Editors’ Note

Computational chemistry is expanding in several new directions, as witnessed by numerous articles published in specialized journals. One such direction is the simulation of colloids and macromolecules aggregate formation, a field which is important in the rationalization of environmental and chemical industrial processes. To given to the readers of Chimia a flavour of the role played by computational chemistry in this new area, we found it useful and timely to publish in our Column the following review paper which has been authored by specialists of this field.

Computer Simulations of Colloids and Macromolecules Aggregate Formation

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Abstract. Understanding colloidal aggregate structures and formation is one of the central issues of colloid science and a very important topic in many industrial, biological, and environmental processes. The aim of this paper is to review and to describe the basic computational aggregation models of colloidal particles and macromolecules, and their developments. The scaling and fractal concepts allowing a quantitative description of the aggregate structure are introduced. The influence of aggregation mechanism on the structure of the resulting aggregates is also discussed. Because of the complexity of these mechanisms, computer simulations combined to experimental verifications is a powerful tool to investigate and understand aggregation processes in many applications.

1. Introduction

Aggregation is a physical process in which initially dispersed basic units (macromolecules or solid particles) stick together, under the action of various attractive forces, to build characteristic structures whose size increases with time. Aggregation phenomena are of great importance in many areas such as biological, medical, environmental, and chemical industrial processes. In natural waters and waste water treatment plants, the transport and fate of both nutrients and toxic compounds largely depend on their interactions with particles, colloids, biopolymers, and their aggregates. The transport and elimination of vital or detrimental compounds will then depend upon the kinetic of formation, the structure, and sedimentation rate of these aggregates. However, because of the complexity and the large number of factors influencing these processes, no rigorous analytical theory can be derived. Computer simulations are then useful because they provide a valuable bridge between theoretical concepts and experimental results, and they allow studying systematically the role of the various physicochemical factors.

Due to the development of powerful computers and to the introduction of scaling concepts, the techniques of computer simulation have been applied since only relatively recently to the investigation of the statistical mechanics of colloidal suspensions. They have proved to be an important tool for the systematic investigation of some of the physicochemical factors influencing the morphology of colloid...
eral structures induced by perikinetic ag-
gregation (e.g. bridging flocculation by
polymers, salt induced coagulation, ag-
glutination, etc.) and field-induced aggrega-
tion which occur, for instance, in sedi-
mentation, filtration, or cathodic depositi-

2. Basic Computational Aggregation Models

The first theoretical work dealing with
aggregation phenomena was introduced
by Smoluchowski in 1916 [1], while one of
the first computational and simple kinetic
model of diffusion limited aggregation
was proposed by Witten and Sanders [2] in
1981 to interpret experiments on smoke
aggregation. This model has been the sub-
ject of a large number of topological in-
vestigations and has found applications in
growth processes governed by Laplace
equations such as electrical breakdowns
or electrodeposition processes, in viscous
fingering often observed at the interface of
two miscible liquids, and in some biolog-
ical growth patterns.

In this model, an aggregate is built in
an infinitely dilute system by addition of
single particles to a growing germ (Fig. 1).
Single particles are introduced success-
vively at random on a circle centred on the
germs, and are submitted to random walks
simulating Brownian motion inside the
circle. If during its random walk, a particle
reaches a site nearest neighbour to the
germs, it sticks to it. This operation is
iterated till the desired aggregate particle
number or aggregate size is reached. With
time, more and more moving particles are
bound to the growing aggregate, leading
to the formation of a typical dendritic
design such as the one presented on
Fig. 1.

It is worthwhile to note that the last arrived
particles are preferentially bound on the
arm tips, rather than inside the structure,
thus leading to the formation of a typical
open structure. The Witten and Sanders
model had a large impact in colloid sci-
ence, as it was the first random aggrega-
tion simulation model able to form a frac-
tal aggregate constituting a starting point
for the development and study of fractal
concepts.

Although a large number of appli-
cations of interest have been found, such a
model has a number of limitations for the
study of real aggregation processes. In-
deed, in the Witten and Sanders model, a
symmetrical situation is imposed where
small individual particles are bound to a
unique motionless aggregate while, in real
systems, the aggregates themselves can

Fig. 1. Two-dimensional off lattice simulation of a Witten-Sanders aggregate containing 2000
particles. The different shades of gray indicate the arrival time of particles.

Fig. 2. Two-dimensional off lattice simulation of a cluster-cluster aggregate (CCA), containing 1000
particles. The different shades of gray indicate the small clusters which have been aggregated into
the final cluster.
diffuse and stick each other to form growing clusters.

In 1983, Jullien and Meakin [3][4] have introduced the cluster-cluster aggregation model (CCA; Fig. 2). At the initial stage, elementary particles are randomly distributed in a cell. Then particles are randomly chosen and moved in all directions in space in order to mimic Brownian motion. When two particles come into a neighbouring position, they irreversibly stick together and form a new aggregate which is also able to diffuse with a diffusion coefficient characteristic of its size. With time, aggregates are formed and irreversibly stick to each other to form larger structures. The iterations are stopped when only one single aggregate remains in the simulation cell. The walls of the cell are characterised by periodic boundary conditions, which assume that individual particles as well as aggregates are allowed to leave the simulation cell and reenter through the opposite wall following exactly the same trajectory. In this way, simulations of only a few hundred particles can be made to mimic macroscopic systems with a much larger number of particles. Fig. 2 shows a typical two dimensional 'CCA' aggregate composed of 1000 particles. The important structural differences between the 'symmetrical' Witten and Sanders aggregate and the 'asymmetrical' CCA cluster must be noted. A key result of the CCA model was the demonstration that the aggregate geometry can be described by using fractal geometry concepts, as discussed below.

3. Fractal Geometry Concepts

The concept of fractal has been introduced in the seventies by the mathematician Benoît Mandelbrot [5]. His approach, essentially based on geometry, became very quickly popular and is now successfully used in many areas of science for the description of apparently very complicated geometrical structures. Full lines, surfaces and volumes have integer linear dimensions of 1, 2, and 3, respectively. Open, complicated structures may have fractal dimensions (between 1 and 2 for surfaces, and between 2 and 3 for volumes). The fractal dimension is then a quantitative measure of the more or less rugose (or open) aspect of the structure of interest. Fractal structures can be divided in two groups: regulars and irregulars. They all exhibit a remarkable property, the self-similarity or invariance against changes in scale or size, which is an attribute of many natural phenomena. Self-similarity means that if we enlarge a given portion of a fractal object, the new enlarged object is identical with the initial one. Regular fractal objects exhibit a regular shape with well defined angles between branches as illustrated on Fig. 3a. They are built with deterministic and iterative rules. Irregular fractals for which some randomness occurred during their growing process are more representative of real aggregation processes. In that case, the self-similarity property is valid on average. The new picture obtained after enlarging a part of an irregular fractal is only statistically equivalent to the original form as presented on Fig. 3b.

The fractal character of Witten and Sanders or CCA aggregates [6] is demonstrated by the power law behaviour of their mass repartition in space. It may be expressed for a space with 2 or 3 dimensions. If we measure the mass contained in a sphere of radius $r$ centred at a given point of an irregular fractal aggregate, the following scaling law is found:

$$ m(r) = r^{D_f} $$

where $D_f$ represents the aggregate fractal or Hausdorff dimension.

The fractal dimension gives a very simple quantitative description of the spatial mass repartition within the aggregates, a higher fractal dimension being representative of more compact structures. In the Table are presented the fractal dimensions for both simulated and 'natural' aggregates.

The study of the influence of aggregation mechanism on the structure of the resulting clusters has become one of the

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**Table. Aggregates Mass Fractal Dimension**

| Space Dimension | Simulated Aggregates | Natural Aggregates |
|-----------------|----------------------|--------------------|
| Witten-Sanders  | 1.70 2.50            |                    |
| CCA aggregates  | 1.44 1.78            |                    |
| CCA aggregates  | 1.55 2.09            |                    |

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![Fig. 3a. Illustration of the self-similarity property of fractal aggregates. Top: shows a regular fractal aggregate. When the central (grey) part of the aggregate is enlarged (as displayed on the right) the same figure is obtained as the original one. Bottom: shows an irregular (disordered) fractal, with some randomness included in its growth. The self-similarity property now is only valid on average.](image-url)
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above considerations also show that two
limiting kinetic processes can be discrim-
inated: a diffusion limited aggregation
process (DLA) with \( P_0 = 1 \), and a reaction
limited aggregation process (RLA) when
the chemical reactivity at surfaces con-
trols the overall sticking probability with
\( P_0 < 1 \).

In order to simulate the aggregation
process of two clusters, formed of parti-
cles for which \( P_0 < 1 \), the probability \( P_j(\sigma) \)
of cluster-cluster aggregation must be re-
calculated based on cluster sizes. The pro-
bability \( P_j(\sigma) \) that a cluster of size \( i \) is
permanently bound to a cluster of size \( j \)
into a new cluster of size \( i+j \) is assumed to
be given by [7]:

### 4. RLA and DLA Concepts

If only the attractive \textit{van der Waals}
forces were operating on suspended par-
ticles in water, we might expect all suspend-
ed particles to stick together immediately
and coagulate. However, particles sus-
pended in water or in liquid of high dielec-
tric constant are usually charged for sev-
eral reasons such as the ionization or disso-
ciation of surface groups or the adsorption of
ions from solution onto the previously
uncharged particle surface. The particles
thus also undergo repulsive electrostatic
forces often originating in chemical reac-
tions occurring at the particle-solution
interface. Particle aggregation occurs when
the attractive \textit{van der Waals} forces exceed
the repulsive electrostatic ones (Fig. 4).
The DLVO theory [11] (Derjaguin, Land-
au, Verwey, and Overbeek) has established
the potential energy-distance relationship
between two particles as a function of the
characteristics of both the particles and the
suspending solution. Combination of \textit{van
der Waals} and electrostatic forces results
in two minima (primary and secondary
minima; Fig. 4) where aggregates are sta-
ble. For two charged surfaces to come into
contact in a primary minimum, their surface
potential or charge must be lowered by the
cloud of electrolyte cou-
terions attracted close to the particle sur-
face. Attraction of two particles then de-
deps on electrolyte concentration. For
highly charged surfaces in dilute elec-
trolyte, there is a strong long-range repulsion
(Fig. 4, curve a). The corresponding ener-
gy barrier is too high to be overcome by
the particles, consequently they remain
totally dispersed in the solution. As a re-
result, when two particles come into a neigh-
bouring position, the sticking probability
steak to form a physical or chemical bond is
practically zero. As the surface charge
approaches zero or in more concentrated
electrolyte solutions, the interaction curve
approaches the pure \textit{van der Waals} curve;
therefore, two particles now attract strongly
and stick together irreversibly (Fig. 4,
curve c). In such a case, the sticking prob-
ability \( P_0 \) is close to one. In the situation
where the thermal motion is not sufficient
to overcome the electrostatic repulsive
barrier (which is typically of a few \( kT \)
in the case of partial screening), parti-
cles bounce on each other many times be-
fore being able to overcome the electro-
static barrier (Fig. 4, curve b), after what
they irretrievably stick together. In that
case, the sticking probability \( P_0 \) is be-
tween zero and one. The above consider-
ations have been implicitly discussed for
single particles. They are also applicable,
however, to the aggregation of two clus-
ters formed of several single particles. The
above considerations also show that two
limiting kinetic processes can be discrimi-
nated: a diffusion limited aggregation
process (DLA) and diffusion limited aggrega-
tion (DLA) processes (Table).

![Fig. 4. Calculated energy profiles of DLVO interactions as a function of the distance between particle surfaces.](image-url)

- **(a)** Surfaces repel strongly; colloidal particles remain stable.
- **(b)** Surfaces come into stable equilibrium at a secondary minimum if it is deep enough; colloids then coagulate reversibly.
- **(c)** The interaction curve approaches the pure \textit{van der Waals} curve; colloids coagulate irreversibly. Conditions used to compute the curves: Particle diameter = 1 \( \mu m \); Hamaker constant = \( 1.5 \times 10^{-18} \) ergs; Salt (NaCl) concentration = 0.001 M (curve a), 0.03 M (curves b–c); Particle surface potential = 35 mV (curve a), 35/30/25 mV (curves b) and 10 mV (curve c).
The following section reports examples obtained with two and three dimensional models simulating a bridging flocculation process in which the size of the polymer chains are much higher than that of the interacting particles [20]. The relative concentration and size of both polymer chains and particles, their conformation in solution and their sticking probability are taken into account.

Two limiting situations are presented below. In the first situation, the sticking probability between particles and chain segments is assumed to be one while it is zero in the other cases. In the second situation, the sticking probability is assumed to be one for particle-particle contact, as well as for particle-chain interactions. The influence of the formation of aggregates composed solely of particles on the overall kinetic of flocculation and aggregate structures can be deduced by comparing the two cases.

**Simulation Model**

Off-lattice simulations have been carried out in which colloidal particles and polymer chains are confined to a cubic cell with normal periodic boundary conditions allowing them to pass freely through the periodic walls. The chains are represented by a succession of several jointed spherical segments, like a pearl necklace. The relative sizes of chains and particles are
controlled by adjusting the diameter of the colloidal particles and the length of the polymer chains through the number and size of the segments. In order to take into account a wide range of chain structural configurations, from coils to rigid rods, angular constraints between the connected segments are imposed, based on the segment excluded volume concept [15]. The size of the excluded volume can be adjusted by varying the diameters of the hard spheres representing the monomers units of the chain with respect to a constant bond length.

The aggregate number evolution is computed using the CCA model: particles, chains, as well as aggregates are allowed to move in space according to their respective diffusion coefficient recomputed at each step from their size and conformation. The Brownian diffusional motion of the particles, chains, and clusters is represented by random walks, the number of steps of these walks during one unit of relative time being proportional to the diffusion coefficients of the moving entities. The link between the relative and physical times is made by correlating the mean displacement of a reference particle or cluster and their diffusion coefficients.

**Bridging Flocculation without Homocoagulation**

Evolution curves of colloid, polymer and aggregate numbers are presented in Fig. 5 for a three-dimensional simulation comprising 100 stiff polymer chains and 100 colloidal particles. Such a concentration ratio induces a fast and complete destabilisation process (good conditions of flocculation). Three distinct successive stages of cluster growth are displayed. In the first mode (region A) aggregates (referred to as type II), consisting of a single chain associated with one or more colloidal particles, are formed rapidly due to the high diffusion coefficient of the free particles and to the high specific surface area of the chains.

In the second mode of cluster growth (region B), aggregates of type II collide with each other or with naked chains to form, via particle bridges, large structures of more than one chain, denoted by type III clusters. Type III clusters associate to form larger aggregates and adsorb the few remaining naked chains. For longer time scales, in the third mode (region C) the number of type III aggregates declines. Finally, type III clusters combine to form one single aggregate which is observed at the end of the calculations. This situation arises owing to the assumption made that the system is closed, i.e., no particles or chains are added to the cell during a simulation run (in experimental conditions this would correspond to a batch experiment).

Simulations demonstrate that aggregation kinetics is strongly dependent on the particle/chain concentration ratio (Fig. 6). At low particle/chain concentration ratio (Fig. 6a), the number of naked chains and of type II and III aggregates does not decrease to zero but reaches a plateau or pseudo plateau value. Such a behaviour is due to the lack of colloidal particles required for linking polymer segments. After a long period of time, the system seems to be frozen; there are no remaining free particles but many naked chains, type II and a few type III aggregates. On the other hand, at a high particle/chain concentration ratio, the polymers are quickly saturated with particles. The system becomes frozen mostly with aggregates of type II, and free particles (Fig. 6b). The rate of saturation is also found to be dependent on the initial particle concentration; a very high initial particle concentration leads to the formation of only type II aggregate, whereas at lower particle concentration, chain saturation is slow enough to allow type III aggregates to be formed. Consequently, the optimal conditions for bridging flocculation are reached for intermediate concentration ratios [20].

Simulation runs using more collapsed chains reveal the formation of more compact clusters. The analysis of the evolution curves shows that the optimal conditions for bridging flocculation are then reached for a lower particle/polymer ratio. This behaviour is due to the fact that the number of particle adsorption sites is lower on
collapsed chains. As a result, a non-negligible fraction of segments into the polymer coil is inaccessible for the particles thus increasing the apparent concentration of the free particles.

**Bridging Flocculation in Presence of Homocoagulation**

When simulations allow the simultaneous formation of aggregates composed both of i) particles and macromolecules and ii) particles only (also referred to as type I aggregates), a different destabilisation process occurs which plays an increasingly important role with increasing the initial particle concentration (Fig. 7).

At low particle concentration (Fig. 7a), the aggregate number evolution curves are similar to those observed without considering homocoagulation and the time scale of the three modes of cluster growth is not change. In such concentration conditions, a small number of aggregates is rapidly formed and associated to the naked chains. Although a small fraction of free particles is involved in the formation of aggregates of type I, particles are preferentially bound to the chains due to their larger specific surface area to form aggregates of type II. A real bridging flocculation occurs, where particles as well as small aggregates act as bridging entities for macromolecules.

At high particle concentration (Fig. 7b), the overall kinetic of coagulation is enhanced by homocoagulation of particles. Large type I aggregates are rapidly formed with a mean size equal to those of the chains and consequently with a similar diffusion coefficient. As a result, both type I and type II aggregates are simultaneously present in the cell. The elementary particles initially adsorbed to the naked chains do not participate significantly to the bridging mechanism of chains. These are essentially bound to each other by type I aggregates. From a structural point of view, several morphological differences can be noticed compared to those observed in the previous situation where the formation of type I aggregates was not allowed. As shown on Fig. 7, bridging flocculation in presence of homocoagulation leads to the formation of quite inhomogeneous structures where particles are preferentially concentrated in 'bridging blobs'.

**6. Examples of Applications of Computer Simulations of Aggregation Processes**

This section gives a few examples showing that computational investigations of aggregation phenomena may greatly assist industrial or medical developments as well as environmental protection by its ability to predict performance before embarking on costly and time-consuming manufacture.

**6.1. Applications to Environmental Protection**

Contaminants introduced in air or water by human activities (such as trace metals or pesticides) often adsorb on suspended particles, and settle down after the coagulation of the latter [16]. In freshwater, two types of colloidal compounds play a predominant role on contaminant circulation: the soil derived inorganic submicron particles and the biogenic organic macromolecules released by organisms. Due to their high adsorbing capacity (small size and large specific surface area), they adsorb most of the contaminants. Even though they do not settle down individually, they can do it after aggregation. Thus, aggregation of particles by organic macromolecules is a key phenomenon which controls the fate and circulation of contaminants in natural waters and must be understood to evaluate long-term impacts of human activities on ecosystems. An analogy exists with the elimination of trace contaminants in the flocculation step of water treatment. Transmission electron microscopic observations using high contrast conditions have revealed that bridging flocculation of small colloidal parti-

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**Fig. 7. Effect of the particles/chains concentration ratio on the bridging flocculation when aggregates of type I can be formed (sticking probability = 1 for both particle-particle and particle-polymer interactions).**

- **Fig. 7a:** Snapshot of a simulation using 25 chains and 100 particles; only a small fraction of free particles is involved in the formation of aggregates of type I. Thus individual particles act as main ligands for the chains.
- **Fig. 7b:** Snapshot of a simulation using 25 chains and 1000 particles. Large type I aggregates are formed with a mean size similar to those of the chains. They may then act as ligands for the chains. In this case, the kinetic of destabilisation and the size of aggregates are greatly enhanced by the high particle concentration and the presence of type I aggregates.
icles by large polymer chains is important both in natural water and water treatment [17][20]. Simulations such as those of Sect. 5.2 thus find important application in environmental protection and management.

6.2. Biomedical Analysis

Immunoassays in medical analysis has become a daily and essential tool of medical science for diagnosis and prevention. Polystyrene latex particles are used today as carriers for antigen and antibody reaction in agglutination tests where the presence of a visible agglomerate shows the presence of a specific cross-linking antigen in a human serum sample. The antibody-coated latex suspended in a buffer solution is aggregated by the antigen which creates a bond between two particles. If a human serum sample does not contain the searched antigen, no agglutination occurs and the colloidal latex suspension remains homogenous. In this reaction, antigen concentration strongly influences the kinetics and mode of aggregation process. The reliability of an agglutination test is then questionable. By comparing experimental agglutination studies with results obtained from computer simulation (by adjusting the $\sigma$ and $\gamma$ values) [18], the aggregation structure and kinetics can be deduced in a wide range of conditions. The results show that although aggregation mechanisms vary with antigen concentration, the aggregate average sizes are of the same order of magnitude at the end of the agglutination process, thus making the test applicable in a wide range of conditions. Computer simulations here allow to precise the limits of these conditions.

6.3. Understanding Powder Disaggregation in Liquid Medium: Fragmentation Processes of Aggregated Colloids

Fragmentation phenomena are encountered in a wide range of applications in industrial processes. For practical and economical reasons, most of materials such as washing powders, dyes in paintings, herbicides in agriculture, food, etc. are available in the form of solid powders which are generally agglomerated together; often before they can be used for the desired purpose, they are mixed with a liquid to dissolve them or make stable suspensions. In material processing, powder disaggregation is then very important. It may be induced by various external forces like shocks and stresses, hydrodynamic forces or forces originating from changes in the chemical potential of colloidal aggregates. When agglomerates of dry powder are immersed in water, hydration of solid-liquid interface contribute to increase the interparticle separation distance. In addition, for electrically charged powder, the formation of an ionic cloud and the presence of the ionic diffuse layer at the solid-liquid interface also produce strong repulsive forces between the particles. The quantitative impact of these forces on fragmentation, however, can only be predicted by computer simulation. A number of models [19] have been developed for that purpose which will not be described here in details.

7. Some Implementation Details

For particle coagulation and bridging flocculation studies (Sect. 5), 'home-made' off-lattice cluster-cluster aggregation programs are used. The executable program file sizes are approximately equal to 50 kbytes. It should be noted, however, that the simulations reported here are extremely CPU demanding, especially when making large scale simulations involving small sticking probabilities (e.g. using 5000 particles with $P_0 = 0.01$ and $\sigma = 0$, particle aggregation requires more than 20 h of CPU time on a DEC 3000-900S). The cluster size distributions are continuously monitored and stored as well as the colloid positions allowing further structural analysis (fractal dimension and space correlation function determination). In addition, movies are created using for the SGI moviemaker tool, permitting thus a direct visualisation (and control) of aggregation processes.

8. Conclusion

Both computational and experimental investigations of aggregation phenomena has vastly progressed over the last years mainly due to the progress in computational physical chemistry and to the development of new powerful concepts such as fractal dimensions and scaling laws. These have allowed quantitative analysis of the aggregate structure and the study of kinetic processes. In addition, close links between simulations and experimental observations have provided a new means to get an insight on the physicochemical processes both in colloid science and engineering by making a direct comparison with experiments possible. Today, this type of 'computer experiments' have become a new research tool in science.

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Glossary

Cluster: synonymous to aggregate
Colloidal particle: particle ≤1 um
Chain: linear polymer chain
CCA: Cluster-Cluster
RLA: Aggregation model
Dla: Reaction Limited
Type I:
aggregates composed solely of particles
aggregates composed of one chain with one or more particles
aggregates composed of more than one chains and particles

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