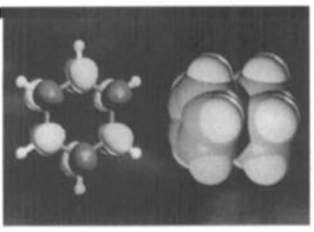
COMPUTATIONAL CHEMISTRY COLUMN



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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.

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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 colloi-

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dal structures induced by perikinetic aggregation (*e.g.* bridging flocculation by polymers, salt induced coagulation, agglutination, *etc.*) and field-induced aggregation which occur, for instance, in sedimentation, filtration, or cathodic deposition.

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 subject of a large number of topological investigations 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 biological 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 successively at random on a circle centred on the germ, 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 germ, 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 dendridic 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 science, as it was the first random aggregation simulation model able to form a fractal aggregate constituting a starting point for the development and study of fractal concepts.

Although a large number of applications of interest have been found, such a model has a number of limitations for the study of real aggregation processes. Indeed, 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

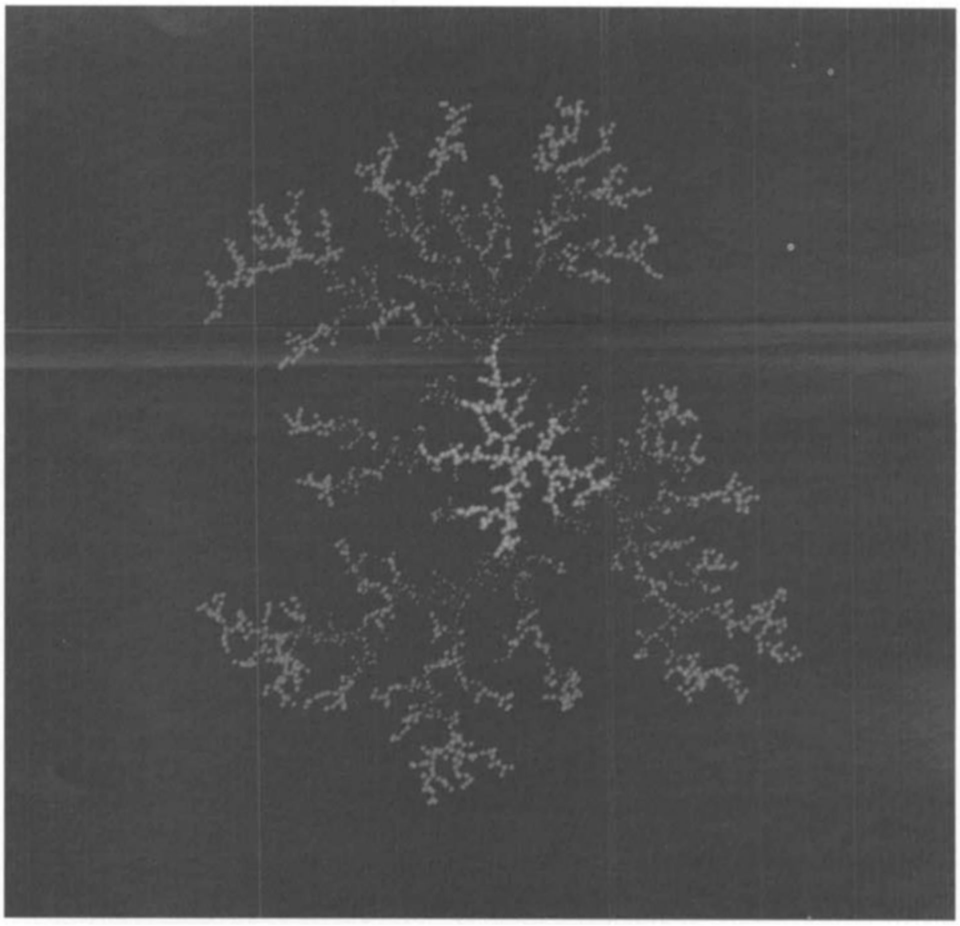


Fig. 1. *Two-dimensional off lattice simulation of a* Witten-Sanders *aggregate containing 2000 particles.* The different shades of gray indicate the arrival time of particles.

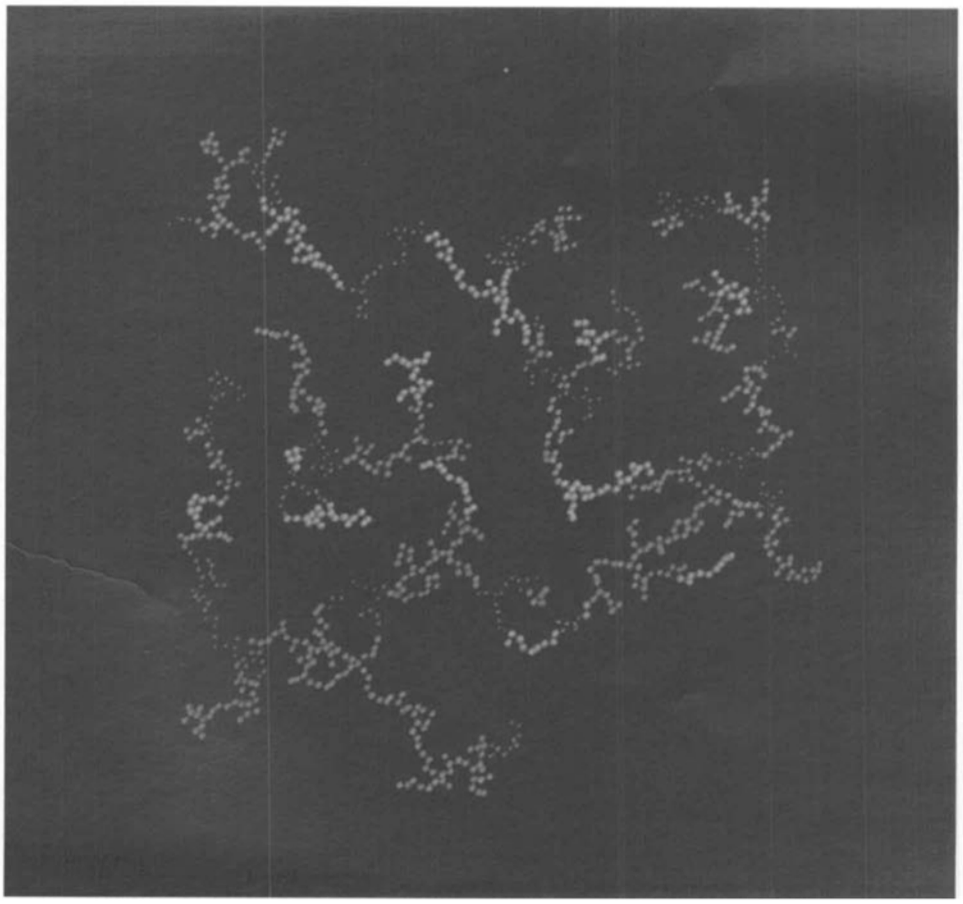


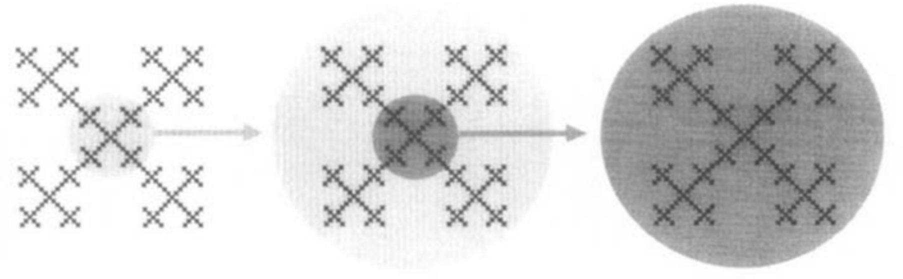
Fig. 2. *Two-dimensional off lattice simulation of a cluster-cluster aggregate (CCA), containing 1000 particles.* The different shades of gray indicate the small clusters which have been aggregated into the final cluster.

diffuse and stick each other to form growing clusters.

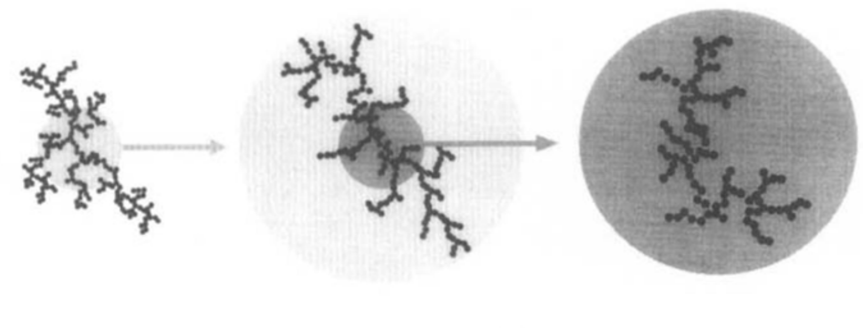
In 1983, *Jullien* and *Meakin* [3][4] have introduced the cluster-cluster aggregation model (CCA; *Fig. 2*). At the initial stage, elementary particles are randomly distributed in a cell. Then particles are randomly chosen and moved in all directions in space in order to mimic *Brownian* motion. When 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 *Benoit 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*.



a) Regular Fractal Object



b) Irregular Fractal Object

Fig. 3. *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.

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 m contained in a sphere of radius r centred at a given point of an irregular fractal aggregate, the following scaling law is found:

$$m(r) \approx r^{D_f}$$

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

Table. *Aggregates Mass Fractal Dimension*

Space Dimension	2	3
Simulated Aggregates [7][8]		
Witten-Sanders aggregates	1.70	2.50
CCA aggregates (DLA)	1.44	1.78
CCA aggregates (RLA)	1.55	2.09
Biological Aggregates [9]		
Estuarine Marine snow	–	1.78
Oceanic Marine snow	–	2.14
Inorganic Aggregates [10]		
Gold colloids (DLA)	–	1.86
Gold colloids (RLA)	–	2.14

major field of investigation in colloidal chemistry. Using a CCA model, simulations have shown that the fractal dimension value depends on whether the aggregation process is controlled by the diffusion rate of the clusters and single particles or by their chemical reactivity at the collision time. This result is in agreement with experimental work on aerosols and colloids, and has led to a new classification of aggregation processes: the reaction limited (RLA) and diffusion limited aggregation (DLA) processes (*Table*).

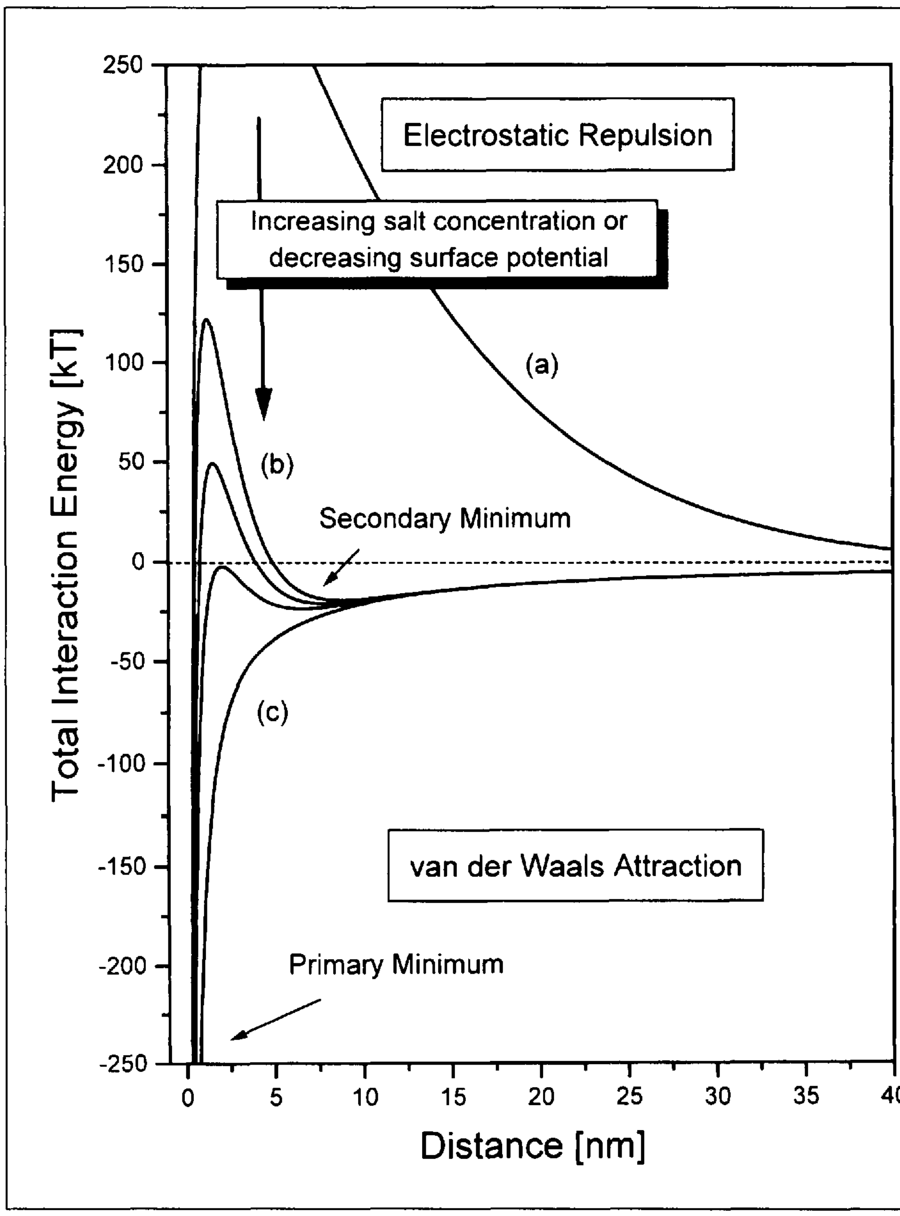


Fig. 4. *Calculated energy profiles of DLVO interactions as a function of the distance between particle surfaces. a*) Surfaces repel strongly; colloidal particles remain stable. *b*) Surfaces come into stable equilibrium at a secondary minimum if it is deep enough; colloids then coagulate reversibly. *c*) The interaction curve approaches the pure *van der Waals* curve; colloids coagulate irreversibly. Conditions used to compute the curves: Particle diameter = 1 µm; Hamaker constant = 1.5×10^{-13} 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*).

4. RLA and DLA Concepts

If only the attractive *van der Waals* forces were operating on suspended particles in water, we might expect all suspended particles to stick together immediately and coagulate. However, particles suspended in water or in liquid of high dielectric constant are usually charged for several reasons such as the ionization or dissociation 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 reactions occurring at the particle-solution interface. Particle aggregation occurs when the attractive *van der Waals* forces exceed the repulsive electrostatic ones (*Fig. 4*). The DLVO theory [11] (*Derjaguin, Landau, 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 *van der Waals* and electrostatic forces results in two minima (primary and secondary minima; *Fig. 4*) where aggregates are stable. For two charged surfaces to come into adhesive contact in a primary minimum, their surface potential or charge must be lowered by the cloud of electrolyte counterions attracted close to the particle surface. Attraction of two particles then depends on electrolyte concentration. For highly charged surfaces in dilute electrolyte, there is a strong long-range repulsion (*Fig. 4*, curve a). The corresponding energy barrier is too high to be overcome by the particles, consequently they remain totally dispersed in the solution. As a result, when two particles come into a neighbouring position, the sticking probability 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 *van der Waals* curve; therefore, two particles now attract strongly and stick together irreversibly (*Fig. 4*, curve c). In such a case, the sticking probability 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), particles bounce on each other many times before being able to overcome the electrostatic barrier (*Fig. 4*, curve b), after what they irremediably stick together. In that case, the sticking probability P_0 is between zero and one. The above considerations have been implicitely discussed for single particles. They are also applicable, however, to the aggregation of two clusters formed of several single particles. The above considerations also show that two limiting kinetic processes can be discriminated: a diffusion limited aggregation process (DLA) with $P_0 = 1$, and a reaction limited aggregation process (RLA) when the chemical reactivity at surfaces controls the overall sticking probability with $P_0 < 1$.

In order to simulate the aggregation process of two clusters, formed of particles for which $P_0 < 1$, the probability $P_{ij}(\sigma)$ of cluster-cluster aggregation must be recomputed based on cluster sizes. The probability $P_{ij}(\sigma)$ 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]:

$$P_{ij}(\sigma) = P_0[ij]^{\sigma},$$

where σ is an arbitrary constant sticking coefficient exponent and $P_{ij}(\sigma) = 1$ if $P_0[ij]^{\sigma} \geq 1$. To account for the effect of size on cluster mobility, it is assumed [8] that the diffusion coefficient D_n of a cluster including n elementary particles is given by:

$$D_n(\gamma) = D_0\, n^{-\gamma},$$

where D_0 is the diffusion coefficient of the elementary particles and γ an arbitrary diffusion coefficient exponent.

Experiments as well as simulations indicate that two different types of aggregate fractal dimensions are obtained depending on the values of the sticking probability. As it approaches unity, highly tenuous structures with low fractal dimensions are formed which are representative of a DLA process. These structures can be explained by the fact that particles cannot penetrate the aggregate since they attach quickly to particles with which they collide first, *i.e.*, on the aggregate exterior. As the sticking probability approaches zero, particles may collide many times before sticking, allowing them to penetrate the aggregate and increase the aggregate density. Thus RLA results in the formation of aggregates with a higher fractal dimension.

Thus fractal scaling relationships constitute a useful and modern approach to identify, from a structural point of view, the aggregate formation mechanisms as well as the reactivity of particles composing aggregates.

5. Heterocoagulation and Bridging Flocculation

5.1. *Heterocoagulation Processes*

Almost all situations of nonequilibrium growth and aggregations (as those reported above) have been carried out under the assumption that all the elementary particles are identical (homocoagulation). However, heterocoagulation involving different constituents is a much more common situation in natural and industrial systems. Such systems are too complicated to enable the development of mathematical theories, and computer simulation based on the concepts presented in *Sect. 1–4* are necessary to understand their behaviour. Simulations relative to the coagulation of a system made up of dissimilar A and B particles have been reported [12][13] and compared to experiments. The structure and growth kinetics of clusters formed by both A and B particles having variable sticking probabilities and the influence of their relative concentrations have been studied. The aim was to determine the influence of the unsuccessful A–A and B–B collisions on the rate of A–B aggregation and to determine the optimal coagulation conditions. In practice, these models are useful for instance in the selective flocculation of minerals, where only one constituent has to be flocculated.

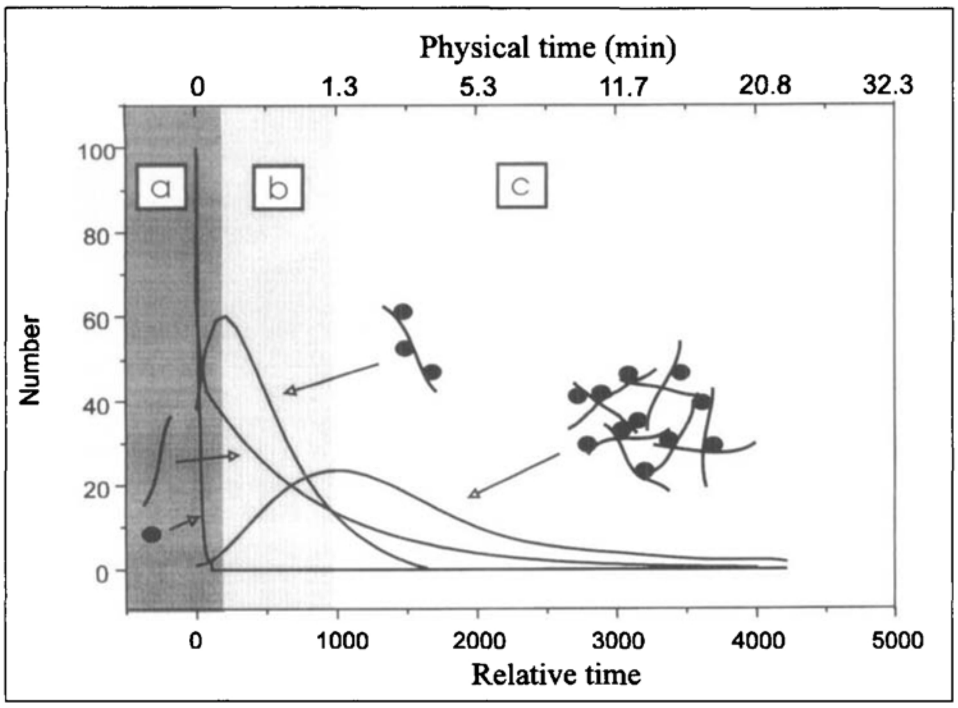


Fig. 5. *Colloid, chain and aggregate number evolutions in a system containing 100 chains of total lengths 1000 nm and 100 particles of a diameter of 60 nm.* The initial particle and macromolecule concentrations are equal to $2.7 \times 10^{15}\ l^{-1}$. After each particle, chain and cluster has been randomly moved, the relative time is increased by one unit. A link between the relative and physical times is made by correlating the mean deplacement of a reference particle or cluster in the cell to its diffusion coefficient.

5.2. Bridging Flocculation between Colloidal Particles and Macromolecules

It is known since a long time that macromolecules may serve as bridges between colloids to form flocs, but very little quantitative information is known on their structure and formation processes, although they play important roles in environmental systems [14]. The particles may not only be bridged by the macromolecules but may also facilitate the formation of larger aggregates due to the adsorption of several macromolecule segments on the same particle. This process can be seen as a case of heterocoagulation in which, in addition, macromolecule configurations and lengths plays an important role. Computer simulation is here the only possible tool allowing to make predictions on the aggregation process.

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

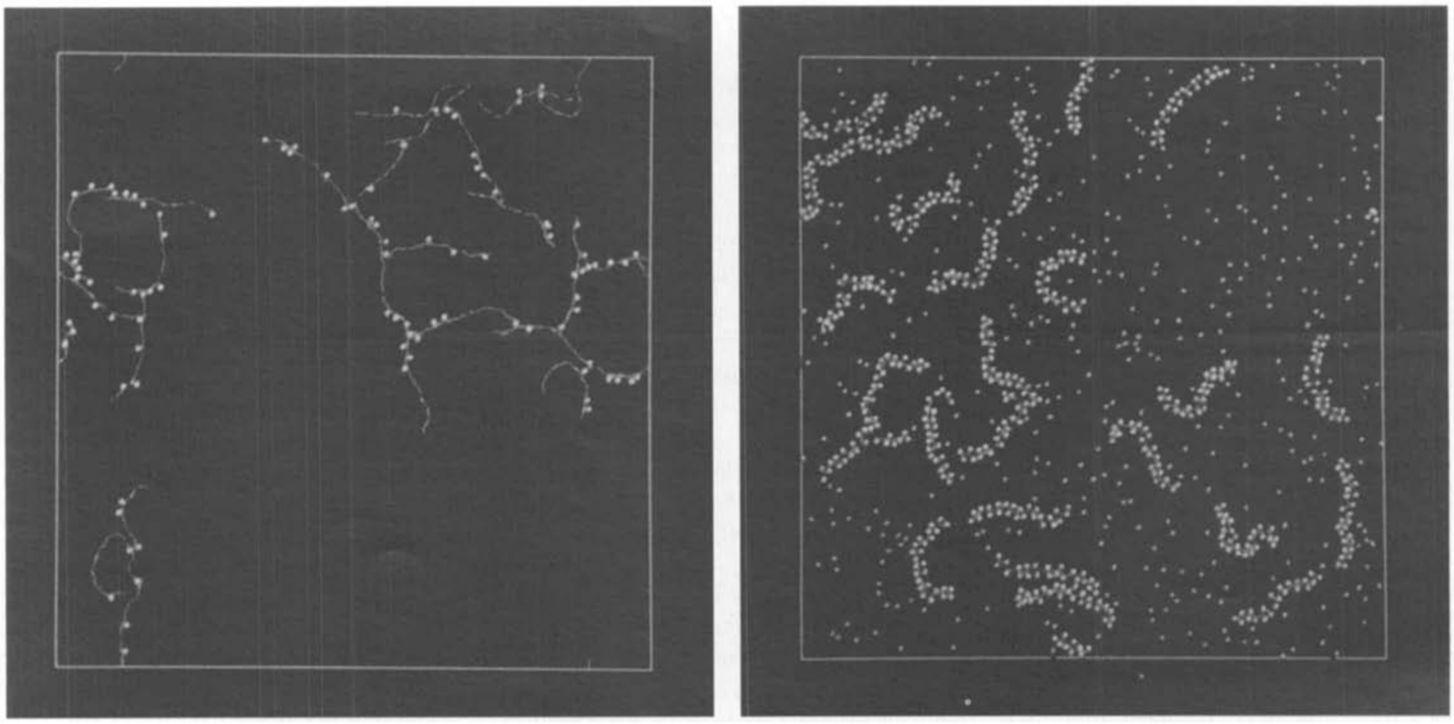


Fig. 6. *Effect of the particles/chains concentration ratio on the kinetics of bridging flocculation when no particle-particle* (type I aggregates) *are formed. Fig. 6a* presents a snapshot of a simulation using 25 chains and 100 particles. The system is destabilised; particles act as ligand for the chains. Large aggregates are present. *Fig. 6b* presents a snapshot of a two-dimensional simulation using 25 chains and 1000 particles. Chains are saturated with particles; the system becomes frozen with aggregates essentially of type II and free particles. In all cases: two dimensional simulation; sticking probability = 1 for particle-polymer and 0 for polymer-polymer and particle-particle interactions.

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 deplacement 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 I 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 inhomogenous structures where particles are preferentially concentred 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-

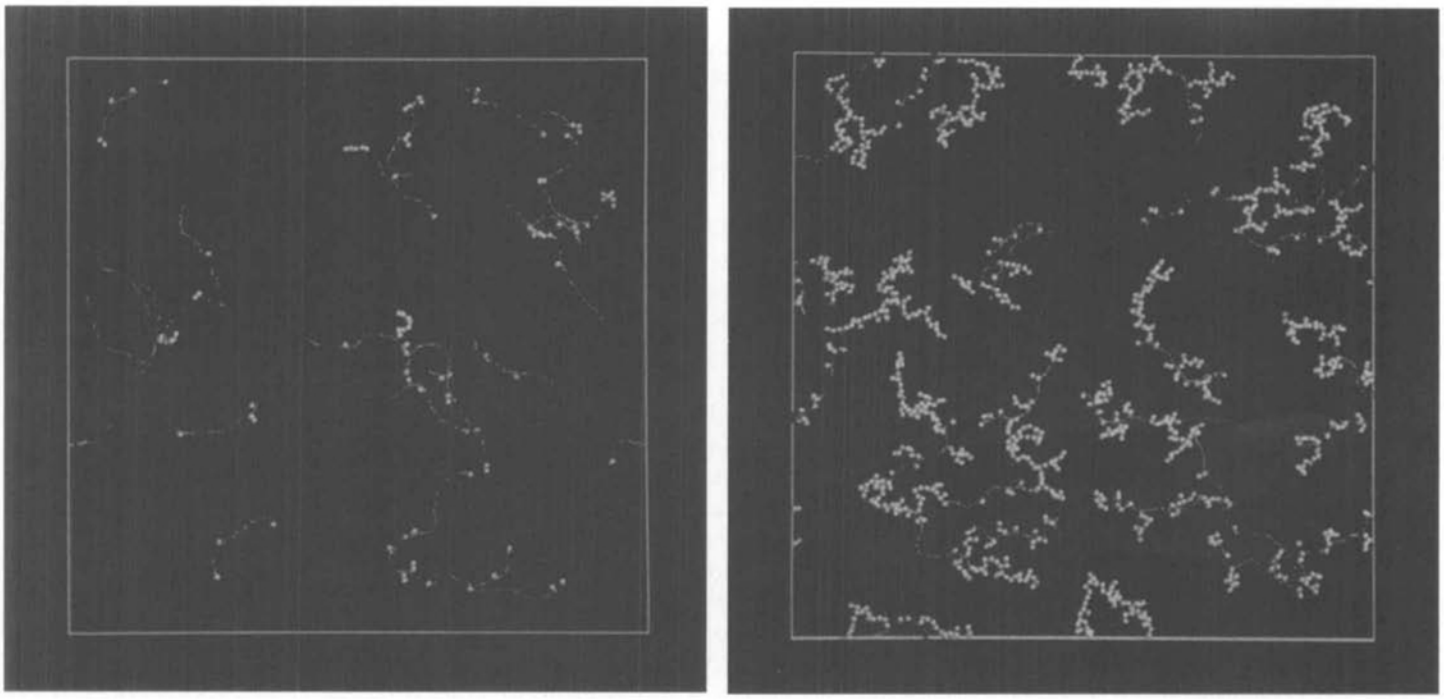


Fig. 7. *Effect of the particles/chains concentration ratio on the bridging floculation when aggregates of type I can be formed* (sticking probability = 1 for both particle-particle and particle-polymer interactions). *Fig. 7a*: snapshot of a simulation using 25 chains and 100 particles; only a small 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.

cles 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 σ and γ 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, 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 Dissaggregation 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 µm
Chain:	linear polymer chain
CCA:	Cluster-Cluster Aggregation model
RLA:	Reaction Limited Aggregation
DLA:	Diffusion Limited Aggregation
Type I:	aggregates composed solely of particles
Type II:	aggregates composed of one chain with one or more particles
Type III:	aggregates composed of more than one chains and particles

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