are not present any longer. The slope of the linear section is 2.0, as expected for a non-fractal 2D system. (b) After 1024 moves. (c) At the percolation time after 4096 moves. The largest aggregate spans the simulation box. The linear fractal region in the DALAI graph has almost reached its final $D_f$ value of 1.46. (d) Final single aggregate after 11967 moves. The fractal-region extent changes little after gelation is reached while the slope remains virtually the same. (e) Corresponding SAXS structure factor patterns for systems (a)–(d) calculated by DALAI.
Cluster-cluster aggregation and SAXS patterns

(a) 

(b) 

(c) 

(d) 

(e) 

\[ \log(\alpha) \text{ vs } \log(q) \]
the reactivity of the monomers decreases while for an \( \omega \) value bigger than 1.0 the monomer reactivity increases upon bond formation. RLCA simulations can be performed by setting the sticking probability for all monomers to a value smaller than 1.0.

The gelation time \( t_g \) can be calculated using percolation theory [29], according to which the moments of the aggregate-size distribution are defined as

\[
M_k = \sum_{s = r_{\text{min}}}^{s_{\text{max}} - 1} s^k n_s. \tag{17}
\]

These summations are called the \( k \)th moments of the aggregate-size distribution \( n_s \). In equation (17) the sum excludes the largest aggregate in the system. When the largest aggregate begins to dominate in the size distribution the moment value \( M_k \) drops sharply. This signals the onset of gelation. From the moments, the ratios are defined [30] as

\[
DP' = \frac{M'_2}{M'_1}, \tag{18}
\]
\[
DP'' = \frac{M'_3}{M'_2}. \tag{19}
\]

These ratios amplify the drop in the value of the moments because the change is larger for the higher moments. Both \( DP' \) values can be used to determine the gelation time as both show a maximum value at the percolation time. In GRASP we use \( DP'_w \). Figure 6 gives the \( DP'_w \) development for 1.0% concentration in 3D. The point at which there is a sudden drop in \( DP'_w \) defines the gelation time (see also figure 5(c) for a 2D simulation at the gelation time).

A kernel of bond-breaking probabilities, similar to that used for RLCA simulations, is used to simulate dissociation events. Various types of bond-breaking procedure may be activated either during aggregation or after the formation of a single aggregate. The aim of this is to attempt to simulate aging processes, whereby mass from already formed fractal aggregates could be redistributed to form stable bonds in regions that would otherwise remain screened and inaccessible during normal DLCA or RLCA aggregation. A variant of this type of algorithm allows for 'reptation' or 'flexing' of branches, which may lead to formation of closed rings of various sizes.

Several system parameters are recorded as the aggregation proceeds for further analysis: the radius \( R_g \) of gyration of each aggregate, the size distribution \( n_s \), the connectivity distribution \( N(q_i) \), the number of sticking or breaking events, the ratios \( DP'_w \) and \( DP'_z \) and the correlation length \( \xi \). Some of these parameters may be used to compare directly with experimental data. For instance, the relative connectivity population may be used to compare with \(^{29}\)Si NMR signals in diluted silica gels. The system coordinates may be further analysed at any stage of the aggregation or as a function of time (move number) to produce other statistics of interest, for instance, the angle correlation, the bond angle distribution, the surface area (defined as the number of remaining free bonds) and, of course, the SAXS pattern

<table>
<thead>
<tr>
<th>( N )</th>
<th>Moves</th>
<th>CPU time (s)</th>
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<tr>
<td>1000</td>
<td>168</td>
<td>23.2</td>
</tr>
<tr>
<td>8000</td>
<td>229</td>
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<td>491</td>
<td>25419.3</td>
</tr>
<tr>
<td>91,125</td>
<td>501</td>
<td>47799.3</td>
</tr>
</tbody>
</table>

Table 1. Execution times on an SGI Indigo R3000 Workstation for different simulation cases.
Cluster-cluster aggregation and SAXS patterns

**Figure 6.** $D_{p_w}'$ development as a function of number of simulation steps for DLCA aggregation of 27,000 monomers in 3D at 1.0% volume concentration.

using DALAI, or indeed the other functions mentioned above used as alternative means of determining $D_t$. Detailed analysis of system properties, including SAXS calculations, will be presented in a forthcoming publication.

GRASP-DALAI can also be used to study the influence on aggregation of low- or high-gravity conditions. Gravity is modelled by changing the $z$-component of the Brownian movements during aggregation. Preliminary calculations have shown only small differences in fractal dimension, although the morphology of the aggregates appeared to be quite different [31]. We summarize graphically the effect these algorithms have on the aggregate morphology in a series of 2D simulations in figure 7.

5. Aggregation simulations for a range of concentrations

To demonstrate the potential of GRASP a series of calculations is presented covering two decades of volume concentration. Figure 8 shows the calculated SAXS patterns in 3D with 27,000 monomers. The patterns are shifted vertically to avoid overlap. The size of the simulation box increases with decreasing concentration and, consequently, the size of the fractal region increases accordingly. Periodic boundary conditions force the preservation of the overall shape of the simulation box, especially at high concentrations. This results in the form factor of the simulation box dominating the structure factor of the system in the low-q region of the pattern. To reduce this effect the coordinates passed to DALAI have been transformed into one continuous aggregate by rebuilding the system following the monomer connectivities. The $D_t$ value in the log-q interval $[0.0, R_8/3.0]$ is within the expected value range of 1.77-1.80 as for zero-concentration 3D DLCA [32] only below 2.50%. The graphs in figure 8 effectively give us the upper concentration limit for fractal scaling behaviour in the DLCA case. The reduction of the linear section, although not sharply defined, is certainly a good guide for comparison with experiment.

The higher-concentration curves show no clearly defined linear region. Due to the limited number of Brownian movements before $t_s$, the screening effect causing the formation of fractal aggregates cannot occur. Gelation occurs within relatively few moves from the start of the aggregation process. Monomers and aggregates of all sizes quickly join up into a dense network. There is no sufficient time for the screening effect of the forming
Figure 7. Comparison of aggregate morphology for different aggregation parameters and algorithms: 2500 monomers in 2D using periodic boundary conditions. (a) Standard DLCA with monomers of bond functionality six. (b) Formation of linear polymers with occasional side contacts produced by using monomers of functionality three and by setting $\omega = 1.0$ and $q_l = 1.0, 1.0, 0.01$.

aggregates to come into operation and to alter the starting Euclidean morphology of the
Figure 7. (Continued.) Comparison of aggregate morphology for different aggregation (c) RLCA aggregate produced by setting $\omega = 1$ and $q_i = 1.0, 0.1, 0.01, 0.001, 0.0001, 0.00001$. (d) Reorganized aggregate following reptation of branches during aggregation.

In order to allow the lattice to 'melt' before onset of gelation, we have...
Figure 8. SAXS structure-factor curves calculated by DALAI for 27 000 monomer 3D systems in the volume concentration range 0.25–30.0%. System parameters are given in Table 2. The small diamonds on the curves indicate the $q_{\text{low}}$ value for the least-squares fit to obtain $D_f$. $q_{\text{high}}$ is zero for all curves.

experienced with very small diffusion-step sizes or allowed several moves to proceed without any sticking events. Although the lattice diffraction peaks do indeed gradually vanish, the structure-factor pattern does not change significantly. The system morphology is that of liquid or disordered solid (glass) or, for the very high concentrations, of a highly distorted (cubic) crystalline solid full of packing defects.

Table 2 contains the system parameters and results for all concentrations given in column 2, using the box size given in column 3. The gelation time in column 4 is determined from the $DP'_{\text{TLS}}$ graphs. The 5th column contains the $R_g$ values of the final single aggregates. The step size was $1/8R_0$ in all calculations, except for 20.0%, 25.0% and 30.0% concentration where the step size was $1/16R_0$.

Column 6 contains the $D_f$ values determined from DALAI ($D_f^{\text{SAXS}}$). For low concentrations up to 2.50% the slopes of the straight lines were fitted by a least squares fit procedure to the calculated SAXS data in the $q$ range [0.0, $R_g/3.0$]. For high concentrations the limiting slope near $q_{\text{low}}$ was taken as $D_f$. Columns 7–9 contain the $D_f$ values determined from the correlation function ($D_f^{\text{Corr}}$), the scaling of the radius of gyration with mass ($D_f^{\text{Gyr}}$)
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Figure 9. Scaling of $R_g$ with mass $M$ for 0.50% concentration. The slope of the straight line fit is 0.565, corresponding to $D_f = 1.77$.

Table 2. Parameters and results for 3D DLCA simulated system of 27,000 monomers in the volume concentration range 0.25–30.0%.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Concentration</th>
<th>Box size</th>
<th>$t_s$</th>
<th>$R_g$</th>
<th>$D_f^{\text{SAXS}}$</th>
<th>$D_f^{\text{Corr}}$</th>
<th>$D_f^{\text{Gyr}}$</th>
<th>$D_f^{\text{Boxc}}$</th>
<th>$\log(q_{R_g/3.0})$</th>
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(see figure 9) and box counting ($D_f^{\text{Boxc}}$). In these columns the abbreviation CO means that a reasonable $D_f$ value could not be fitted to the data by a straight line due to cross-over effects. Finally, column 10 contains the $q$ value corresponding to one third of the $R_g$ value of the single aggregate.

Inspection of the derivatives of the DALAI graphs reveals a gradual departure from the expected linear dependence at length scales between $q_{\text{low}}$ and $q_{\text{high}}$ at non-zero concentrations starting from approximately 2.50% upwards. Such departures from linearity.
have been interpreted [33, 34] as signifying multi-fractal, surface-fractal or simply non-fractal behaviour. More detailed analysis of the statistics of the (small) aggregates is needed here in order to properly quantify the cross-over from fractal to Euclidean systems with increasing concentration, and, in particular, the different degree of screening exercised by intermediate aggregates on each other's inaccessible inner regions. Intuitively we can see that the freedom for morphological variation is much reduced at high concentration. We will revisit this problem and its quantification in future studies.

Comparison of the $D_f$ values from the other methods shows that all methods predict the expected increase of the fractal dimension with increasing concentration. The low- and high-concentration values are all in excellent agreement. Only in the cross-over concentration region between 2.50% and 20.0% is it very difficult to estimate $D_f$. The curves for all four methods show no well defined straight fractal parts, but it should be noted that the DALAI curves in the cross-over region of concentrations show a straight line with slope $\sim 1.0$. This slope is also present in the box-counting results.

The development of the fractal properties during the aggregation and gelation process can be visualized by calculating the DALAI scattering of the coordinates of the system at the different stages. This is demonstrated in figures 5 and 10. In figure 10 the development of the fractal properties during the aggregation process is shown.

In curves a–d we see the buildup of a linear section with slope 1.78 in the log $q$ interval $[0.0, R_g/3.0]$. At move 14182 gelation occurs and the fractal region continues to grow slowly between curves e and f. As expected from experimental scattering data [12], no significant change of slope is observed before and after gelation.

The cross-over from Euclidean morphology to a fractal one as a function of aggregation time is more clearly seen in 2D simulations, where a greater extent of length scales can be studied for a given number of monomers. Figure 5 shows the real-space morphology of the corresponding 2D simulations and the $q$-space ‘fingerprints’. At $q \approx 0.25$ (reciprocal distance of $\sim 7 R_0$) in figure 5 all curves cross. This isobestic point marks the $q_{\text{high}}$ limit of fractality, while the $q_{\text{low}}$ is determined by the size of the largest aggregate in the system which is constrained by and determined from the size of the simulation box.

The time evolution graphs in figure 5 show very clearly the change of slope from the Euclidean starting value of $d = 2.0$ to the ultimate fractal dimension $D_f = 1.46$. Just as in the 3D case in figure 8, the extent of the fractal region increases as the largest aggregate size increases until percolation occurs. From then on only little change in the pattern is observed up to the formation of a final single aggregate.

6. Conclusions

GRASP incorporates all the main features of box CCA algorithms and makes feasible the study of very large systems. The combination of model simulations of diffusion- or reaction-limited aggregation and calculation of SAXS patterns offers specific advantages. The most important one is that the scattering patterns calculated provide information that can be readily compared with frequently used experimental techniques, such as SAXS, SANS, STXM and light scattering, employed in the characterization of materials of technological importance, e.g., silica gels and zeolite precursors, in contrast to conventional methods for determining fractal dimensions, over comparable length scales. DALAI enables the determination of fractal properties (if present) at different aggregation conditions and the study of the time evolution of the system.

We have restricted ourselves in this paper to demonstrating the application of the code to DLCA concentration studies. We have shown how the cross-over from fractal to Euclidean
Cluster–cluster aggregation and SAXS patterns

Figure 10. Evolution of aggregation monitored by the calculated structure factor patterns. Periodic boundary 3D DLCA for 27000 monomers at 1.0% volume concentration and step size 1/8 of monomer radius. Moves 512 (curve a), 1024 (curve b), 2048 (curve c), 4096 (curve d), 8192 (curve e), 16384 (curve f), 32768 (curve g), 69474 (curve h, single-aggregate formation). Gelation occurs at move 14182. The ripples in the patterns of curves a–e in the log q range [-1.5, 0.25] are due to the form factor of the cubic simulation box. The aggregate boundaries are less well defined at this concentration and as the aggregation proceeds, they totally disappear.

...morphology exhibits itself in terms of the changing extent (length scale) and measure $D_f$ of the fractal region over a range of volume concentrations not explored before. Future publications will deal in greater detail with other applications of both the GRASP and DALAI programs, particularly methods for studying reorganization processes.

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technical assistance during SAXS measurements, Dr C E Dean for implementing and running the parallel DALAI version on the Intel iPSC/860 hypercube at Daresbury Laboratory and Mr J B West for his various contributions in the development of the GRASP program.

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