Volume fraction dependence and reorganization in cluster–cluster aggregation processes

H. F. van Garde, W. H. Dokter, T. P. M. Beelen, and R. A. van Santen
Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands

E. Pantos
DRL Daresbury Laboratory, Warrington Cheshire WA4 4AD, United Kingdom

M. A. J. Michels and P. A. J. Hilbers
Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands and Koninklijke/Shell-Laboratorium, Amsterdam, Badhuisweg 3, 1031 CM Amsterdam, The Netherlands

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Off-lattice diffusion limited cluster aggregation simulations in two dimensions have been performed in a wide volume fraction range between 0.001 and 0.60. Starting from a system of 10 000 monomers with radius 0.5, that follow Brownian trajectories, larger aggregates are generated by bond formation between overlapping aggregates. No rings are present in the nonaged structures. The influence of the initial monomer volume fraction on the fractal properties of the gels is studied and interpreted by calculation of small angle scattering structure factor patterns to find the fractal dimension. It is found that an increase of the volume fraction leads to the development of two distinct fractal regions. The fractal dimension at short length scale shows the diffusion limited cluster aggregation value of 1.45 up to the correlation length, while the long range fractal dimension gradually increases from 1.45 to 2.00, the Euclidean dimension of the simulation space. It is shown that high volume fractions lead to changes in the local morphology of the monomers as a function of the volume fraction with corresponding changes in the high-\( q \) region of the structure factor pattern. A new method to simulate aging of aggregates at modest (low \( p \)H and temperature) reaction conditions by an off-lattice nonbreaking reorganization process, called shaking, is presented. The shaking process induces small changes in the local mass distribution, causing ring formation, but does not affect the radius of gyration of the aggregates. It is found that shaking leads to the formation of a polydisperse collection of new primary scatterers with a volume fraction dependent radius between 6 and 8 initial monomer radii. For low volume fractions the fractal dimension decreases approximately by 0.2, due to the formation of the new primary scatterers. The shaking process induces changes in the fractal properties at length scales up to \( \sim 40 \). A simple theory that relates the volume fraction with the correlation length and describes the influence of aging on fractal properties such as monomer radius, fractal dimension, and correlation length is developed. The diffusion limited cluster aggregation simulation results of nonaged and aged gels are compared with this theory. Satisfactory quantitative agreement between simulated and theoretical results is found. © 1995 American Institute of Physics.

I. INTRODUCTION

Chemical and physical aggregation processes in the nanoscopic regime have been studied extensively during the last decade.\(^1\)–\(^9\) Scattering techniques such as small angle scattering (SAS) of neutrons or x rays, light scattering (LS), and microscopic experiments (in this paper chemical or physical experiments will be referred to as “experimental.” Computer models will be referred to as “simulated” or “model.”) have provided more insight into both the fundamental scaling behavior and kinetics of these processes.

This knowledge, however, could have never been built up without the concomitant usage of computer models. Starting with simple particle-cluster aggregation (DLPCA or DLA) the models have been extended to a family of aggregation algorithms including reaction limitation (RLPCA), and cluster–cluster aggregation (DLCA,RLCA).\(^10\)–\(^23\) These last cluster–cluster models have received particular attention recently\(^24\)–\(^29\) as they can be used to simulate a wide range of experimentally observed aggregation processes. We have studied experimental aggregating silica systems and use the cluster–cluster aggregates as typical starting structures for modeling the gel transformations preceding zeolite synthesis.\(^30\),\(^31\)

Experimental silica aggregation systems can be found (at low volume fractions) that obey the two types of mass-fractal behavior predicted by DLCA (\( D_f = 1.8 \)) and RLCA (\( D_f = 2.1 \)). The existence of these two distinct fractal aggregate systems, and the switch from DLCA to RLCA as a function of reaction conditions, has also been shown experimentally by Wijnen et al.\(^32\) When a higher initial monomer volume fraction (\( \phi_0 \)) is used, this ideal behavior is disturbed and at realistic zeolite synthesis conditions, where volume fractions over 0.50 are commonly used, the fractal properties change from mass-into surface-fractal.\(^30\)

In both volume fraction regimes the aggregates formed in the aggregation process are subject to aging. The effect of aging depends, among others, on \( \phi_0, \) \( pH \) (reactivity), temperature and chemical composition of the gel and is believed...
to play a major role in zeolite synthesis. Before zeolite crystallization can start the gel has to reorganize into a gel with suitable morphology.\textsuperscript{31}

Relatively few attempts have been made to analyze the effect parameters such as volume fraction, sticking coefficients, diffusion and relaxation have on aggregation and aging processes. In particular, relations between experimental aging effects and aging models have not been fully investigated. Most cluster–cluster models do not include the volume fraction as a parameter and contain no aging algorithms to study the dependence of fractal structures as a function of aging steps. The simulations are performed without allowing for internal reorganization and breaking of aggregates.

There are a few examples of simulated aging in fractal aggregates. Random bond-breaking\textsuperscript{33} and rotational aging (instantaneous large ring formation)\textsuperscript{34,35} algorithms have been published and used by Jullien \textit{et al.} (see references in Ref. 28) and others to investigate the short-range correlations in fractal aerogels. Recently, the sintering of fractal aggregates was theoretically addressed by Sempéré \textit{et al.}\textsuperscript{36} based on mass conservation. No simulations were reported.

We have recently developed an off-lattice simulation program\textsuperscript{37} (GRASP) that includes parameters such as the volume fraction of the monomers, the stepsize and aggregation kernels\textsuperscript{27} together with several aging algorithms to describe aging processes. Aging types implemented are

\begin{itemize}
  \item[(a)] internal flexibility of aggregates (used in this paper).
  \item[(b)] single and random bond breaking that use dissociation kernels to select bonds to break as a function of monomer connectivity $Q$.
  \item[(c)] bond breaking depending on the local density of the
\end{itemize}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{(a) Nonaged aggregate of 10 000 monomers in 2D at $\phi_0 = 0.05$. The structure resembles that of an intrinsic mass-fractal. The aggregate is built using periodic boundary conditions and therefore some of the connecting bonds reach over the boundaries. (b) Nonaged aggregate of 10 000 monomers in 2D at $\phi_0 = 0.25$. The short-range structure is intrinsically mass-fractal while the long-range morphology is denser than at $\phi_0 = 0.05$. (c) Nonaged aggregate of 10 000 monomers at $\phi_0 = 0.50$. No fractal properties can be identified, the structure looks homogeneous at all length scales.}
\end{figure}
monomers; this enables breaking of bonds in selected regions of aggregates such as highly ramified areas, densest regions, or outmost branches.

The effects of aggregation parameters on the long-range morphology, formation of fractal systems, and changes therein due to aging can be analyzed via simulated SAS scattering patterns. We use the program DALA\textsuperscript{19} which is an implementation of the Debye formula\textsuperscript{39} optimized for model systems build of monodisperse spheres. Using parallel computers systems consisting of up to one million spheres have been handled.

Here we present simulations as well as a theoretical analysis on aging of gels aggregated by diffusion limited cluster–cluster aggregation in two dimensions. In a later paper we will compare these results with simulations in three dimensions, and with simulations that allow shrinking of aggregates during aging. We emphasize the effect the shaking process, detailed below, has on the morphology of the aggregates and on both the short-range and long-range (fractal) density correlations as shown by simulated SAS patterns.

II. ALGORITHMS AND THEORY

A. Aggregation algorithm

The simulation system consists of 10 000 monomers, where a monomer is modeled as a disk with radius \( R_0 = 0.5 \), which are placed in the simulation space on a square 100 by 100 two-dimensional lattice. Two distinct models exist to control the volume fraction. The first method (used by GRASP), varies the size of the box \( L \) (and consequently the lattice spacing) depending on \( \phi_0 \) using a fixed number of monomers \( N_0 \). This method allows a \( \phi_0 \) range up to the theoretical packing maximum density of an hypercubic lattice, i.e., \( \pi/4 \) in two dimensions and \( \pi/6 \) in three dimensions. Using a hexagonal starting lattice instead of a hypercubic lattice it is possible to enhance the \( \phi_0 \) range of this method even further. The second method\textsuperscript{40,41} is called the sequential addition method. A simulation space of fixed size \( L \) is defined and filled with \( N_0 \) monomers by random sequential placing of the monomers until the desired volume fraction has been reached. The available \( \phi_0 \) range for this method is smaller and limited to 0.55/0.38 in two/three dimensions. The first method is preferable since it enables the study of a wider \( \phi_0 \) range and it nicely links up with theoretical considerations of fractal scaling behavior that use \( N_0 \) as a scaling parameter, such as the theory we present in Sec. II C.

An important difference between the aggregation method used here and previously presented box-aggregation methods is that we move all aggregates during an iteration, similar to the practice of molecular dynamics simulations. Other box-aggregation methods move only one aggregate per iteration and scale their time units accordingly. Within our method time is equal to the iteration number. This difference is similar to the practice of molecular dynamics (MD) and Monte Carlo (MC) simulations.\textsuperscript{42} In MD all molecular coordinates are updated per time step, while in MC only one molecule is moved.

The lattice is melted to generate an off-lattice random system (i.e., to remove initial distance correlations) during a number of moves, typically 10 for low volume fractions to 250 for high \( \phi_0 \). During the melting period no bonds are allowed to form and any detected overlap is removed by restoring the center–center distance of the overlapping pairs to the hard-sphere contact distance of \( 2R_0 \). The melted systems are checked off-line for remaining preferred distance correlations of the starting lattice by inspecting the distance histogram. Next, the monomers start to move along Brownian trajectories. The step size used for the melting and the aggregation is \( R_0/5 \) for all densities higher than 0.05. For the 0.001, 0.01, \( \phi_0_{0.5} \), and 0.05 calculations step sizes of length \( R_0 \) were applied to take advantage of the increased intermonomer distances and thus reduce the computation time.

In DLCA, reaction limitations are ignored and instantaneous bond formation is assumed. So all values of the aggregation kernel are set to unity in all simulations. Overlap between two aggregates leads to formation of exactly one new bond, even when more than one overlapping monomer pair is found. First, for the multiple overlapping aggregates the largest overlapping monomer pair is searched for and all other overlap is removed by iterative separation of the aggregates. Next, all the overlapping aggregate pairs, that now each have only one overlapping monomer pair, are separated, and one new bond per aggregate pair is formed. The resulting nonaged DLCA aggregates therefore contain no ring structures.

The newly formed aggregates (we will still refer to the connected monomers that make up that aggregates as monomers) continue to follow their Brownian trajectories as rigid bodies. The aggregation process stops when one aggregate of mass 10 000 has been formed. In this paper we will refer to these 10 000-monomer aggregates, formed at the very end of the aggregation process, as the nonaged aggregates. In Fig. 1 three nonaged aggregates grown at volume fractions 0.05 (a), 0.25 (b), and 0.50 (c) are shown. At \( \phi_0 = 0.05 \) the mass-fractal properties are well developed and the aggregate has a very ramified structure. At \( \phi_0 = 0.25 \) the mass-fractal properties are only present at short length scales. The long-range structure seems almost homogeneous. At \( \phi_0 = 0.50 \) no mass-

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{(a) A small DLCA aggregate built of five monomers that are bonded by four bonds. Shaking steps \( S \) are shown as arrows. (b) The shaking steps have been applied causing both longer and shorter bonds as well as a new overlap, indicated as a dotted line between monomers 1 and 4. (c) Existing bond lengths have been constrained to length 2\( R_0 \) and a new bond between monomers 1 and 4 has formed a new 4-ring. The number of bonds equals five now.}
\end{figure}
fractal structure is visible and the morphology resembles a high density 2D random network.

The maximum allowed monomer connectivity \( Q \) is six for these simulations. The actual average connectivity \( \langle Q \rangle \), however, is lower and can be calculated since the structure contains no bond-sharing rings. The nonaged aggregate can be regarded as a set of connected chains of monomers. One of these chains has to be taken as the starting chain and all monomers that make up that chain have a \( Q \) of 2 except for the two ends. Other chains can be regarded as branches of the starting chain. The branches can have subbranches and so on. Each (sub)branch causes one of the monomers of another chain to have its \( J \) raised by one but the other terminus remains single-connected leading to a \( \langle J \rangle \) of exactly two for all branches. The total connectivity for an aggregate of mass \( N_0 \) that contains no rings therefore equals \( 2N_0 - 2 \) leading to an average connectivity of:

\[
\langle Q \rangle = \frac{2(N_0 - 1)}{N_0} = \frac{19998}{10000} = 1.9998.
\]

This result is independent of the connectivity distribution, i.e., the relative number of \( Q_1, \ldots, Q_6 \) connected monomers may differ between aggregates, but \( \langle Q \rangle \) will remain constant as long as no rings are formed in the structure.

The number of chains \( N_c \) in a nonaged aggregate is equal to the number of \( Q_1 \) connected monomers minus one, as all chains are connected (\( Q_2,3,\ldots \)) to another chain on one side and are not connected (\( Q_1 \)) on the other side. It is only the starting chain that has two single connected ends.
coordinates, shown in Fig. 2, are labeled as arrows. The shaking steps are added to the monomer aggregate of five monomers is shown. The steps $S_s$ are indicated as arrows. The shaking steps are added to the monomer aggregate of five monomers is shown. The steps $S_s$ are added to the monomer aggregate of five monomers is shown. The steps $S_s$ are added to the monomer aggregate of five monomers is shown. The steps $S_s$ are added to the monomer aggregate of five monomers is shown.

The branching frequency $N_b$, i.e., the average number of monomers in a chain equals the number of monomers in the system divided by the number of chains

$$N_b = N_0 / N_c.$$ 

(3)

B. Aging shaking algorithm

The nonaged aggregates are subjected to the shaking algorithm. The monomers of the aggregate being aged are moved (shaken) with respect to each other by a step $S_s$ the size of which depends on the connectivity. Single connected monomers ($Q_1$) are "shaken" most rigorously, higher connected monomers ($Q_{2,3,4,...}$) are subjected to smaller steps since their movements are restricted by their bonds:

$$S_s(Q) = \frac{R_0}{4(Q + 1)}.$$ 

(4)

In Fig. 2(a) a small artificial nonaged off-lattice DLCA aggregate of five monomers is shown. The steps $S_s$ are indicated as arrows. The shaking steps are added to the monomer coordinates, shown in Fig. 2(b). Since this aging process is performed off-lattice the shaking movements cause existing bonds to stretch or shorten. The bond between monomer pairs 1–2 and 2–3 are stretched and the bond-lengths between pairs 3–4 and 3–5 are decreased. The steps $S_s$ have a random direction so apart from bond-length changes, the angles in the branches also change. The rotations may cause new overlaps between previously nonoverlapping, and therefore nonbonded monomer pairs, this has happened with monomers 1 and 4 in Fig. 2(b).

Bond breaking and monomer fusion are not allowed in these simulations so the lengths of existing bonds have to be constrained to their intrinsic, hard sphere contact distance of $2R_0$. Figure 2(c) shows the shaken aggregate after all previously existing bonds have been constrained to their intrinsic length and the new overlap has been turned into a new bond thereby increasing $Q$. 

The shaking process is continued for 25 000 iterations. This number has been chosen by comparing the SAS patterns of the systems after every 1000 shaking iterations. Clear differences between the starting pattern and the pattern for the systems shaken 1000 times could be observed. After applying shaking for some 7000 iterations no further changes in the pattern could be measured in the development of $D_f$ and $R_g$, the fractal dimension and the primary particle size of the aged aggregates, respectively. By continuing the simulations up to 25 000 times it could be established that the shaking process had reached its final stage.

In Fig. 3 the effect shaking has on the morphology is shown. Visual comparison of aged and nonaged structures shows that the shaking process has "folded" all short side-chains onto the backbone of the aggregate, leading to formation of a "strengthened" backbone consisting predominantly of 3-rings which pack closely to form "semicrystalline" hexagonally packed structures. Occasionally larger rings have been formed by inter- or intrabranch bonding. At low $\phi_0$ the aged aggregate looks stringy while at high $\phi_0$ it becomes coarse-grained. At medium $\phi_0$ both effects are visible. The long-range structure and the size of the aggregate do not

<table>
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<th>$L$</th>
<th>$R_g$</th>
<th>$2R_g/L$</th>
<th>Simulation</th>
<th>Theory</th>
<th>Short</th>
<th>Long</th>
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<td>$186.8$</td>
<td>$1.45 \pm 0.012$</td>
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</table>

$N_c = N_0 - 1$. 

(2)
change, the backbone of the aggregate moves only slightly, preserving long-range distance correlations.

C. Theoretical expressions

1. Expressions for aggregation

Suppose a $D$-dimensional simulation space contains $N_0$ monomers of mass $M_0$, radius $R_0$, and density $r_0$. The initial volume fraction of the monomers is $f_0$. The monomers have formed $N$ aggregates of mass $M$ that are fractal on a length scale between $R_0$ and $R_1$. The mass $M$ of the aggregates as a function of length scale $R$ is:

$$M = M_0 \left( \frac{R}{R_0} \right)^{D_f}.$$  \hfill (5)

For distances $R$ shorter than $R_0$ we set the density $\rho_0$ of the initial primary scatterer to 1.0. The density $\rho$ of the fractal region can be expressed analogous to Eq. (5) as:

$$\frac{\rho}{\rho_0} = \left( \frac{R}{R_0} \right)^{D_f - D}. \hfill (6)$$

The aggregate mass distribution, as found in polydisperse aggregation models such as the DLCA model used in this paper, has to be simplified to enable a theoretical description that includes $\xi$, the correlation length associated with the length scale over which the structures exhibit fractal properties. We take the mass distribution to be a delta function, just as in the hierarchical DLCA model. The $N$ aggregates are assigned mass $M$, while $NM = N_0 M_0$ to ensure mass conservation during aggregation. Then for the number of fractal aggregates in the system holds:

$$\frac{N}{N_0} = \left( \frac{R}{R_0} \right)^{-D_f}. \hfill (7)$$

Each aggregate can be regarded as a porous sphere of radius $R$. The effective volume $V_e$ of an aggregate is then:

$$\frac{V_e}{V_0} = \left( \frac{R}{R_0} \right)^D. \hfill (8)$$

The total volume of the aggregates $\phi_e = NV_e$ so that the following relation holds for the effective volume fraction $\phi_e$:

$$\frac{\phi_e}{\phi_0} = \frac{NR^D}{N_0 R_0^D} = \left( \frac{R}{R_0} \right)^{D - D_f}. \hfill (9)$$

It is necessary to distinguish between two situations for the formation of the nonaged aggregate and the upper length scale $R$ of fractality. Depending on $\phi_0$ the aggregates formed can become so large that they span (percolate) the box before the final aggregate has been formed (gelation). This happens for high volume fractions (situation A). At low $\phi_0$ however,
the aggregate is too small to percolate and only gelation occurs (situation B). The premature percolation at high volume fractions limits the fractal growth. The upper length scale \( R \) of fractality therefore depends on \( f_0 \) and is smaller for high volume fractions.

For high volume fractions (situation A) percolation occurs before gelation: \( \phi_A = 1 \) and \( N_A > 1 \). From Eq. (9) so follows then for \( R \) that:

\[
\frac{R_A}{R_0} = \phi_0^{1/(D_f-D)}.
\]  

For low volume fractions (situation B) gelation occurs, but there is no percolation: \( \phi_B < 1 \) and \( N_B = 1 \)

\[
\frac{R_B}{R_0} = N_0^{1/D_f}. \tag{11}
\]

The critical volume fraction \( \phi_{0,c} \) for the crossover between situation A and B can be calculated by combining Eqs. (10) and (11):

\[
\frac{R_C}{R_0} = \phi_{0,c}^{1/(D_f-D)} = N_0^{1/(D_f-D)} \Leftrightarrow \phi_{0,c} = N_0^{(D_f-D)/(D_f)} \tag{12}
\]

Equation (12) shows that the occurrence of percolation depends on \( N_0 \), the numbers of monomers used in the simulation.

2. Expressions for aging

Aging processes like random bond breaking, ring formation, or more sophisticated processes as “Ostwald ripening”\(^4\) will induce changes in the (fractal) properties of the system, such as

(a) formation of new primary scatterers of radius \( R'_0 \) with density \( \rho'_0 \).

(b) shrinking of the aggregates, due to sintering or resolution, thereby inducing changes in the correlation length \( \xi \), the cutoff length \( R_1 \) and/or the long-range density \( \rho \).

(c) changes in the fractal dimension \( D_f \).

Often, several changes in the fractal properties appear simultaneously. Using these modified system parameters an expression equivalent to Eq. (6) can be written down for the aged system:

\[
\frac{\rho'}{\rho_0} = \left( \frac{R'}{R_0} \right)^{D_f-D}. \tag{13}
\]

Equations (6) and (13) allow us to relate the fractal properties of nonaged and aged aggregates. When we take the log of Eqs. (6) and (13) and subtract them we get after some rearrangements:
The properties of the fractal aggregates used in Eqs. (5)–(14) are functions of $\phi_0$. The correct values for upper limit $R_1$ of fractal behavior, given by Eqs. (10) and (11), can be substituted into Eq. (14):

$$\log \left( \frac{\rho'}{\rho} \right) - \log \left( \frac{\rho'_0}{\rho_0} \right) = (D'_j - D) \left[ \log \frac{R'}{R} - \log \frac{R'_0}{R_0} \right] + (D'_j - D) \log \frac{R}{R_0}. \tag{14}$$

The correlation length can be calculated by combination of the definition of the radius of gyration and Eq. (6):

$$\xi^2 = \frac{\int R^2 \rho(R) dR}{\int \rho(R) dR} = \frac{2 - D + D_f R_1}{4 - D + D_f R_1} R_1. \tag{16}$$

$R_1$ is the maximum radius of the aggregates and can be calculated using Eqs. (10)–(12) depending on $\phi_0$. For $D_f = 1.45$ we find for the relation between $R_1$ and $\xi$:

$$\xi = \sqrt{\frac{D_f}{2 + D_f}} R_1 \approx 0.65 R_1. \tag{17}$$

3. Effect of particle growth on $D_f$ with mass preservation

The effect of the shaking process on the morphology of DLCA aggregates is depicted in Fig. 4. In Fig. 4(a) all (black) monomers have size $R_0$ and density $\rho_0$. On the length scale of the copies the system is homogeneous with density $\rho$. In Fig. 4(b) shaking has caused ring formation represented by white monomers. The long-range density $\rho'$ is still $\rho$, but new primary scatterers with size $R'_0$ and density $\rho'_0$ have been formed, as shown schematically in Fig. 4(c).
Equation (14) describes the relations between the fractal parameters of aggregates. Below we determine how the fractal dimension changes when aging causes $R_0$ and $r_0$ to change to $R_0'$ and $r_0'$ while $R_1$, $R_1'$ and the mass of the aggregate are constant. We can reduce Eq. (14) since we can identify $R$ and $R_0'$ as $R_1$ and $R_1'$, which we expect not to change as a result of the shaking procedure. The same holds for $r$ and $r_0'$; therefore,

$$\log \frac{S_{r_0}}{S_{r_0'}} = \frac{(D_2 - D_1) \log (\frac{R_{1}}{R_0}) - (D_j - D_f) \log (\frac{R_{1}}{R_0})}{\log (R_{1}/R_0) - \log (R_{1}'/R_0)}. \tag{18}$$

Solving Eq. (18) for $D_j$ gives

$$D_j = \frac{\log (\rho_{0}'/\rho_0) + D \log (R_{0}'/R_0) - D_f \log (R_{1}/R_0)}{\log (R_{0}'/R_0) - \log (R_{1}/R_0)}. \tag{19}$$

Depending on $\phi_0$, Eq. (10) or (11) has to be used for the ratio $R_1/R_0$.

Consider now the following aging process. An aggregate of 10 000 monomers grown by 2D DLCA aggregation is used as the starting structure. The parameters describing the nonaged fractal system are $R_0=0.5$, $\rho_0=1.0$, and $D_f=1.45$. The critical volume fraction, calculated from Eq. (12), is $\phi_{0,c} \sim 0.0304$.

The aggregate has been grown in a box with volume fraction $\phi_0=0.001$, i.e., the aggregate is grown below the critical volume fraction. Using Eq. (11) an upper length scale of fractal behavior $R_1$ of 286.8 is found. Using Eq. (17) the expected correlation length $\xi(R_1)$ becomes 186.8.

Suppose that the aging process causes the formation of a new primary scatterer with a radius $R_0' = 8R_0$. The growth of the primary scatterer has been achieved by a local densification without disrupting the backbone of the aggregate. Furthermore we assume that the new primary scatterers are built of hexagonal-close-packed disks with density $r_0'$. The theoretical value for the density of 2D hexagonal-close-packed disks $\rho_0' = \sqrt{3}/2 = 0.87$, relative to the density 1.0 of the initial primary scatterer.

Since the backbone of the aggregate is only locally distorted, the long range morphology of the aggregate remains fractal and the $\xi$ of the aggregate is not changed. Using Eq. (19) and the value $\rho_0'$ the value of $D_f'$ is calculated to be 1.22. So formation of a larger primary scatterer formed by an aging process that preserves the size of the aggregate (no shrinking) will lead to a decrease in the fractal dimension by approximately 0.23.

4. Simulation of scaling data

The simplified form of the size distribution for DLCA used in Sec. II C 1 does not occur in the simulations. The system will evolve from a monodisperse collection of 10 000 monomers into a system containing a polydisperse set of...
aggregates with masses $M_i$. The radius of gyration $R_{g,i}$ and maximum radius $R_i$ of a centered aggregate, can be calculated using the distances $r_j$ of the monomers to the center of mass:

$$R_{g,i}^2 = \frac{1}{M_i} \sum_{j=1}^{M_i} r_j^2,$$

$$R_i = \text{MAX}(k: 1 \leq k \leq M_i; j_k).$$

From the gyration radii of the aggregates, the correlation length $\xi$ can be calculated:

$$\xi^2 = \frac{\sum_{i=1}^{N} R_{g,i}^2 M_i}{\sum_{i=1}^{N} M_i}.$$

Using the maximum radii the effective volume fraction $\phi_e$ can be calculated from the volumes $V_i$ occupied by the aggregates, using $V_i = C_D R_i^D$. The constant $C_D$ equals $\pi$ and $4\pi/3$ in 2D and 3D respectively:

$$\phi_e = \frac{\sum_{i=1}^{N} C_D R_i^D}{L^D}.$$

The aggregates grow in time until finally one aggregate is formed. For volume fractions higher than $\phi_0$, percolation will occur. At a certain stage of the simulation, the $\phi_e$ reaches 1.0. At this moment the total effective volume of the aggregates has become equal to $L^D$, the volume of the simulation space. The growing aggregates touch causing percolation before one aggregate has been formed. This limits the development of fractal properties, leading to a decrease of $\xi$.

For volume fractions below $\phi_0$, the aggregate is grown in a simulation space that is too large to span for the given the number of monomers, and percolation does not occur. The $\xi$ of the nonaged aggregate is used as the $\xi$ for that volume fraction. From Eq. (22) we see that for such a system $\xi$ is identical to $R_\xi$, as the summation contains only the $R_\xi$ of the nonaged aggregate. These results are analogous to effects found in percolation theory.$^{45,46}$

### III. RESULTS

#### A. Aggregation

##### 1. Tabulated aggregation results

System parameters and results for all aggregation simulations are presented in Table I. For all volume fractions ten simulations were performed except for 0.001 at which one simulation has been done. For the $R_\xi$ and $\xi$ values the standard deviations are given. The $D_f$ values were determined by averaging the SAS patterns first. Consequently no standard
deviations are presented. The horizontal lines around the $f_0$, $c$ data indicate the crossovers between aggregation regimes.

The size of the simulation space $L$, that increases as the volume fraction decreases, is given in column two. The spacing of the starting lattice can be derived from $L$ by dividing it by 100. We see that for $f_0 = 0.001$ the lattice spacing is very large, more than twenty-eight monomer diameters. For $f_0 = 0.60$ the spacing is very small, just over one monomer diameter.

The radius of gyration $R_g$ of the nonaged aggregates and the ratio between $2R_g$ and $L$ are given in columns three and four. For $f_0$ higher than $f_{0,c}$ the growth of the aggregates has been restricted by the size of the simulation space, leading to constant ratios. For $f_0$ lower than $f_{0,c}$ no simulation space restrictions are present and the aggregate size becomes independent of the size of the simulation space and the $2R_g/L$ ratio decreases.

The values for $\xi$, in column five, are determined from the simulated coordinates using Eq. (22). For $f_0 = 0.01$ and 0.001 no percolation occurs and the $\xi$ of the nonaged aggregate equals the $R_e$ value as indicated in Sec. II C 4. For volume fractions higher than $f_{0,c}$ the development of $\xi$ during aggregation stops when the system percolates, i.e., when the effective volume fraction $f_e$ becomes 1.0. Consequently $\xi$ is smaller than the $R_g$ value of the nonaged aggregate in column three. From $f_0 = 0.25$ upward the value of $\xi$ becomes so low that fractal behavior does not occur anymore. The value of $\xi$ becomes equal to distances representing the first and second coordination shells of the monomers. The aggregation process has become “space-limited”, there is simply no space available to build fractal structures.

The theoretical $\xi$ values in column six of Table I are calculated using Eq. (17). For $f_0 = 0.001$ and 0.01, $R = R_B$ is calculated from Eq. (11). For $f_{0,c}$ $R_C$ is obtained using Eq. (12) and for higher volume fractions $R_A$ is calculated by Eq. (10). For $f_0 = 0.01$ and 0.001, the simulated $\xi$ are slightly higher than the theoretical values, due to the anisotropic (not spherical) shape of the aggregates. This leads to the overestimation of $\xi$. At the critical volume fraction and higher the values agree quite well. However, the values for $\xi$ are smaller than predicted by the theory. This reflects the theoretical assumption of a homogeneous aggregate size distribution. Also the absolute value of $\xi$ might depend on choice made to take the $\xi$ value at the moment when the $f_e$ becomes 1.0.

The $D_f$ values in columns seven and eight are measured from the SAS patterns shown in Fig. 5. In column seven the $q$ interval $[q(\xi) - q(4)]$ is used. For a wide range of volume fractions up to $f_0 = 0.20$ the short-range fractal dimension on length scales smaller than $\xi$ remains equal to the intrinsic DLCA $D_f$ as predicted in Sec. II C. For the high volume

FIG. 10. Scattering patterns of aged aggregates as a function of $f_0$. The shaking algorithm has been applied 25 000 times causing the growth of densely packed primary scatterers between approximately 3.0 and 4.0 ($6\sim8R_0$) and a slope between 1.75 and 1.85.
fractions between 0.25 and 0.60 the q interval is too small to determine D_f properly.

The longest straight section of the SAS patterns is used to determine the long range D_f in column eight. The q(R_g) value was taken as the upper limit of the q interval. The fractal dimension appears to increase gradually starting from the DLCA value of 1.45 to 1.99 (~52), the Euclidean dimension of the simulation space. This effect is analogous to the mass-fractal behavior of DLCA in 3D. In 2D however the effects are clearer because the ratio (R_1/R_0) is larger for the same number of monomers in 2D than it is in 3D.

Figure 5 shows that the SAS patterns are affected by \phi_0 on all length scales. Nevertheless, for all volume fractions the SAS patterns can be separated into two regions, i.e., the fractal region in the low-q interval [q(R_g)-q(4)] and the nonfractal, or local density, region in the high-q interval [q(4)-q(R_0)]. The radial distribution function patterns (RDF) of the nonaged aggregates in Fig. 6 show that the long-range (fractal) properties indeed start at distances larger than four.

2. Long and short range effects of \phi_0

For the low-q region the effect of increasing volume fraction is clear. We know from the data in column seven of Table I that the short range morphology of the aggregates for volume fractions below 0.25, has a fractal dimension of 1.45. The scattering data show that D_f gradually increases with \phi_0. The reason that D_f does not immediately increase to 2.0 at length scales larger than \xi must be interpenetration or packing of the fractal blobs. Both interpenetration and packing will increase with \phi_0, leading to a gradual increase of D_f until the short range fractality has disappeared and no interpenetration is further possible and a close packing is reached at high volume fractions. As said before, the aggregation process becomes space-limited at high \phi_0 and no fractal structures can be formed. The system then is nonfractal, and homogeneous on all length scales larger than 2R_0. It is further worth noticing that the increase of D_f cannot arise from finite size effects as the ratio between L and \xi is high (>10) at all volume fractions, between 0.10 and 0.60, for which D_f is higher than the DLCA zero concentration limit of 1.45. Therefore the effect of \phi_0 on D_f can be attributed to the decrease in \xi.

For the high-q region we observe that the increase of \phi_0 also affected the short-range mass-distribution. In the inset of Fig. 5 the patterns for \phi_0 higher than 0.30 show a deepening of the first minimum around q=4.5, and a gradual shift of the minimum to lower q. Also a crossing point at
q = 1.25 (R = 5.0) is observed. The shift of the first minimum indicates that the size of the primary scatterer R₀ is growing. The deepening of the first minimum must be due to an increase in the local density of these primary scatterers.

The RDF patterns in Fig. 6 confirm the idea that increased volume fraction affects the local density. For φ₀ = 0.05 the RDF pattern shows the hard sphere contact distance peak at distance R = 1.0 and two discontinuities at distances R = 2.0 and 3.0. Even at distance 4.0 the RDF shows a discontinuity. This marks the end of the nonfractal region and the onset of fractality at higher distances. This shape is typical for a fractal system at low φ₀. The discontinuity at R = 2.0 is clearly visible in all RDF patterns but for φ₀ = 0.15 and 0.50 the typical fractal shape changes with increasing volume fraction. The discontinuities at R = 3.0 and 4.0 present at low φ₀ become less and less pronounced and are hardly visible at φ₀ = 0.50.

Figures 7 and 8 show the connectivity histograms of the nonaged aggregates and the dependence of the branching frequency Q on φ₀. Both figures provide us with direct information concerning changes in the local morphology around the monomers. From Fig. 7 we can conclude that the population of the first coordination shell increases with the volume fraction as the number of Q₁,₄,₅ connected monomers increases with φ₀, at the expense of the number of Q₂ connected monomers. This is accompanied by a decrease in the branching frequency as shown by Fig. 8. The decreased chain length is also visible in Fig. 1(a)–1(c), that show the gradual change in local morphology from chains in the inset of Fig. 1(a) to dense packing and a higher branching frequency in Fig. 1(c). The effect of increased population of the first coordination shell with φ₀ is also shown by the bond-angle distribution plot in Fig. 9. We observe that at low volume fractions the angles between 60.0° and 90.0° are less populated, with respect to the interval between 90.0° and 180.0°. Higher volume fractions lead to an increased number of angles in the range between 60.0° and 90.0° and thus to an increased number of short monomer–monomer distances.

Due to the increase in local density around a monomer for high volume fractions, the first minimum around q = 4.5 both deepens and shifts towards lower q values. The shift of the first minimum towards lower q values can be attributed to the increasing number of high-connected monomers forming “primary” particles of which the structure factor has a first minimum at lower q. The deepening causes the high φ₀ SAS patterns to lie below those for low φ₀. Since Dₐ increases with φ₀ the SAS patterns for higher φ₀ must cross the low φ₀ patterns leading to the crossing around q = 1.25 (R = 5.0).

### B. Aging shaking

The influence shaking has on (long-range) fractal properties of aggregates is shown in Fig. 10 where the SAS structure factor patterns are shown and Fig. 11 that shows the (short-range) radial density functions (RDF) for both nonaged and aged aggregates. In Table II the results of the shaking procedure on the fractal properties of the aggregates are presented. The shaking simulation has been performed once for every volume fraction.

In the second column the Dₐ on long length scales and the Dₐ' on the intermediate length scales of the aged aggregates are presented. The longest straight section in the q interval [q(R₀')–q(R₀)] of the SAS patterns was used to determine Dₐ'. The theoretical value for Dₐ' using Eq. (19) is given in the third column. We find very good agreement between theory and simulation.

The intrinsic effect of shaking on long-range morphology is best seen at low φ₀. For φ₀ = 0.01 and 0.001 two distinct fractal dimensions can be identified. The shaking process has affected the Dₐ of the aggregate up to a maximum (intermediate) length scale. For distances larger than this intermediate length scale the fractal dimension of the system has not been changed. In Fig. 12 the SAS patterns of the nonaged and aged aggregates at φ₀ = 0.001 are plotted together. It is clear that the growth of the primary scatterer...
from $R_0$ to $R'_0$ has been achieved by a "mass-transfer" from low $q$ to higher $q$, i.e., the number of short-range interactions has been increased at the expense of the long-range interactions. Consequently the short-range density increases and the intermediate-range $D_f$ decreases.

The longest length scale affected by shaking is smaller than the $R_g$ or $j$ of the nonaged aggregate. The maximum length scale for the influence of shaking lies around 40 ($80R_0$) as can be seen in Fig. 12. For $f_0 > 0.05$ no long-range $D_f$ is found. The $j$ of these systems is smaller than 40 so that shaking affects the morphology over the entire fractal range length scale.

$D_p$, defined as the negative slope of the dense packing region (high-$q$) is given in the fourth column. $D_p$ was determined in the $q$ interval. For low $f_0$ we find values around 1.85 decreasing to 1.75 for high $f_0$. This indicates that the new primary scatterers are not completely closed packed, as this would lead to a $D_p$ value of 2.0. The packing shown in Figs. 3(a)–3(c) are schematically illustrated in Fig. 4 suggest new primary scatterers of various shapes and sizes.

The radius of gyration $R'_g$ of the aged aggregates is tabulated in column five. When we compare the $R'_g$ values with the $R_g$ values of Table I we see that the size of the aggregates indeed has not been changed by the shaking process. So Eq. (19) may be used to calculate $D_f$.

In column six, the size of the new primary scatterers, $R'_0$ formed by the shaking process, as measured from the SAS curves is tabulated. Around $q = 2.0$ ($R = 2.0$–5.0) there is a crossover between the dense packing region and the fractal region. $R'_0$, was taken to be the first deviation from the $D_p$ slope on the low-$q$ side. We find values between 3.0 and 4.0, and observe a gradual increase with $f_0$.

Finally the average connectivity $\langle Q \rangle$ is tabulated is columns 7. The $\langle Q \rangle$ increases with $f_0$. In Fig. 13 the connectivity distribution of the aged aggregates is shown. Figure 13 shows that the increase of $\langle Q \rangle$ with increasing $f_0$ has been achieved by an increase of $Q_5$ and $Q_6$ connected monomers at the expense of the number of $Q_2$ and $Q_3$ monomers. It is further clear that the aging process has caused the total disappearance of $Q_1$ connected monomers, indicating that all chain end-points have folded back or contacted a neighboring chain.

The SAS patterns for the aged systems have a common course in the $q$ interval $[q \sim 3.0 – q \sim 0.5]$, and show only minor differences for higher $q$ values as can be seen in the inset of Fig. 10. The $R'_0$ is almost constant for all aged aggregates. It is only the average connectivity that increases with the volume fraction from 3.86 to 4.29.

It is clear that the shaking process has transformed the widely varying local densities of the nonaged aggregates into...
a dense local morphology that is (almost) volume fraction independent. This is reflected by the $R_0$ and $D_p$ columns of Table II that show that the aging process has formed a new densely packed primary scatterer with an $R_g$ between 3.0 and 4.0 ($6 \sim 8R_0$) with a $D_p$ between 1.75 and 1.85. The long-range fractal behavior in column $D_f$ shows that for low $\phi_0$ the $D_f$ decreases approximately by 0.2, in very good agreement with the prediction of Eq. (19). Even in the system with high $\phi_0$, where the mass-fractal properties are highly disturbed or even absent, the growth of $R_0$ to $R'_0$ is present and the predicted $D_f$ values are in close agreement with the simulated $D_f$ values.

The increase of $\langle Q \rangle$ with $\phi_0$ can be easily explained. We have seen in Sec. III A that the nonaged aggregates have a local density that increases with $\phi_0$. For low $\phi_0$ the monomers have a low number of neighboring monomers due to the well-developed fractal properties. Consequently, the reorganizations are local since monomers can only form new bonds with monomers that are in the same branch, other branches are too distant to connect. The reorganizations can be called “neighbor-limited”. For high $\phi_0$ local rearrangements also take place between monomers in the same branch but also between branches due to the higher local density leading very rapidly to interbranch connections and a higher average connectivity. Still, the reorganizations and constrained at high volume fractions also since the movements of the monomers are highly obstructed by all the other monomers in their neighborhood. The reorganizations are “free-space-limited.”

IV. CONCLUSIONS

We have discussed a series of 2D DLCA aggregation simulations, followed by an aging gel-transformation process that simulates local nonbreaking reorganizations in off-lattice aggregates. We have also presented a theoretical model that describes both the effect of volume fraction on the properties of the aggregates and in a general way relates the properties of nonaged and aged systems.

We have shown that DLCA systems with a volume fraction above the critical volume fraction show two different fractal dimensions at length scales shorter (high-$q$) and larger (low-$q$) than $\xi$. Below and at the critical volume fraction no low-$q$ region exists and the systems can be characterized by one fractal dimension. In addition, for distances shorter than four the system has no fractal properties.

In the high-$q$ region, at short length scales between distance four and the correlation length of the system, $D_f$ equals
1.45, the intrinsic DLCA value, over a wide range of volume fractions up to 0.20. For higher volume fractions $\xi$ becomes smaller than four and fractality is absent. In the nonfractal region differences in scattering behavior between systems with low and high volume fractions are found. These differences can be attributed to changes in the local density of the monomers.

For systems with a volume fraction higher than the critical volume fraction, the low-$q$ region represents distances between $\xi$ and the radius of gyration of the nonaged aggregate. Increasing $\phi_0$ causes a continuous change in the long range $D_f$. Starting from 1.45, the fractal dimension gradually increases and for high $\phi_0$ it equals the Euclidean dimension 2.0 of the simulation space.

The shaking process leads to growth of $R_0$ with a concomitant decrease of $D_f$, since $R^*_0$ ($R_g$) remains constant. This can be explained by a simple model based on scaling relations in which $\phi_0$ and $R_g$ are kept constant while $R_0$ and $\rho_0$ change.

The maximum length scale at which shaking affects $D_f$ is $\sim 40 (80 R_0^*)$ as could be measured from the simulation below $\phi_{0,c}$. These show the formation of a new primary scatterer, the decrease in $D_f$ for length scales smaller than 40 and the remaining fractal region of the starting aggregate.

The simulations presented here, when repeated in three dimensions, will make possible the comparison with experimental scattering data of aging silica systems under mild conditions. Other experimentally observed effects such as shrinking (sintering) and pH dependence of aggregation and aging processes should be allowed for in the simulations to study their effect on the fractal properties of the gels. Finally, application of bond-breaking and solvent effects ("Ostwald ripening") should be studied to explain the aging effects found in experimental systems as a functions of reaction conditions.

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