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Application of the Stochastic Lattice Model for Describing Aggregation Processes in the Disperse Systems Flowing through a Tubular Reactor

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The paper deals with results of the numerical experiment conducted to study the kinetics of the aggregation process occurring in a dispersed system flowing through a tubular reactor. The model is based on the discrete-event simulation paradigm (DES). Previously, a lattice model was used to simulate the process of aggregation of a dispersed system in a periodic reactor. The main result of the given work is the development of a lattice aggregation model applicable to a flow reactor. For creating the model the mathematical apparatus of a random walk on mathematical lattices has been used. As shown in the work, this approach allows removing the problem linked to accounting the effect of many-particles collisions, and as a result it gives the way for describing both a diffusion-limited aggregation and the competition of different kinetic mechanisms taking place on different characteristic times. In this paper, the algorithm that allows taking into account the impact of fresh flow with a dispersed phase entering the flow reactor in the working volume of which aggregation takes place on the kinetic parameters of the process has been submitted.

1. Introduction

Aggregation processes play an exceptionally important role in nano-technologies, chemical and pharmaceutical engineering, metallurgy etc. (Chen et al., 2015). However, despite of long standing interest of researchers and exist of many outstanding works, theoretical analysis of many issues remains poorly developed. The first obvious problem is that a known model accounting multi-particles collisions (Krapivsky, 1991) is, so far, little effective in practical calculations, and only binary collisions are considered in most models (Wattis, 2006). However, it was also theoretically shown that multi-particles collisions can make a significant contribution to the kinetics of aggregation, especially at a high concentration of the dispersed phase and high intensity of a random fine particle drift (Brener, 2014).
Besides this, another problem is that the concentration of dispersion can be distributed unevenly in the volume of the apparatus (Markus et al., 2015), and during the aggregation process (Chowdhury et al., 2015) this local inhomogeneity changes in time and space (Andreassen, 2005).
Both these aspects, namely multi-particle collisions and spatial heterogeneity, are of great practical importance. For example, the problem of creation of stable dispersion should be considered both for ensuring a narrow fractional composition in the volume of the apparatus (Kazenova et al., 2017), and from the point of view of the uniformity of the spatial distribution of fractions (Kébaili et al., 2009). These problems are important in the processes of sedimentation of suspensions (Conway et al., 2015) and stratifying the creams and ointments (Morganti et al., 2016). At the same time, the known models (Wattis, 2006) do not give enough opportunities to take the mentioned aspects into account.
In the work (Brener et al., 2017), a new approach for describing aggregation processes in disperse systems based on the random walk model on mathematical grids (Brener et al., 1981) with using the discrete-event

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simulation paradigm (DES) (Zeigler et al., 2000) has been proposed. It was shown that the proposed approach allows for accounting the contribution of multi-particle collisions into the rate of aggregation process.
In this work, the problem is also considered from the standpoint of the algorithmic approach (Zeigler and Sarjoughian, 2012). The authors of the mentioned paper (Brener et al., 2017) were limited themselves to the case of a periodic reactor in which the average flow velocity was assumed to be zero, and only random walks of the particles were considered.
At the same time, the aggregation processes in the flow reactors can proceed under specific conditions because of impact of the fresh stream with a dispersed phase entering the flow reactor (Boer et al., 1989). It should be also considered the specific interaction between averaged flow and turbulent-Brownian drifts (Zatevakhin et al., 2015). The regularities of coagulation at these conditions have a lot of little studied features (Pnueli et al., 1991).
In this paper, the algorithm that allows taking into account the impact of fresh flow with a dispersed phase entering the flow reactor on the aggregation process in the working volume has been submitted.

2. Details of the algorithm and code

The used approach is based on the algorithm submitted in the previous work (Brener et al., 2017). The brief exposition of this algorithm will be given anew, but with adaptation to the case of flow reactor.
In according with DES, 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) in the cells of the lattice that is caused by particles drifts and aggregation processes is described. Thus, the kinetically competing processes of diffusion, aggregation, and sedimentation in an external force field if the one exists, can be described from a unified view (Brener et al., 2017).

2.1 Concept

In the case of diffusion-limited aggregation (DLA) the aggregation of clusters occurs immediately in the moment of their collisions (Meakin, 1983). In terms of the lattice model this phenomenon is interpreted as the hit of clusters in the common cell. Therefore in this case the characteristic aggregation time is determined by the characteristic diffusion time of the particles, i.e. the time of drift of particles from one cell to another. This time can be accepted as a characteristic time unit.
In the case of mixed kinetics (Zhou et al., 2015) the unit of the time pace was assumed as equal to the characteristic coagulation time of clusters falling into one cell. It means that particles that reach a common cell can have not necessary time to form a single cluster, but can continue drift separately (Brener et al., 2017). Besides, it is hypothetically assumed that the particles are glued together 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 is considered as completed. Thus, the competition of time intervals of diffusion and the characteristic time of aggregation is simulated. Such approach, probably, is not the only possible. However it was accepted for creation of the submitted model.
In order to simulate the random drift of a particle along a lattice, the technique worked out earlier (Brener et al., 2017) was applied. A random selection of the components of the particle movement in the vertical and horizontal directions was made before each time pace. This choice was made from a given set of possible displacements in a new column and a new row of the matrix.
Let the term "cluster order" means the number of cluster-forming monomer particles. In this case, the possibility that clusters of different orders have different mobilities should be taken into account (Brener et al., 2017). The specific critical value of the cluster order, for which the mobility decreases significantly (Clemmer and Jarrold, 1997), depends on physic-chemical characteristics of the real system (Wang et al., 2012).
Thus, the mathematical expectation of displacement decreases when the cluster order increases (Tammet, 1995). 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) (Brener et al., 2017). The mobilities of clusters are also dependent on the cluster dislocation regarding the wall of apparatuses (Waite et al., 2001).
The main parameters of numerical experiment were accepted like ones in previous work (Brener et al., 2017), but with one principle change. Movement in the horizontal direction on each time unit consisted of two terms, namely: of a fixed displacement with an average axial flow velocity and of a horizontal component of the random drift. This circumstance required some changes in the calculation scheme.
First, it is assumed that displacements of particles trapped in the boundary cells nearby the walls are equal to zero under selection of random drift which leads outside the boundaries of the lattice under consideration.
Second, unlike the algorithm was used to modelling a periodic reactor (Brener et al., 2017), clusters leaving due to the random drift or mean flow to the left or to the right beyond the tube domain, drop out of further calculations.

2.2 Calculation scheme for DLA case

During the calculation, four matrices are formed.
The first matrix A* simulates the entire lattice with clusters of different orders, obtained in the process of displacements and aggregation at each time unit.
The second matrix U simulates an analogous lattice with clusters that fall into the reactor with a fresh flow that flows into the reactor with a given average horizontal velocity.
The third matrix A, which simulates the situation at the end of the calculation time unit and generates the initial situation for the next unit, is formed as the sum of the two previous matrices: A=A*+U.
The fourth matrix S indicates the number of collisions of particles in each cell at each time unit.
Figure 1 depicts the described procedures. The shaded area in the matrix (first W columns) denotes the domain occupied by the fresh flow during the time unit.

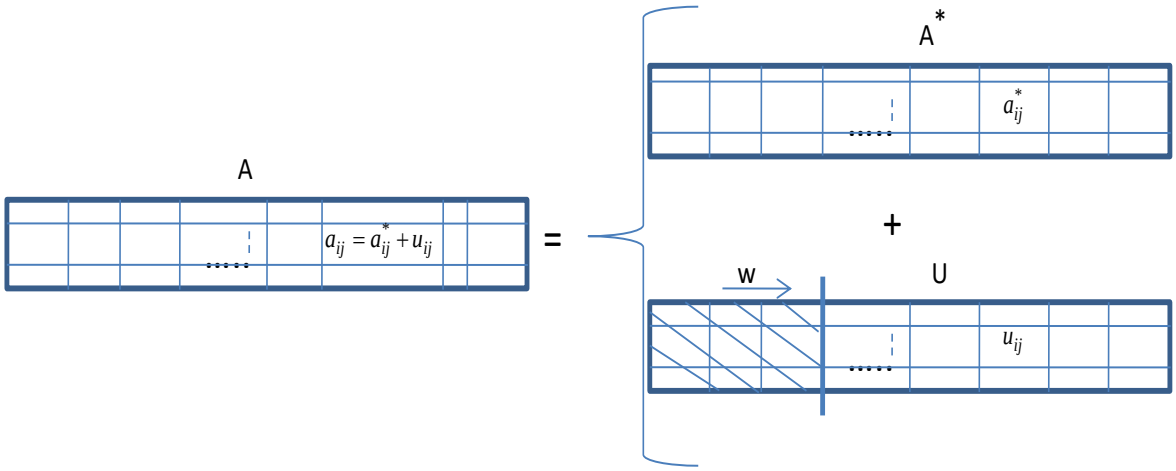

Figure 1: Scheme of the calculation procedure.

At the initial moment, a cluster of order 1 was placed in each cell. Then random selection of displacements for each particle is made as it was explained above, and further aggregation of the particles is carried out as described above too.
Then the process has repeated at each time step by the same principle. Numerical experiments were carried out on planar matrices of dimensions 4X40, 8X40, 5X20, 4X100, which simulated the flow reactors with the length of 20, 40 and 100 cells and with the width of 4, 5 and 8 cells.

2.3 Calculation scheme and main code for the case of mixed kinetics

During the calculation, five matrices are formed.
The first, second and third matrices A*, U and A have the same meaning, as in previous section. The fourth matrix S indicates also the number of collisions of particles in each cell at each time unit.
Along with this, a fifth matrix B is formed (Brener et al., 2017). This three-dimensional array B(I, J, M) serves 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. The matrix B can be denoted as an aggregation-witness matrix.
For demo purpose the main code used for occurring the numerical experiment reads below (Figure 2). The created algorithm and code provide a sufficiently high calculation speed. For example, the time for calculating the matrix of 4 x 100 in the case of mixed kinetics to a depth of 100 conventional time units takes about 5 minutes with using a laptop.

```
procedure Tform1.calc3d;
var k,l,u,t,t1,ii,uu:Integer;// description of variables
begin
 for i:=1 to n2+1 do // n2- number of columns in the table
  for j:=1 to n1 do// n1- number of rows in the table
    begin ss[i,j]:=0; // initial data for the collision matrix
    for u:=1 to coln1 do
      begin
        c[i,j,u]:=0;  U0_3d[i,j,u]:=0; // initial data for intermediate variables
      end;
    end;
 for i:=1 to n2 do
  for j:=1 to n1 do
   for u:=1 to coln1 do // coln1- the number of internal cells of each table cell
       begin
        if (a[i,j,u]<>0) then // if the cell is not empty
          begin
            if (i+vg3w[i,j,u]<1) or (i+vg3w[i,j,u]>n2) then begin k:=n2+1; end
            else k:=i+vg3w[i,j,u]; // check the boundary conditions of the table
            if j+vv3[i,j,u]<1 then  l:=1;
            if j+vv3[i,j,u]>n1 then  l:=n1;
            if (j+vv3[i,j,u]>=1) and (j+vv3[i,j,u]<=n1) then l:=j+vv3[i,j,u];
            t1:=0; // calculation of labels
            for t:=1 to coln1 do if b[k,l,t]=((i-1)*n1+j) then t1:=t;
            if t1<>0 then c[k,l,t1]:=c[k,l,t1]+a[i,j,u];
            if t1=0 then begin t:=1; while (c[k,l,t]<>0) and (k<>n2+1) do t:=t+1; end;
            c[k,l,t]:=c[k,l,t]+a[i,j,u];  // calculation of particle moving
            b[k,l,t]:=(i-1)*n1+j; // b- label matrix
            ss[k,l]:=ss[k,l]+1;  calculation of collision matrix
          end;
        if (i+vg3[i,j,u]<1) or (i+vg3[i,j,u]>n2) then begin k:=n2+1; end
        else k:=i+vg3[i,j,u]; //there is a U flow calculation
        if j+vv3[i,j,u]<1 then l:=1; // account for boundary conditions
        if j+vv3[i,j,u]>n1 then l:=n1;
        if (j+vv3[i,j,u]>=1) and (j+vv3[i,j,u]<=n1) then l:=j+vv3[i,j,u];
        U0_3d[k,l,u]:=U0_3d[k,l,u]+U_3d[i,j,u];
       end;
 i:=n2+1; // coordinate of the right boundary
 for j:=1 to n1 do
 c[i,j,1]:=c[i,j,1]+a[i,j,1]; // calculation of particles at the right boundary
end;
```

Figure 2: Main code used for occurring the numerical experiment

3. Results of simulation

Figures 3a, 3b, 4a and 4b depict some numerical results for matrices, where each point is averaged over ten series of calculations. As a conventional unit of time in the simulation process, the calculation step is used. Clusters of higher than order 5 were not observed practically, so they are not depicted on the graphs.

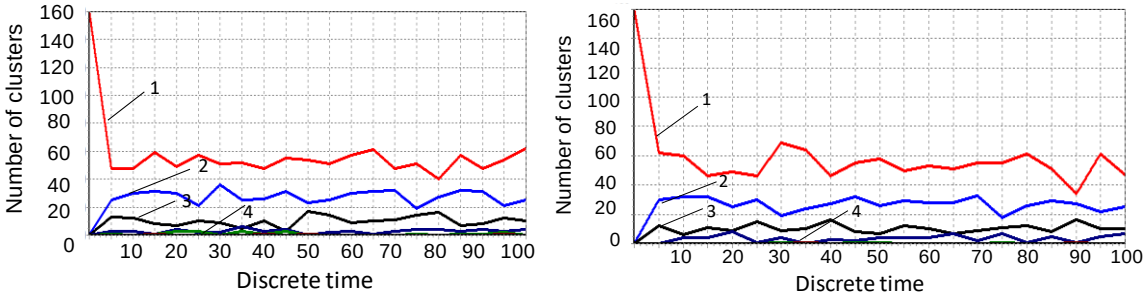

Figure 3: (a) Time history of the numbers of clusters of different orders for w=2, table 4X40. (b) Time history of the numbers of clusters of different orders for w=8, table 4X40. Experiment of the DLA case. Cluster orders: 1-first, 2-second, 3-third, 4-fourth

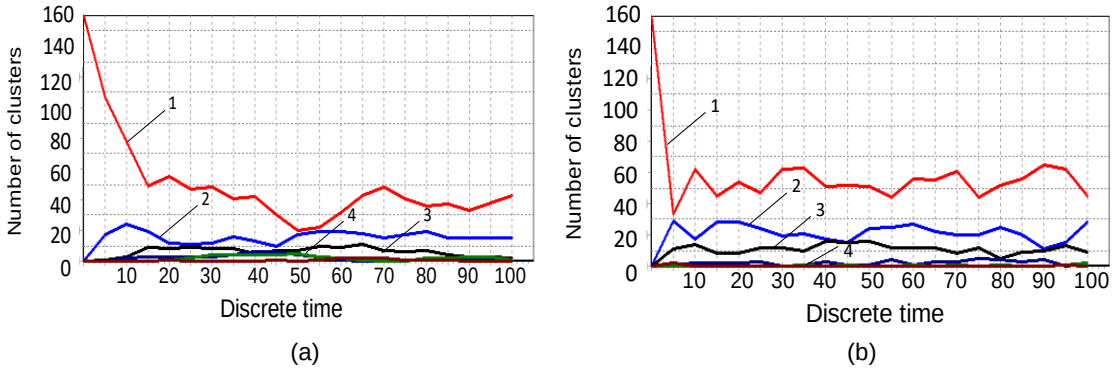

Figure 4: (a) Time history of the numbers of clusters of different orders for w=2, table 4X40. (b) Time history of the numbers of clusters of different orders for w=8, table 4X40. Experiment of the mixed kinetics case. Cluster orders: 1-first, 2-second, 3-third, 4-fourth.

The results of numerical experiments have shown that sharp change in the distribution of clusters in orders occurs during several initial time units after the start of the process, and then the fraction composition lefts practically stable. This observation is correct both for DLA and mixed kinetics cases. However, the drop of the concentration of 1-order clusters in the initial period is sharper for DLA case, and that is easy to explain, of course. At the same time, in the case of mixed kinetics, a more uniform fractional composition is established. Uniformity also improved with increasing average velocity of the flow.
However, the average order of clusters is set at a lower level especially in the case of mixing kinetics. Hence, it can be concluded that the average flow through the reactor can serve as a control parameter not only for achieving a certain performance, but also in order to stabilize the required fractional composition. Like it was observed for periodic reactor model (Brener et al., 2017), numerical experiments for flow reactor confirmed that total number of collisions of multiplicity greater than two cannot be accepted as negligible compared to the number of binary collisions. It is especially correct at the initial stage of the process.
Of course, the above results illustrate only the possibilities of the proposed mathematical tool, and their further verification and discussion are necessary in comparison with other methods and experimental data.

4. Conclusions

Specific comments and conclusions are given at the end of the previous section 3 when discussing the results of numerical experiment. The general conclusion from the results of the research is that an algorithmic approach based on the DES paradigm can be used quite effectively for calculating the kinetics of aggregation in heterogeneous systems both for periodic and for flow reactors. The created mathematical tool allows numerically solving the problem linked to accounting the impact of many-particles collisions, and it gives possibility for describing both a diffusion-limited kinetics of aggregation and the competition of different kinetic mechanisms taking place on different characteristic diffusion, kinetic and flowing times.
Simulation and numerical experiments confirmed that the contribution of multi-particle collisions of clusters to the kinetics of aggregation is noticeable not only in periodic reactors but this phenomenon in flow disperse systems is even more significant. Obviously, the intensity of multi-particle collisions will increase with increasing turbulence level of the flow.
The complexity of implementing the approach proposed in this paper does not increase significantly when taking into account the noted phenomena. Certainly, it is necessary to have reliable experimentally established values of the control parameters for the effective use of the new approach. Apparently, it needs also a lot of work in developing a methodology of calculation convenient for engineering practice on the basis of the submitted approach.

References

Andreassen J.P., 2005, Formation mechanism and morphology in precipitation of vaterite - nano-aggregation or crystal growth?, Journal of Crystal Growth, 274(1), 256-264.
Boer G.B.J de, Hoedemakers G.F.M., Thoenes D., 1989, Coagulation in turbulent flow. Part II, Chemical Engineering Research and Design, 67, 308-315.
Brener A.M., Bolgov N.P., Sokolov N.M., Tarat E.Ya., 1981, Application of methods of grid statistics in describing liquid distribution on stacked shelf packing, Theoretical Foundations of Chemical Engineering, 15(1), 62-67.

Brener A.M., 2014, Model of many-particle aggregation in dense particle systems, Chemical Engineering Transactions, 38, 145-150.
Brener A.M., Musabekova L.M., Jamankarayeva M.A., 2017, Stochastic Lattice Model of Aggregation in Heterogeneous Disperse Media, Chemical Engineering Transactions, 60, 70-84.
Chen H., Lin L., Li H., Li J., Lin J.M., 2015, Aggregation-induced structure transition of protein-stabilized zinc/copper nanoclusters for amplified chemiluminescence, ACS Nano, 9(2), 2173-2183.
Chowdhury I., Mansukhani N. D., Guiney L. M., Hersam M. C., Bouchard D., 2015, Aggregation and stability of reduced graphene oxide: complex roles of divalent cations, pH, and natural organic matter, Environmental Science & Technology, 49(18), 10886-10893.
Clemmer D.E., Jarrold M.F., 1997, Ion mobility measurements and their applications to clusters and biomolecules, Journal of Mass Spectrometry, 32(6), 577-592.
Conway J.R., Adeleye A.S., Gardea-Torresdey J., Keller A.A., 2015, Aggregation, dissolution, and transformation of copper nanoparticles in natural waters, Environmental Science & Technology, 49(5), 2749-2756.
Gambinossi F., Mylon S.E., Ferri J.K., 2015, Aggregation kinetics and colloidal stability of functionalized nanoparticles, Advances in Colloid and Interface Science, 222, 332-349.
Kazenova A., Brener A., Golubev V., Kenzhalieva G., 2017, Modelling the formation of particulate composition in aggregating disperse media with account of the clusters age aspect, Chemical Engineering Transactions, 57, 835-840.
Kébaili N., Benrezzak S., Cahuzac P., Masson A., Bréchignac C., 2009, Diffusion of silver nanoparticles on carbonaceous materials. Cluster mobility as a probe for surface characterization, The European Physical Journal D, 52(1-3), 115-118.
Krapivsky P.L., 1991, Aggregation processes with n-particle elementary reactions, Journal of Physics A: Mathematical and General, 24, 4697-4703.
Markus A.A., Parsons J.R., Roex E.W.M., De Voogt P., Laane R.W.P.M., 2015, Modeling aggregation and sedimentation of nanoparticles in the aquatic environment, Science of the Total Environment, 506, 323-329.
Meakin P., 1983, Formation of fractal clusters and networks by irreversible diffusion-limited aggregation, Physical Review Letters, 51(13), 1119-1122.
Morganti P., Del Ciotto P., Stoller M., Chianese A., 2016, Antibacterial and Anti-inflammatory Green Nanocomposites, Chemical Engineering Transactions, 47, 61-66.
Pnueli D., Gutfinger C., Fichman M., 1991, A turbulent-brownian model for aerosol coagulation, Aerosol Science and Technology, 14(2), 201-209.
Tammet H., 1995, Size and mobility of nanometer particles, clusters and ions, Journal of Aerosol Science, 26(3), 459-475.
Waite T.D., Cleave, J.K., Beattie J.K., 2001, Aggregation kinetics and fractal structure of γ-alumina assemblages, Journal of Colloid and Interface Science, 241(2), 333-339.
Wang B., Yoon B., König M., Fukamori Y., Esch F., Heiz U., Landman U., 2012, Size-selected monodisperse nanoclusters on supported graphene: Bonding, isomerism, and mobility, Nano Letters, 12(11), 5907-5912.
Wattis J.A., 2006, An introduction to mathematical models of coagulation–fragmentation processes: a discrete deterministic mean-field approach, Physica D: Nonlinear Phenomena, 222(1), 1-20.
Zatevakhin M.A., Ignatyev A.A., Govorkova V.A., 2015, Numerical simulation of Brownian coagulation under turbulent mixing conditions, Izvestiya, Atmospheric and Oceanic Physics, 51(2), 148-155.
Zeigler B.P., Praehofer H., Kim T.G., 2000, Theory of modeling and simulation: integrating discrete event and continuous complex dynamic systems, Academic Press, San Diego, CA, USA.
Zeigler B.P., Sarjoughian H.S., 2012, Guide to Modelling and Simulation of Systems of Systems (Simulation Foundations, Methods and Applications), Springer-Verlag, London, UK.
Zhou X.H., Huang B.C., Zhou T., Liu Y.C., Shi H.C., 2015, Aggregation behavior of engineered nanoparticles and their impact on activated sludge in wastewater treatment, Chemosphere, 119, 568-576.