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Short Communication

Cluster-cluster aggregation for particles with different functionalities

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Abstract. — An extended lattice model for reaction limited cluster-cluster aggregation is studied, where different kinds and states of bonds between monomers are considered. The decrease of the numbers of possible bonds per monomer yields decreasing fractal dimensions, which differ from the usual values obtained for diffusion limited and reaction limited cluster-cluster aggregation regimes, respectively.

The investigation of aggregation models and nonequilibrium growth has become a main-stream topic in the last few years. The concept of fractal geometry according to Mandelbrot [1] proves to be a suitable tool for the description of structures forming as a consequence of very different processes. A great variety of aggregation models is developed (see [2-5]) and produces aggregates whose fractal dimensions $d_f$ agree very well with experimental results obtained for example by small angle X-ray scattering and light scattering [6-11]. However, so far the theoretical models were designed, mainly, to study principal features of aggregation processes and experimentally important details are missing. In this paper a computer algorithm for fractal growth is studied, which allows more realistic simulations by considering different kinds and states of bonds between monomers allowing a further step in the interpretation of experimental results.

We consider an aggregation model taking into account the various kinds and states of chemical bonds between monomer [12]. Similar models were proposed and studied by Leyvraz [13], Meakin et al. [14, 15] Warren [16] and Kallala et al. [17] without distinguishing bonds.

We start from a list of clusters (monomers or primary particles are clusters of size 1) and randomly select two clusters. In the next step a random particle of the first cluster and a random particle of the second cluster are chosen. Our model allows us to select clusters or particles with different probabilities, e.g. as a function of the cluster size or the particle position in the chosen cluster. Here we use an extended on-lattice model, the centers of all the particles being located on lattice points of a quadratic or cubic lattice in 2- or 3-dimensional simulations. Usually lattice models allow bonds along the directions of the lattices axes only.
In our model bonds also can be established along the diagonals of the lattice. This yields 8 possible directions for bonds in the 2-dimensional and 26 bonds in the 3-dimensional case (comparing with 4 or 6 bonds in the usual lattice model) and should be a step forward to more realistic simulations of systems consisting of spherical or polyhedral monomers with a long number of possible bonds avoiding the large expense of computational capacity in off-lattice simulations.

Moreover, in our model the bonds between monomers may be different, since we distinguish all bonds by their type, that means their strength or binding energy and their state, which can be:

0 if the bond is free (dangling bond)

1 if this bond connects two particles

2 if this bond is forbidden.

In the third step, one of the possible binding directions is selected randomly and the monomers (respectively, the two clusters) are brought into neighboring positions along this direction. If there is overlap, i.e., if two monomers use the same lattice site, the configuration is rejected and a new pair of clusters and another pair of particles are chosen. An alternative way consists in only selecting a new pair of particles in the selected clusters after obtaining an overlap. This alternative yields a difference in the cluster size distribution, which will be discussed in another paper.

Following an idea of Kallala [18] the hindered bonds correspond to chemical systems, where bonds (respectively parts of the surface of the particles) are blocked by surfactants or, for the case of aggregation in silica-gels, by an incomplete hydrolysis of the monomers [9].

The algorithm was used for 2- and 3-dimensional aggregation starting from a list of 10000 monomers and generating clusters until a cluster of size greater than 500 monomers is reached. In an alternative model the generating of clusters will be continued until only one cluster containing all monomers remains in the system. With this model we get clusters of definite size, but it leads to slightly lower fractal dimensions, because the aggregation of clusters with similar sizes occurs in the last steps of the simulation. The relationship between the fractal dimension and the cluster size distribution in the system (the polydispersity of the distribution) will be investigated by simulations using larger computers than that we used for this paper.

Initializing the system, for every monomer a given number of randomly chosen bonds were set to be in state 2. It means, according to the mentioned rules, that this bond is blocked.

Figures 1a-e show clusters obtained from 2-dimensional simulations for different numbers of possible bonds per monomer. With decreasing numbers of bonds from 8 of 8 possible bonds to 4 of 8 possible bonds the clusters become more tenuous and chain like. The limiting case of 2 bonds corresponding to chain like polymers we could not realize in our simulations because of the large computational time needed for it. The fractal dimensions \(d_f\) were calculated from the relation

\[
M \sim R_G^{d_f}
\]

where \(M\) is the mass and \(R_G\) the radius of gyration of a cluster (monomers have a mass 1), by minimizing

\[
\sum_M \left( \ln R_G(M) - \frac{1}{d_f} \ln M \right)^2
\]
for all clusters and subclusters during the aggregation in one simulation (or for the last clusters containing all monomers using the second model mentioned above) with \( M \geq 10 \). Figure 2 shows a log-log plot of the mass versus size for clusters of 4, 8, 16, .., 1024 monomers for different numbers of blocked bonds. Tables I and II show the fractal dimensions for 2- and 3-dimensional simulations. It can be seen that with a decrease of the number of bonds the fractal dimension decreases also. This decrease is particularly significant when the number of free bonds is reduced from 8 to 7 (or from 26 to 25 in the 3-dimensional model). The subsequent reductions are less significant.

In this paper we introduced a computer model for reaction limited cluster-cluster aggregation which allows us to consider various kinds and states of bonds corresponding to different chemistry of the experimental system. We detect a decrease of the fractal dimension \( d_f \) with a decreasing functionality of the monomers. This could explain low fractal dimensions in disperse systems at very long gelation times, like a fractal dimension of \( d_f = 1.38 \) in silica-gels with incomplete hydrolysis as a result of blocked bonds [9]. This conclusion is in contrast to the usual classification of fractal cluster aggregation as fast aggregation with low fractal dimensions \( d_f \approx 1.7 \) in the case of diffusion limited cluster-cluster aggregation and slow aggregation

Fig. 1. — Aggregates consisting of about 500 particles grown for different number \( k \) of blocked bonds per monomer in a 2-dimensional simulation with 8 possible bond directions: (a) \( k = 0 \), (b) \( k = 1 \), (c) \( k = 2 \), (d) \( k = 3 \), (e) \( k = 4 \).
Fig. 2. — Mass $M$ (expressed as number of monomers) versus radius of gyration $R_G$ (in lattice spacings) for different number $k$ of blocked bonds in 3-dimensional simulations. The simulations were carried out until one cluster containing all monomers was reached. The straight lines correspond to the fitted fractal dimensions. (□) $k = 0$, $d_f = 2.17$, (●) $k = 1$, $d_f = 1.68$, (△) $k = 10$, $d_f = 1.60$.

Table I. — Fractal dimension $d_f$ for different numbers of bonds per monomer in a 2-dimensional simulation with 8 possible bond directions.

<table>
<thead>
<tr>
<th>Blocked bonds per monomer</th>
<th>$d_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (8)</td>
<td>1.62 ± 0.02</td>
</tr>
<tr>
<td>1 (8)</td>
<td>1.44 ± 0.02</td>
</tr>
<tr>
<td>2 (8)</td>
<td>1.40 ± 0.02</td>
</tr>
<tr>
<td>3 (8)</td>
<td>1.39 ± 0.02</td>
</tr>
<tr>
<td>4 (8)</td>
<td>1.39 ± 0.02</td>
</tr>
</tbody>
</table>

Table II. — Fractal dimension $d_f$ for different numbers of bonds per monomer in a 3-dimensional simulation with 26 possible bond directions.

<table>
<thead>
<tr>
<th>Blocked bonds per monomer</th>
<th>$d_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (26)</td>
<td>2.20 ± 0.02</td>
</tr>
<tr>
<td>1 (26)</td>
<td>1.71 ± 0.02</td>
</tr>
<tr>
<td>2 (26)</td>
<td>1.67 ± 0.02</td>
</tr>
<tr>
<td>4 (26)</td>
<td>1.65 ± 0.02</td>
</tr>
<tr>
<td>8 (26)</td>
<td>1.63 ± 0.02</td>
</tr>
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with higher fractal dimensions $d_f \simeq 2.1$ in the reaction limited regime \cite{19-21}. Moreover, it can be seen from the results of the simulation that the dependence of the fractal dimension $d_f$ on the number of free bonds shows a certain saturation behaviour. Whether this is true also for larger clusters and an increased number of different bonds will be proved in future simulations. Finally we would like to mention that simulations with decreasing binding strengths yield higher fractal dimensions compared to usual reaction-limited aggregations in a similar way to the effect of restriction processes \cite{5}. A thorough discussion of this relationship will be presented in a forthcoming paper.

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