Study of the Structure of Fractal Aggregates:
Off-lattice Monte Carlo Simulations

S. Diez Orrite, S. Stoll and P. Schurtenberger
Analytical and Biophysical Environmental Chemistry (CABE)
Department of Inorganic, Analytical and Applied Chemistry
University of Geneva, Switzerland

E-mail: Silvia.Diez@cabe.unige.ch

Overview

Introduction

The characterisation of the structure of colloidal aggregates is strongly related to the study of the mechanism and kinetics of aggregation. In the first part of our work, an irreversible aggregation process is considered. In this case the interaction between particles is so strong that once particles (or clusters) are connected, they cannot break up due to the deep attractive well. We centre our study in the diffusion-limited cluster aggregation (DLCA) where the aggregation is limited by the time taken for the clusters (or free colloidal particles) to encounter each other by diffusion. Finally, we simulate a system in which the inter-particle interaction is relatively weak so that the system temperature is so high that the break up of aggregates is promoted. This system is described by reversible cluster-cluster aggregation.

- Irreversible aggregation process (DLCA)
  - Study of the aggregate structure over a wide range of concentrations
  - Calculation of \( R_g \) during the aggregation process, the radial distribution function and the structure factor of the final structure.

- Reversible aggregation process
  - Study of aggregate structure over a wide range of concentrations
  - Influence of the inter-particle interaction at a given particle concentration
  - Influence of the particle concentration
  - Comparison with DLCA results

Results

Irreversible process (DLCA)

- Calculations of the radius of gyration
  - Flocculation regime in very diluted systems:
    - Transition from flocculation to percolation regime in semidilute and concentrated systems.
  - Calculation of pair correlation function
    - In the cluster-aggregation process:
      - Calculations of \( R_g \) during the aggregation process, the radial distribution function and the structure factor of the final structure.

Conclusions

DLCA aggregation:

- At non-diluted conditions, the structure of the clusters cannot be described by a single fractal dimension.
- The analysis of \( S(Q) \) and \( g(r) \) shows that the definition of fractal region, and consequently the calculation of \( z \), is difficult at semidiluted and high particle concentration, the fractal dimension is almost non-existent at \( \phi > 0.1 \).

Reversible cluster-cluster aggregation:

- Our results show that the interaction between particles plays an important role in the aggregation process. Thus, the average mean square radius increases with the inter-particle interaction. However, the appearance of the fragmentation process makes that the clusters cannot grow indefinitely.
- The aggregates obtained by reversible process are more compact than DLCA ones.

Comparison with DLCA results

Non-overlap identical colloidal particles are positioned randomly in a cubic box of edge length \( L \) according to the volume fraction \( \phi \).

- The interaction between the colloidal particles is represented by a square-well potential: the well-depth goes to infinity and the well-width is given by the parameter \( \epsilon \), whose value is related with the diameter of the colloidal particle, \( d \).

- Once two particles are connected, the bond is not broken during the aggregation process (irreversible conditions). Once a single aggregate is reached, the simulation is stopped.

Simulation model

Overview

Non-overlap identical colloidal particles are positioned randomly in a cubic box of edge length \( L \) according to the volume fraction \( \phi \).

- The interaction between the colloidal particles is represented by a square-well potential: the well-depth goes to infinity and the well-width is given by the parameter \( \epsilon \), whose value is related with the diameter of the colloidal particle, \( d \).

- Once two particles are connected, the bond is not broken during the aggregation process (irreversible conditions). Once a single aggregate is reached, the simulation is stopped.

Fig. A. Temporal evolution of irreversible aggregation process at \( \phi = 0.01 \)

Reversible process:

- The procedure is divided in two parts
  - The first part corresponds to the diffusion of the colloidal particles and clusters. During this part once two clusters are connected, the bond is not broken.
  - The second part simulates the thermal motion of a particle within cluster allowing to arrange its position in the cluster or break apart from it.

1. The inter-particle interaction is given by: 
   \[ \epsilon = \begin{cases} 
   \phi d & \text{if } \phi \leq 0.11 \times 10^{-4} \\
   \phi d & \text{if } \phi > 0.11 \times 10^{-4}
   \end{cases} \]

2. The movement is accepted by metropolis rule and the process evolves until a thermal equilibrium state is reached.

Fig. B. Reversible cluster-cluster aggregation. System conditions: a. Initial DLCA cluster, b. Initial system, c. Equilibrated system.

Fig. C. The time dependence of the total energy and the maximum fraction of particles that are directly connected.

Reversible process

- Influence of the inter-particle interaction
  - Possibility to find sol-gel transition with an increase of the volume fraction

Fig. D. Initial DLCA cluster

Fig. E. Initial system

Fig. F. Equilibrated system

Fig. G. Maximum average number of particles connected to a given particle

Fig. H. Plot \( N \) vs. \( \phi \) for three different steps of the aggregation process

Fig. I. Influence of \( \phi \) on the inter-particle interaction at three different particle concentrations.

Conclusions

- The analysis of \( S(Q) \) and \( g(r) \) indicates that the definition of fractal region, and consequently the calculation of \( z \) is difficult at semidiluted and high particle concentration, the fractal dimension is almost non-existent at \( \phi > 0.1 \).

Acknowledgements

The authors express their thanks to M. Rottereau and J. C. Gimel for their encouraging discussions and to the Commission for Technology and Innovation, CTI, for financial support (Project no. 6056.2).