CHEMICAL ENGINEERING TRANSACTIONS
VOL. 60, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Luca Di Palma, Elisabetta Petrucci, Marco Stoller

ISBN978-88-95608- 50-1; **ISSN** 2283-9216
DOI: 10.3303/CET1760014

Stochastic Lattice Model of Aggregation in Heterogeneous Polydisperse Media

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The submitted paper proposes a new model algorithmic approach to describing aggregation processes, which is based on mathematical tool of a random walk over mathematical lattices. Such approach agrees as a whole with the DES paradigm. This tool allows removing the problem linked to accounting the effect of many-particles collisions, and it gives the way for describing both a diffusion-limited aggregation and the competition of different kinetic mechanisms that take place on different characteristic times, without significantly complicating the model. The paper deals with the concept of the model, and the results of the numerical experiment based on software developed by the authors have been also described.

1. Introduction

As it is well known aggregation processes play an exceptionally important role in nano-technologies (Chen et al., 2015). However, despite of long standing interest of researchers and many outstanding works, theoretical analysis of many issues remains poorly developed (Wattis, 2006). Below it is a summary of such complex issues.

A preliminary asymptotic analysis showed that the assumption of a strong predominance of the number of binary collisions over multi-particle collisions of clusters is not unconditionally correct (Brener, 2014). It was shown that the contribution of multi-particle collisions into the rate of aggregation process can be comparable with the contribution of binary collisions for dense disperse systems (Bardotti et al., 1995), especially at the initial period. Another aspect of the problem is that the dispersion density can be distributed unevenly in the volume of the apparatus (Markus et al., 2015), and during the aggregation process (Chowdhury et al., 2012), this local inhomogeneity changes in time and space (Andreassen, 2005). Therefore, the problem of stabilizing dispersion can be considered from the point of view to ensure a narrow fractional composition in the volume of the apparatus (Chowdhury et al., 2015), and from the point of view of the uniformity of the spatial distribution of fractions (Kébaili et al., 2009). The latter question is important in the processes of sedimentation of suspensions (Conway et al., 2015) and stratifying the creams and ointments (Morganti et al., 2016).

In this work the problem is considered from the standpoint of the algorithmic approach (Zeigler and Sarjoughian, 2012). The region in which the diffusion and aggregation processes take place become covered by a fixed spatial lattice, and then the change in the local distribution of the fractional composition (Gambinossi et al., 2015) of the dispersion in the cells of the obtained lattice is described. With this approach, in fact, the kinetically competing processes of diffusion, aggregation, and sedimentation in an external force field if the one exists, are described from an unified position. In the planar case the appropriate equation for the expected value $M(R_{ij})$ of the cluster order R at time unit $(n+1)$ in the cell with indices (i,j) for diffusion-limited aggregation (DLA) reads

$$M(R_{ij}^{(n+1)}) = -R_{ij}^{(n)}\left(1 - P_{ij}^{ij}\right) + \sum_k \sum_l R_{kl}^{(n)} P_{kl}^{ij} \,. \tag{1}$$

The appropriate equation for aggregation with mixed kinetics reads

Please cite this article as: Brener A., Musabekova L., Jamankarayeva M.A., 2017, Stochastic lattice model of aggregation in heterogeneous polydisperse media, Chemical Engineering Transactions, 60, 79-84 DOI: 10.3303/CET1760014

$$M(R_{ij}^{(n+1)}) = -R_{ij}^{(n)}\left(1 - P_{ij}^{ij}\right) + \sum_k \sum_l R_{kl}^{(n)} P_{kl}^{ij} \hat{P}_{kl}^{ij} \cdot \quad (2)$$

Here P_{kl}^{ij} is the probability of the cluster transfer from the cell (k,l) to the cell (i,j) for the one time unit which is chosen to be equal the characteristic aggregation time; $\hat{P}_{kl}^{ij}$ is the probability of aggregation of the clusters transferred from the cell (k,l) to the cell (i,j) during the characteristic aggregating time.

2. Description of the algorithm

To implement the above concept, the discrete-event simulation paradigm (DES) (Zeigler et al., 2000) was actually used. The algorithm was designed to establish and conduct two numerical experiments.

2.1 Diffusion-limited aggregation

The first experiment simulated aggregation in a cluster system for the case of DLA (Lin et al., 1990). Aggregation of particles occurred immediately, i.e. without any delay, after they hit the common cell (Figure 1).

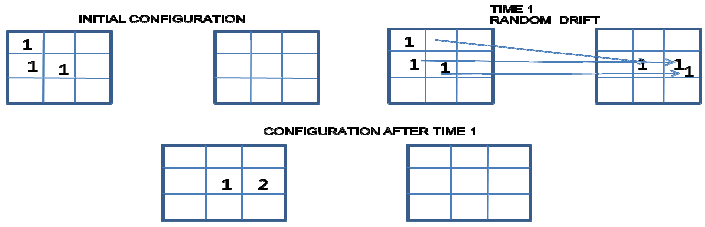


Figure 1: Scheme of the algorithm for diffusion-limited aggregation (an example).

Thus, the characteristic aggregation time was completely determined by the characteristic diffusion time of the particles (Meakin, 1983), i.e. the time of drift of particles from one cell to another. At each time unit, a random selection of the drift components of the particle in the horizontal and vertical directions was made. The choice was made from a given set of characteristic displacements. This set was formed taking into account the order of the cluster being moved, namely: the mobility of the cluster was assumed to depend on its order (Clemmer and Jarrold, 1997). For clusters of a higher order, the mobility decreased, which corresponds to the known physics of the random drift of particles both in the volume (Tammet, 1995) and in the surface layer (Wang et al., 2012). The specific critical value of the cluster order, for which the mobility decreases significantly, depends on physic-chemical characteristics of the real system. In the described numerical experiment, such a critical value was assumed to be equal to 3.

For example, if a random choice of one time displacements along a given direction for clusters of orders 1 or 2 can be made from the sequence (-3; -2; -1; 0; 1; 2; 3), then for clusters having orders higher than two and less than four, the choice can be made from the sequence (-3; -2; -2; -1; -1; 0; 0; 1; 1; 2; 2; 3). Thus, the mathematical expectation of displacement decreases. Then, the last decrease in mobility was set for clusters of the order more than 5. Of course, a physically reasonable choice of the shift of mathematical expectation should be carried out for each specific physical system after analyzing the necessary physical characteristics (Willaime et al., 2005). The behavior of clusters near the walls (Waite et al., 2001) can also be taken into account in the general case by modifying the sequence of random selection of displacements. In this experiment, it was assumed for particles trapped in the boundary cells to zero the displacements in the case of random selection, which leads outside the boundaries of the lattice under consideration.

The process of numerical experiment was organized as follows.

At the initial moment, a cluster of order 1 was placed in each cell. Then random selection of displacements for each particle was made and further aggregation of the particles was carried out as described above. Then the process was repeated at each time step by the same principle. During the calculation, two matrices were formed. The first matrix A modeled the entire lattice with particles of different orders, obtained in the process of displacements and aggregation at each time unit. The second matrix S indicated the number of collisions of particles in each cell at each time unit. The second series of experiments was performed for a more sparse matrix, i.e. at the initial moment single clusters were placed not in each cell, but in a staggered order. Thus, a dispersion with a smaller spatial density of particles was modelled. In order to simplify the debugging of the algorithm and code, a numerical experiment was performed on planar matrices.

2.2 Mixed kinetics aggregation

The second experiment simulated aggregation in a cluster system for the case of mixed kinetics aggregation (Zhou et al., 2015). In this case, the unit of the time pace was assumed to be equal to the characteristic coagulation time of clusters falling into one cell. This means that particles that fall into one cell do not necessarily have time to form a single cluster, but can continue further drift separately.
In the course of the experiment, it was assumed that the particles aggregate only if, once they hit the common cell, they again migrate to the common cell at the next time unit. In this case, the aggregation was considered as completed (Figure 2). Thus, the competition of time intervals of diffusion and the characteristic time of aggregation was modelled.
Apparently, this approach is not the only possible one. It can be also specified a fixed probability of aggregation of clusters in a common cell. But this model has not been studied in this paper.
The random choice of displacements for clusters of different orders was carried out in the same way as in the case of diffusion-limited aggregation.
The process of numerical experiment was organized as follows. At the initial moment, a cluster of order 1 was placed in each cell. In contrast to the previous case (DLA), it was now possible to find several non-aggregated clusters in one cell in different time units. Therefore, two three-dimensional arrays were formed.

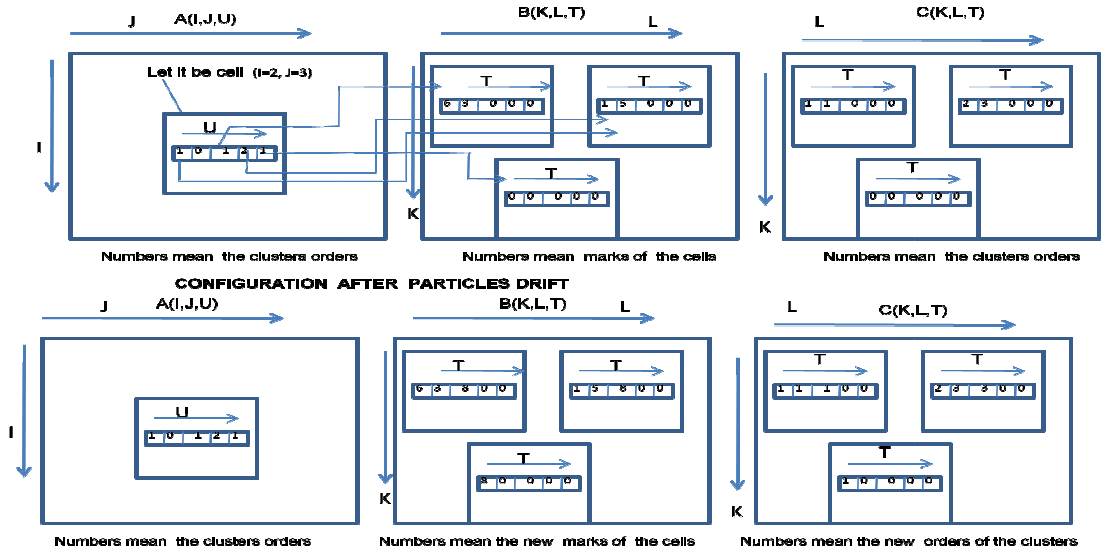
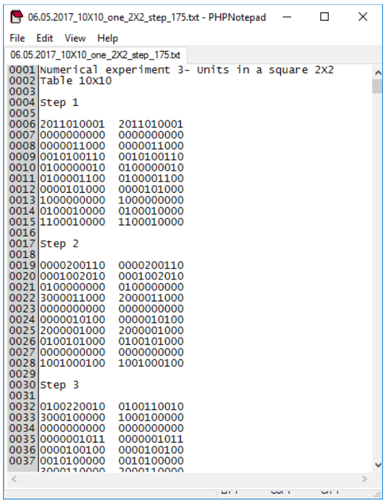


Figure 2: Scheme of the algorithm for mixed kinetics aggregation (an example).

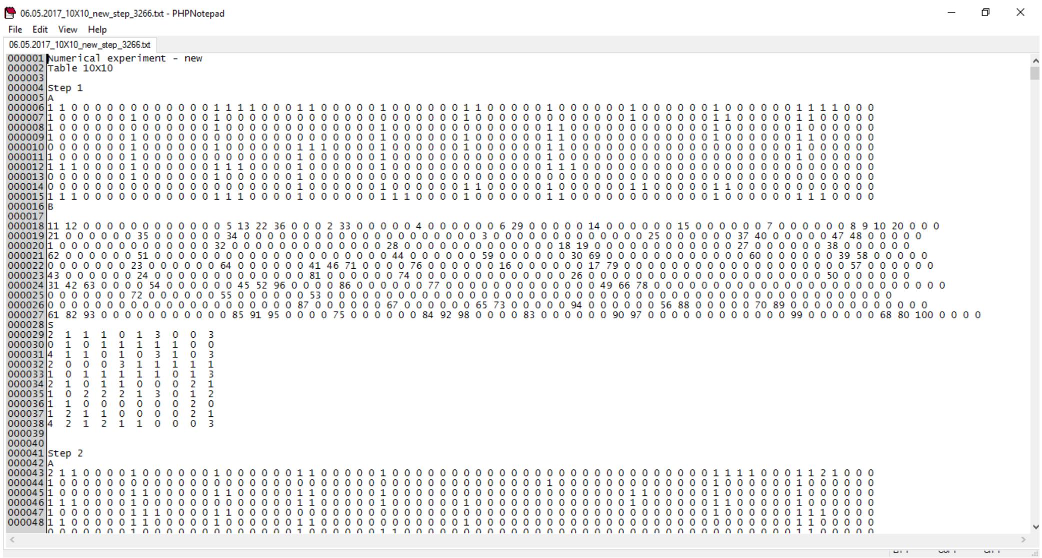
The first array A(I,J,U) served to define two cell indices (I, J), and also for assigning a number U to each cluster in the given cell. The second three-dimensional array B(I, J, M) served to identify the previous cell from which the given cluster entered the new cell. To do this, in addition to the two cell indices (I, J) into which the cluster falls on a given time interval, the third index M indicates the label of the cell ((I-1)*N+J) in which the cluster was before the start of the drift. Thus, it is possible to identify clusters with the same labels, which, according to the proposed model, should be aggregated. Clusters with different labels continue separate migration. Array C(K, L, T) is used as intermediate for organizing the code. The third two-dimensional matrix S indicated the number of collisions of particles in each cell at each time unit like the case of DLA.
Like it was done in the experiment with DLA, in the case of mixed kinetics the second series of experiments was performed for a more sparse matrix, where at the initial moment single clusters were placed not in each cell, but in a staggered order. Embarcadero Delphi 10.1 was used as a software. Embarcadero Delphi 10.1 expands developers' ability to use a single codebase to rapidly develop applications for any device.

3. Results of simulation

Numerical experiments were carried out on planar matrices of dimensions 5X5, 10X10, 20X20. Figure 3 shows some screenshots illustrating the visualization of calculations both in the case of DLA (N1) and in the case of mixed kinetics (N2). Figures 4, 5 and 6 depict some numerical results for dense matrices, where each point is averaged over ten series of calculations.



N1



N2

Figure 3: Examples of windows visualizing the results of calculations. N1- *DLA case;* N2- *mixed kinetics.*

The results of numerical experiments for both DLA and mixed kinetics have shown that the situation with more than five collisions in a common cell is unlikely. In any case, it was not observed in any series of calculations although there were no special restrictions on the number of collisions in one cell.

At the same time, it is easy to see that the total number of collisions of multiplicity greater than two cannot be considered negligible compared to the number of binary collisions, especially at the initial stage of the process. In the first three, and often four, time intervals, the ratio of the number of multiple collisions to the number of binary collisions exceeds 0.25 in practically all series of calculations for dense matrices (Figure 5). This confirms the conclusion that accounting for multiple collisions in dense disperse systems is important (Brener, 2014). Moreover, it is in the initial stage of the process that the most intensive aggregation takes place. Then the partial density of the system falls, and the rate of aggregation also drops sharply (Figure 4, 6). Comparison between the aggregation rates with DLA and mixed kinetics shows that the aggregation process with mixed kinetics, i.e. when the characteristic times of diffusion and coagulation are comparable in order, is much slower, which is quite expected (Sokolov et al., 2015). Since the phenomenon of the decay of clusters in this paper was not considered, the process in all cases ends in the formation of a single cluster. However, in the case of mixed kinetics, the gelation occurs after several thousand time units.

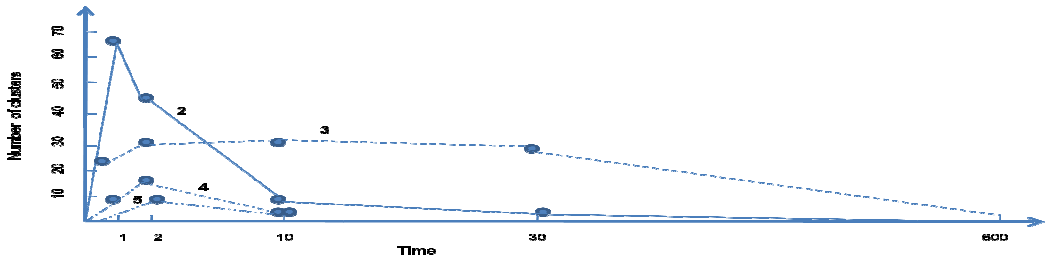


Figure 4: Time history of the numbers of clusters of different orders for DLA case (matrix 10X10). The numbers above the curves indicate the appropriate orders.

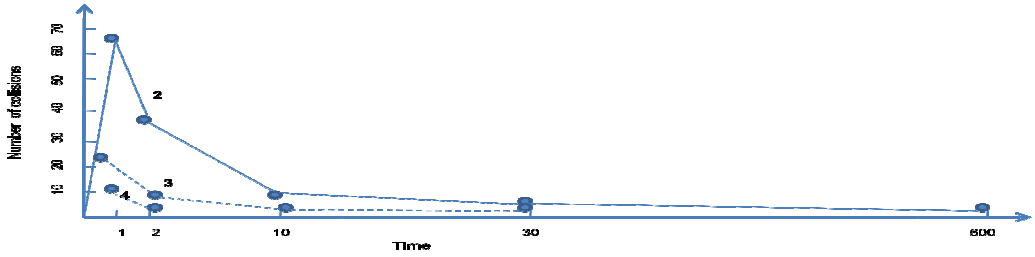


Figure 5: Time history of the numbers of collisions of different multiplicities for DLA case (matrix 10X10). The numbers above the curves indicate the appropriate multiplicities.

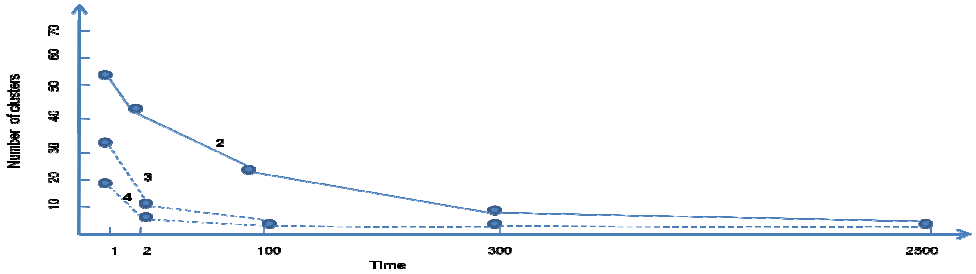


Figure 6: Time history of the numbers of clusters of different orders for mixed kinetics case (matrix 10X10). The numbers above the curves indicate the appropriate orders.

Account of the rate of decay of clusters under this model approach is also possible without a special complication in the calculation. However, even without considering the kinetics of the decay of clusters, this model can be used to estimate the time of stabilization of the fractional composition of the dispersion, since it allows calculating the period of the most intensive aggregation and estimating the average order of clusters at the end of this period.

4. Conclusions

The general conclusion from the results of the research is that an algorithmic approach based on the DES paradigm can be used quite effectively to calculating the kinetics of aggregation processes in dense disperse systems. This mathematical tool allows removing the problem linked to accounting the effect of many-particles collisions, and it gives simple way also for describing both a diffusion-limited kinetics of aggregation and the competition of different kinetic mechanisms that take place on different characteristic times, without significantly complicating the model. Simulation confirmed that the contribution of multi-particle collisions of clusters in dense disperse systems to the kinetics of aggregation is quite noticeable and can attains 25 and more percents in the early stage of the process. This effect is most noticeable in the case of DLA, but the neglect of multi-particle collisions is hardly correct also for mixed kinetics at the initial stage of aggregation at a high partial particles density.

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