# Simulation of Higher Order Self-Assembly

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## Abstract

*Self-assembly of particles with certain surface properties is a topic which becomes more and more interesting in many research areas. The main problems of self-assembly of different particles are of two kinds: First, one has to find a method that determines a set of particles with certain properties so that an assembly into a desired structure is achieved. Second, once these particles are found, they have to be created as real chemical or biological components. The model proposed in this paper only considers the first problem: finding a set of particles that self-assembles into higher order structures. It uses a simple hard-sphere description of particles with circular patches on the particle surface, called binding sites. These binding sites allow the particles to attach to each other. Further the model is split into two parts of which the first one simulates the aggregate growth while the second part simulates the internal dynamics of the aggregate. The model is capable of creating a broad range of different structures, ranging in size from a few particles up to several hundreds. The paper also introduces current research, that tries to combine this model with evolution.*

## 1 Introduction

Self-assembly is the spontaneous formation of ordered matter from separated or linked components. The length scales at which self-assembly can be observed range from molecules to galaxies. Some examples of self-assembly are protein folding, formation of molecular crystals, colloids and lipid bilayers [1].

There are several reasons for the increasing interest in self-assembly: First, material science and engineers are investigating and exploring the creation of nano- and mesocale structures. But at this length scale it is not possible to use current technologies to assemble structures. Self-assembly might offer a solution to this problem. Second, self-assembly plays an important role in the cell as well as on the level of multicellular clusters and is therefore important for the understanding of the cell and life itself. Third, self-assembly also occurs in systems with length scales larger than nano, and therefore it may be a general way of assembling structures and thus interesting for material science [1–3].

Different types of self-assembly systems are known. Whitesides and Grzybowski [3] differentiate between

1. Static self-assembly: Systems at a global or local energy minimum, and in an equilibrium state. One example is a crystal.

2. Dynamic self-assembly: Systems that use free energy and only by this energy use self-assembly can take place. These systems assemble into an out-of-equilibrium state. Simple examples are reaction-diffusion systems. A more complex example of such a dynamic system is a living cell.

They further describe templated self-assembly in which the interactions with the environment are important for the structure formation. One example of templated self-assembly is crystal formation on a surface. In addition they also point out the rich variety and complexity of structures that is created by self-assembly in biological systems.

Further Whitesides and Boncheva [1] identify the five important characteristics of a self-assembling system as the components, the interactions, the adjustability of the bindings, which is crucial for the self-assembling process, the environment and the mass transport, which can be of different types on different length-scales.

Beside a classification of a self-assembly system and a description of its major characteristics, statistical properties of self-assembling systems are known. Hogg[4] outlines several of these properties. If these statistical properties are fullfilled, the self-assembly of the structure should become a robust process that creates the desired target structure with a high probability.

In order to gain a deeper understanding of self-assembly systems two paths are followed by the scientific community: First, computer experiments are conducted in which self-assembly systems are simulated. One example of such a computer simulation is the model introduced in this article, while more examples are given in [5–7]. These articles describe the creation of a conceptual framework for nanoparticle self-assembly which also has been successfully used to simulated particles that form diamond structures [7]. The second path involves experiments with chemical structures. Examples of such chemical systems and structures are given in [8, 9]. A review of chemical self-assembly techniques can be found in [10], while a review of the interplay between aggregation and crystallization in self-assembly is given in [11].

In our model, which is similar to the model proposed by Zhang, Keys, Chen, and Glotzer [7], we do not only simulate the self-assembly process, instead we also want to combine it with evolution in our future research. This combination can be used as a guide for creating particle sets that self-assemble into a certain structure.

## 2 Model

The model introduced in this paper is based on the Diffusion Limited Aggregation (DLA) model introduced by Sanders and Witten [12], extended with a mechanistic simulation to drive the system towards an equilibrium state. Each

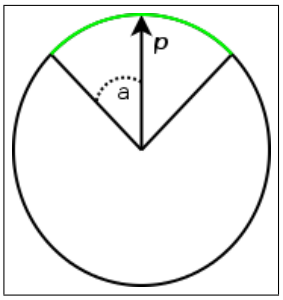


Figure 1: Schematic view of a particle with a binding site. The green area marks the surface area at which the particle can bind to other particles. $a$ is the opening angle of the binding site, and $\boldsymbol{p}$ is position vector of the binding site. The position is defined by the center point of the binding site on the particle's surface.

model step consists of two parts: first the DLA step in which new particles are attached to the aggregate and second the simulation of the internal dynamics of the aggregate. In this model, particles are not considered to be of the same type (unlike the standard DLA model), but to be of different types that are distinguished by their surface features. The different particle types get concentrations assigned at the beginning of a simulation which determine the probabilities for generating the different particle types, when they are inserted. The particles are modeled as hard spheres with a diameter $D_p$ and with circular patches on the surface, called binding sites, through which the particles can bind to each other. A binding site has three properties: the position $\boldsymbol{p}$ on the surface of a particle, the opening angle $a$, and a set of other binding sites $S$ to which it can bind. Figure 1 shows a schematic view of a particle with a binding site. Using the binding site model, two particles $i$ and $j$ can bind if the conditions given in figure 2 are fullfilled. During the DLA step, new particles attach to the aggregate which leads to a growth of the aggregate. In the second step, the internal dynamics of the aggregate is simulated. This is done by simulating the Newtonian trajectories for each particle. During this phase, binding sites can exhibit a mutual attraction force if the binding conditions 2 and 3 (shown in figure 2) and the additional condition $\lambda \geq dist(i,j) > D_p$ are fullfilled, where

$$
\begin{aligned}
dist(i,j) &= D_p && (1)\\
f(i,j) &= 1 \text{ where} && (2)\\
f(i,j) &= \begin{cases} 1 \quad \text{if} \begin{cases} (\vec{p_i} \cdot \vec{r_{ij}} \geq cos(a_i)) & \text{for some binding site } b_i \text{ on particle i} \\ & \text{with type } t_i \text{ where } \vec{r_{ij}} = \vec{P_j} - \vec{P_i} \\ \text{and} & \\ (\vec{p_j} \cdot \vec{r_{ji}} \geq cos(a_j)) & \text{for some binding site } b_j \text{ on particle j} \\ & \text{with type } t_j \text{ where } \vec{r_{ji}} = \vec{P_i} - \vec{P_j} \end{cases} \\ 0 \quad \text{otherwise} \end{cases} \\
T(b_i,b_j) &= 1 \text{ where} && (3)\\
T(b_i,b_j) &= \begin{cases} 1 & \text{if } t_j \in S_i \text{ and } t_i \in S_j \\ 0 & \text{otherwise} \end{cases}
\end{aligned}
$$

Figure 2: Two particles $i$ and $j$ with position $\vec{P_i}$ and $\vec{P_j}$ and some binding sites on both particles can bind if all of the conditions are fullfilled for any pair of their binding sites. Condition 1 and 2 are similar to the ones used by Kern and Frenkel[13].

$\lambda$ determines the distance where bonds break. Further, if the necessary conditions for binding are fullfilled for an unbounded pair of particles a bond is established between the two particles. If any of the three binding conditions is violated for a bond, the bond breaks. During the dynamics simulation the bonds are represented as stiff, damped springs. Collisions between particles that do not result in new bonds are handled as momentum and energy conserving collisions. Before each step of the dynamics simulation, the velocity of each particle gets assigned a random value from a normal distribution. Also, the velocity of each particle gets periodically random contributions.

# 3 Results

In order to explore some of the possible structures, randomized simulations were executed. Particle and binding site types were created at random and then used in simulations. Each simulation had five different particle types with at most eight different binding sites, while three binding site types were created. The diffusion step was executed until ten particles had attached to the aggregate. Then the physics simulation was executed to allow for rearrangements in the cluster. The final aggregate size was 300 particles for each of the aggregates. The results show examples of different structural properties. First, some simulations were encountered in which several small instead of one big aggregate were formed. Further, cyclic bindings can be observed in most obtained structures. Examples of these structures are given in figure 3. In addition to the above described observations, the influence of the particle type concentration on the aggregate growth was examined. To study this topic, an engineered example was created. In this example only one binding site type existed with an opening angle of $20^\circ$ degrees with only itself as binding partner. In addition, two particle types were defined. The first one (type $P0$) had six binding sites. Each of them was placed in such a way, that its position vector pointed along a local coordinate frame axis in the positive or negative direction. The second particle type (type $P1$) had two binding sites. Both of these were placed on opposite positions on the particle surface. Two experiments were conducted of which the first one was about the effect of a high $P0$ concentration and a low $P1$ concentration, while the second one examined the effect of a high $P1$ and a low $P0$ concentration. The results are shown in figure 3 (d) and (e). These experiments were conducted using an older version of the model in which the internal dynamics of the aggregate were not simulated.

# 4 Discussion

The introduced model allows for conducting computer simulations of self-assembly. The first obtained results seem promising and allow us already to draw a few conclusions of this model. First of the all, the model is capable of creating structures with a wide variety of shapes and sizes. The simulation of the internal dynamics of the cluster allows for creation and destruction of bonds. We consider this to be an important feature of the self-assembling process and therefore important to include. The model also allows for the formation of cycles in the aggregate's structure, something that has not been observed in an older version of the model that did not include the internal dynamics simulation, and that is not typically observed in traditional DLA. Further, the results of the concentration experiment show that the concentrations of the different particle types can influence the growth and structure of the aggregate quite significantly. Thus, not only the design of the particle (the particle surface with its binding sites) but also the concentrations of each particle type can be used as a mean of growth control.

Current research conducted on this model is in the area of how evolution can be incorporated into the model. The approach considered in the current research is to use a genetic algorithm to evolve particle and binding site types that assemble into an aggregate with a desired form or function (also called target structure). The main point of concern is the choice of the fitness function, since several statistical features of the resulting particle type set are important for the self-assembly process as outlined by Hogg [4]. First, it is desirable that the set of particles assembles into the desired structure in most of the experiments, even if the process is disturbed by noise of various type. Some examples of disturbances are small errors in the particle properties or deviations of the environmental conditions, like concentrations of different particle types. This means that we would like the fitness function to favor the evolution towards a set of particles that results in an assembly process where most aggregates have the target structure. Hogg refers to this as "designability" while we prefer to view this as the fidelity of the self-assembly process. If one can find a set of a few particle types that by variation of concentration can lead to a variety of final aggregate structures, then we would consider that to be a set of high designability. We can in that case control the self-assembly process by simply controlling the inflow of particle types to the process. Hogg further discusses another important property that takes into account how well the aggregate can resist environmental noise after the assembly. Hogg considers the energy gap between different global structures. This energy gap can change (become smaller or larger) due to a small change in the environment or the component or particle set which may result in a shift of the lowest energy state and consequently a shift in the aggregate that is formed. He concludes that the component or particle set should be composed in such a way that the resulting target structure has a big energy gap between all other global possible structures to withstand environmental noise.

The aim of our research is to design and investigate a number of fitness criteria for self-assembly in the presented model. We expect that at least some of Hogg's suggested properties will characterize the self-assembly process if the fitness function leads to a robust process. One may also try to explicitly incorporate some of the properties as part of the fitness function. Further, two possible ways of defining a target structure are currently discussed. One way is to define certain functional properties that the aggregate should fullfill. To evaluate the aggregate under this aspect one could for example simulate the functional aspect of the aggregate in a more physically realistic simulation, e.g., dissipative particle dynamics. Another way of defining the target structure would be by giving a desired shape to which the grown aggregate's shape is compared and ranked by the degree of similarity. Future research will examine to what extent either of the ways is suitable for incorporation of evolution into the proposed model.

## Acknowledgement

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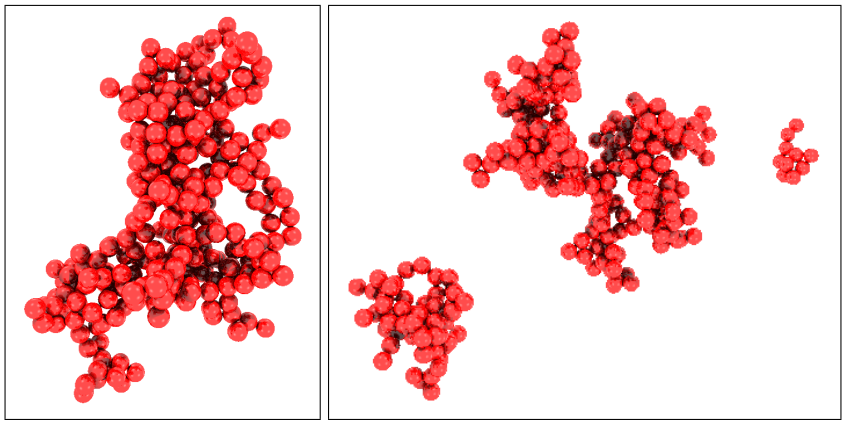
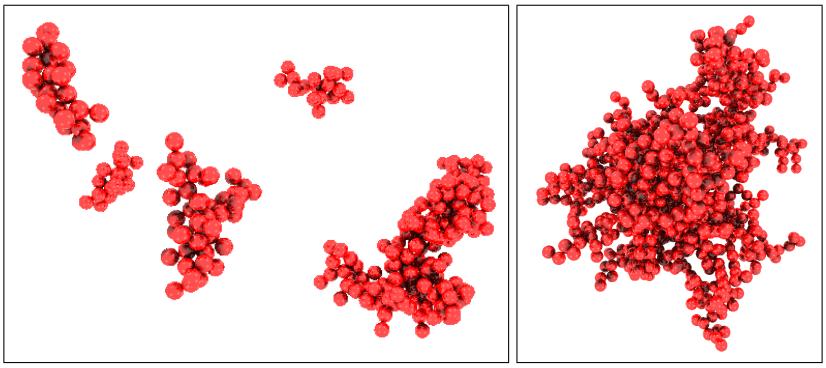
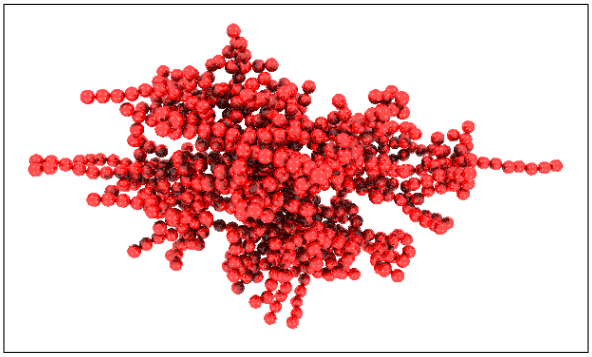


(a) (b)



(c) (d)



(e)

Figure 3: (a) - (c) show different results from the random experiments. (a) is the only simulation result that consists of only one aggregate. The results shown in (b) and (c) consist both of several aggregates of different size. One can observe loops in the structure of the aggregates in (a) (right hand side of the aggregate) and (b) (aggregate in the bottom left corner). (d) shows the result from the experiment with a high concentration of $P0$, while (e) shows the result for the experiment with a high concentration of $P1$. The aggregate in (d) has a much denser structure, while in (e) strings of particles are seen.