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Modelling the Formation of Particulate Composition in Aggregating Disperse Media with Account of the Clusters Age Aspect

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The work deals with the simplified approach to develop modelling of the integrated effect of geometric and thermodynamic factors on the stability of the dispersion fractional composition. The influence of the age factor is described in the form of the ultimate reduction of the aggregation activity of colliding clusters when increasing their orders. Some experimental data evidencing the possibility of such simplified approach are also resulted. The novelty of the submitted models is determined by the fact that the kinetics of internal transformations of clusters structure is included in the description of the cluster aggregation process as whole.

1. Introduction

The contemporary view of the mechanism of formatting the new (insoluble) phase in the system lies in the fact that the intensive transition of the component to insoluble state is thermodynamically similar to the formation of crystals nuclei in supersaturated solutions, although solid particles may be only partially crystallized (Kaschiev, 2000). An intensive transition to the insoluble state starts when the critical concentration of the component forming insoluble phase is reached (De Groot and Mazur, 2013). New phase of nuclei may have different sizes and masses, but the probabilities of arising the nuclei of different masses are different (Leyvraz, 2003). Therefore the particles of the smallest possible size of the insoluble phase, corresponding to the negative work of nucleate formation, can be regarded as 1-mers with the most probable size (Sonntag et al., 1987).
Taking this hypothesis, it is reasonable to assume that the equilibrium distribution of the dispersed phase in the volume of the medium, i.e. the formation of the fractional composition, is determined mainly by two factors. The first factor is the rate of coagulation (Sonntag et al., 1987) and the second one is the fragmentation of the solid clusters phase (Zahnov et al., 2011).
The rate of coagulation depends on the sign and magnitude of the total interaction energy, which, in accordance with the theory of Deryagin-Verwey-Overbeek (DFO) is determined by the superposition of ionic-electrostatic repulsion forces and the van der Waals-London attraction forces (Voloschuk and Sedunov, 1975).The relationship between the components of the total energy of clusters interaction is determined by two geometric factors: the effective size of the cluster, which depends on its order, and the characteristic distance between the clusters (Aldous, 1999). At the same time, the cluster has a complex structure, and its fractal dimension is also dependent on cluster order (Conoglio and Stanley, 1984). The aggregation activity of the cluster depends on the number of active centers on its surface (Ernst, 1986). When the process of capturing the new particles by the cluster surface slows down significantly, then after a while the inner structure of the cluster can be changed under the influence of internal transformations. Thus the cluster acquires a stable structure which characterizes by an absolute or local minimum of the free energy of its surface. It is correct unless, of course, the system has no interactions that can overcome the energy barrier of the local extreme of the surface energy (Mirlin, 2000). Thus, a quasi-stable equilibrium distribution of the dispersed phase is achieved at a certain aggregation activity of its surface, which in turn depends on the cluster order and the age (Brener and Dil'man, 2016).
The purpose of this work is to offer a simplified approach to modeling the integrated effect of geometric and thermodynamic factors on the stability of the dispersion fractional composition. The influence of the age factor

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is described in the form of the ultimate reduction of the aggregation activity of colliding clusters when increasing their orders. Some of experimental results confirming the prospect of such a simplified approach are presented here in this work.

2. Theoretical considerations and heuristic models

In terms of formal kinetic models the two main mechanisms controlling stabilization of the dispersion composition can be distinguished. Firstly, it is the balance between the rates of disaggregation and aggregation and, secondly, it is reducing of the aggregation activity with increasing the order of clusters and with growth of the cluster age (Dairabay et al., 2016).

In some cases, the first mechanism is, apparently, dominant (Alexander and Orbach, 1982). In other cases, such as phase transitions and aggregation processes in supersaturated systems, a second mechanism of stabilizing the fractional composition becomes prevalent after the transition of the process to the diffusion-limited stage (Blackman and Marshall, 1994).

It can be also considered systems with comparable kinetics of both mechanisms. If due to certain prerequisites a highly concentrated dispersion of the monomer-embryos arises, the fast many-body aggregation (Brener, 2014) can begin as the mobility of the monomers is large enough, and the diffusion resistance is small (Doering and ben-Avraham, 1988).

Then, when after a certain transition period the clusters having high orders arise, and the diffusion resistance increases due to the decrease in the concentration of particles in the dispersion, the process proceeds to the diffusion-limited type (Happel, Brenner, 2012), and at the same time, the large clusters start structuring with reducing their mobility and aggregation activity (Brener and Dil'man, 2016). Apparently, the frequency of many-body collisions on this period reduced (Brener, 2014).

Thus, the process of adding new particles to a high-order cluster can be significantly slowed down, and after a while it can acquire a pseudo-stable structure of the cluster surface (Barabasi and Vicsek, 1991). Formation of these stable (screened) structures can be described as a process of reducing local fluctuations (Coniglio and Stanley, 1984). Each reduction means a transition into a new state with its own free energy level of the cluster surface (Mirlin, 2000).

The characteristic times of local relaxation processes is significantly less than the global stabilization time (Brener, Dil'man, 2016). Moreover, it is most likely the transition to a stable global state for higher order clusters will move through a series of local stabilization, while the total stabilization time can exceed the characteristic time for the process.

Based on these considerations, let us consider the process of stabilizing the fractional composition by the way of the second of above mentioned mechanisms using the modified Smoluchowski model of binary coagulation (Brener and Dil'man, 2016).

$$\frac{dC_1}{dt} = -\sum_{J=1}^{\infty} \int_0^t \int_0^t \Phi_{1,J} C_1(t_1) C_J(t_2) dt_1 dt_2 \tag{1}$$

$$\frac{dC_I}{dt} = \frac{1}{2} \sum_{J=1}^{I-1} \int_0^t \int_0^t \Phi_{J,I-J} C_J(t_1) C_{I-J}(t_2) dt_1 dt_2 - \sum_{J=1}^{\infty} \int_0^t \int_0^t \Phi_{I,J} C_I(t_1) C_J(t_2) dt_1 dt_2 \tag{2}$$

The above heuristic arguments can be interpreted as reducing the probability of mutual particles capture with an increase in the total order and ages of the colliding clusters. In terms of the formal kinetic model it can be described as follows

$$\lim_{i+j\to\infty} \Phi_{i,j} = 0 \tag{3}$$

At the same time the requirement of the spatial homogeneity of the distribution of the clusters is consistent with the decrease of elements of the aggregation matrix with increasing orders of the colliding particles. This approach offers the simplified model instead of an inner kinetic equation for describing the transformation of clusters structure with their ages (Brener, Dil'man, 2016). The proposed approach allows passing from the infinite chain of coagulation equations to a closed finite system of equations that can be effectively investigated with the help of qualitative methods and subjected to computational experiments.

On the other hand, regarding to the small orders of clusters it can play a main role the increase in the effective capture cross section with increasing the particle radius, and decrease in the mobility of the particles with increasing their order (Duprat and Stone, 2016).

Here we propose to use the model elements of the matrix in the form of an even function of the following parameter (Brener et al., 2009).

$$\lambda = \frac{i-j}{i+j} \tag{4}$$

The expansion of this parameter to the Taylor series reads

$$\Phi_{i,j} = a_0 + a_2\lambda^2 + a_4\lambda^4 + \ldots \tag{5}$$

Here $a_s \to 0$ when $s \to \infty$.

It is obvious that under condition $a_0 = const$ expression (5) contradicts to hypothesis (3). To resolve this contradiction it is possible to set the coefficient a_0 in the form of decreasing function of $(i+j)$, such as:

$$a_0 = \frac{k}{(i+j)^{\beta}} \tag{6}$$

Confining ourselves to two terms of the expansion in a Taylor series in the expression (5), the following approximate model of the aggregation matrix can be obtained:

$$\Phi_{i,j} \approx \frac{k}{(i+j)^{\beta}} + a_2\left(\frac{i-j}{i+j}\right)^2 \tag{7}$$

The derivative of the matrix elements by an order of one of the components is:

$$\frac{\partial\Phi_{i,j}}{\partial i} = -\frac{\beta k}{(i+j)^{\beta+1}} + 4a_2\left(\frac{i-j}{i+j}\right)\frac{j}{(i+j)^2} \tag{8}$$

Hence, for the reason of the symmetry of the aggregation process for each component (Brener et al., 2009), it is sufficient to consider the stabilization of the disperse composition for the aggregation of globules of the same orders, i.e. at $i = j$.

Since the intensity of the process according to our model and in accordance with the conclusions of the DFO theory (Voloschuk and Sedunov, 1975) decreases with increasing the orders of the particles, the consideration can be limited by two terms on the right hand in the usual Smoluchowski equation for aggregating the two *i*-mers of great orders (Wattis, 2006):

$$\frac{dC_{2i}}{dt} = \frac{1}{2}\Phi_{i,i}C_i^2 - \Phi_{i,2i}C_iC_{2i} = 0 \tag{9}$$

From the condition of the process stationarity we obtain the ratio between concentrations of 2*i* -mers and *i*-mers, what value will be called the instability factor:

$$\tilde{W} = \frac{C_{2i}}{C_i} = \frac{\Phi_{i,i}}{2\Phi_{i,2i}} = \frac{(3/2)^{\beta}}{1+(zi)^{\beta}} \tag{10}$$

Here

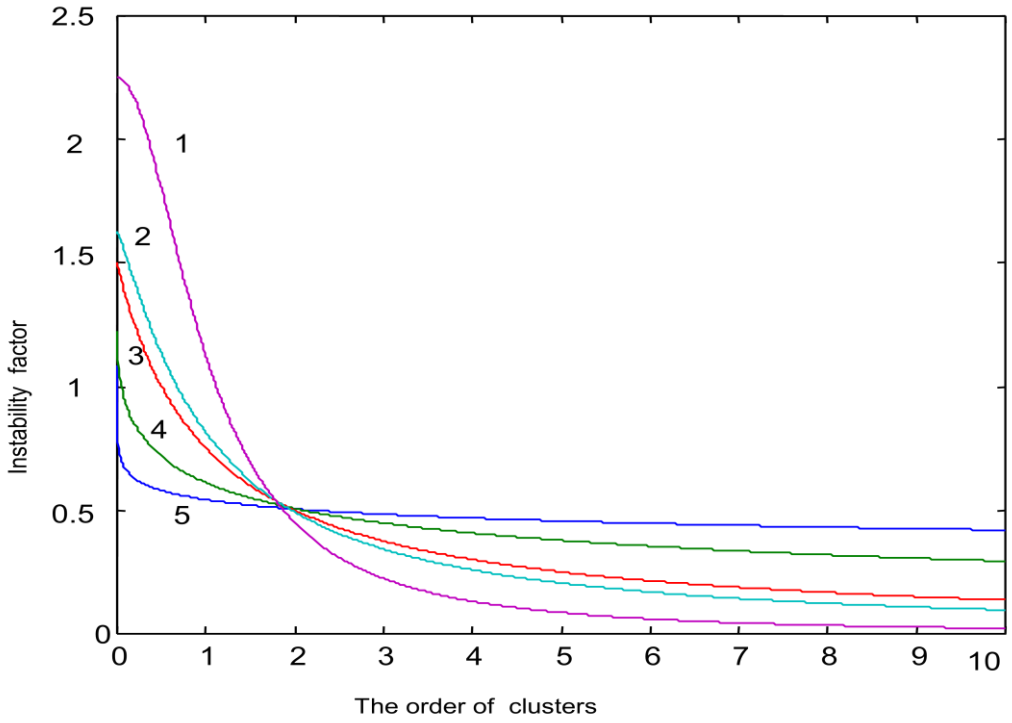
$$z = 3\left(\frac{a_2}{9k}\right)^{1/\beta} \tag{11}$$

Figure 1 depicts some results of the numerical experiments for the instability factor as a function of the orders of collided clusters. Figure 1 shows the feature of the behaviour of curves, namely, all the curves intersect in a small neighbourhood of the point $zi \approx 2$.

This allows counting on being able to relate the two parameters controlling the stability of the disperse systems with two parameters that control the scale of the intermolecular interaction energy in the theory of van der Waals-Hamaker (Dairabay, 2016 b):

$$V_m = -\frac{A^*}{12\pi h^2}, \tag{12}$$

where V_m is the energy of interaction, A^* is the van der Waals-Hamaker constant, *h* is the distance between particles (Sonntag et al., 1987).



1- $\beta = 0{,}2$; 2- $\beta = 0{,}5$; 3- $\beta = 1$; 4- $\beta = 1{,}2$; 5- $\beta = 2$

Figure 1: The instability factor $\tilde{W}$ as a function of the parameter β (look formula (6))

Thus, the heuristic model of stabilization of disperse systems in the aggregation process provided in this section, acquires some physical justification, since it is possible to calculate the control parameters of the model for the known physical media.

3. Some experimental data

In this section, the brief review of some experimental data obtained by research group led by Professor V. Golubev in the State University of South Kazakhstan has been submitted. These data are described in detail in the PhD thesis by Dairabai D.D. (Dairabay, 2016 b), and here we will try to give them an interpretation in the spirit of the considerations outlined in the previous section.

The main impetus for this experiment was to test the conclusion that under the high initial density of primary nuclei dispersion the conditions of the aggregation process for creating the dispersions with high level of the uniformity of the cluster distribution by sizes and orders can be chosen.

Experimental studies of the nucleation and subsequent coagulation of the solid particles of SiO_2 which are arisen when desublimation from the gas phase mixture $(NH_4)_2SiF_2 + NH_3 + H_2O$ were carried out on the special laboratory-scale plant (Dairabay, 2016 b). The above gas mixture has been given off by the help of heat treatment of Karatau phosphorite by the ammonium fluoride. The dispersion characteristics were studied with the help of electron microscopy. The scanning electron microscope JSM-6490LV (SEM) was used.

Figure 2 shows some representative photographs of the dispersions obtained through experiments.

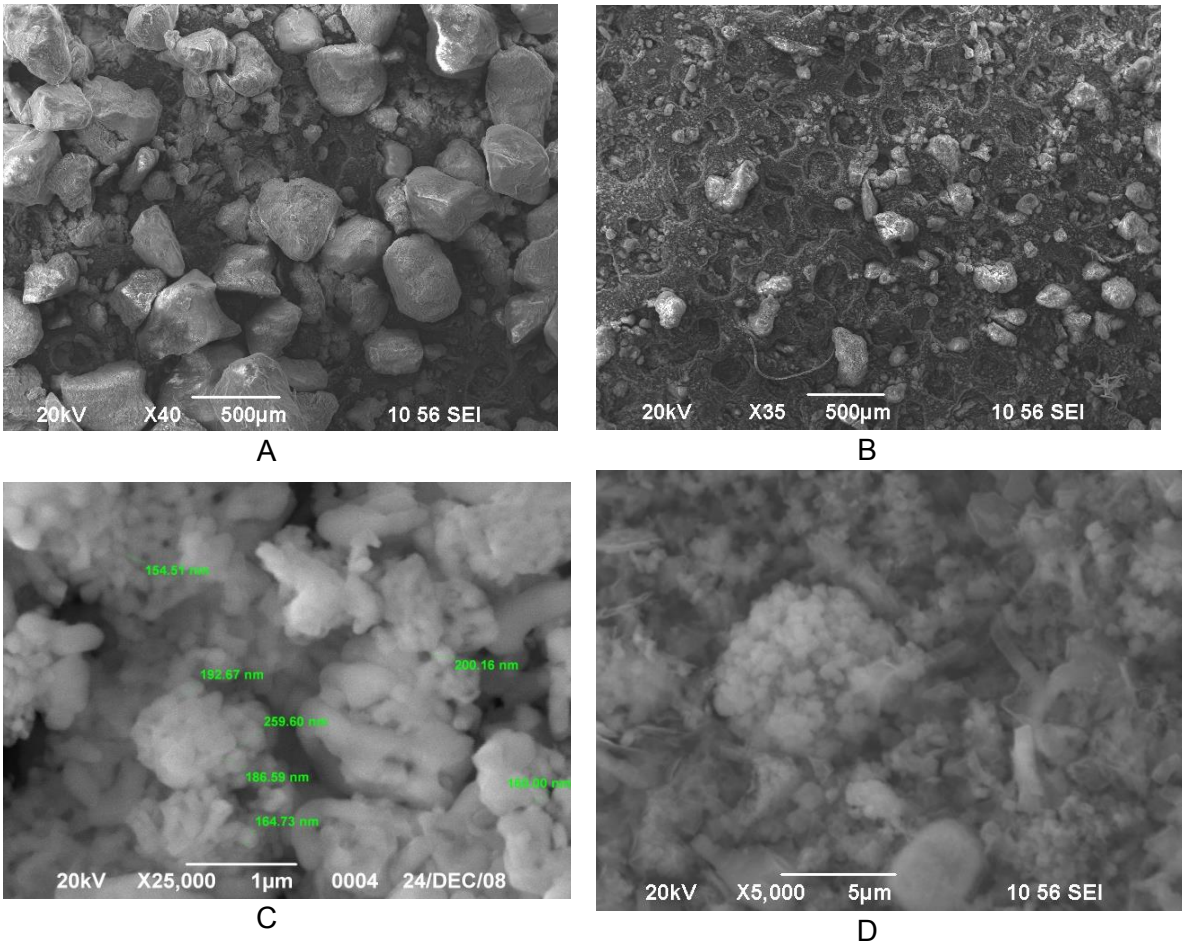


Figure 2: Photomicrographs of the cluster dispersions in the processes of silica vapour desublimation.

Figure 2A is a photomicrograph of a dispersion which arose under the relative supersaturation of 4.5 as a result of a sharp discharge of the vapour pressure. The average cluster size is 380 µm (micrometers), the standard deviation is of the order of 25 µm.

Figure 2B is a photomicrograph of a dispersion with the initial supersaturation of 1.4 which arose while the sudden depressurization. It is clearly seen that the degree of the homogeneity of the dispersion is significantly lower than in the first case (4A). The average size of the clusters is less than 160 µm, at the same time the standard deviation exceeds 90 µm.

Figure 2C corresponds to the first case, i.e. the relative supersaturation is 4.5, but the picture was taken in the zoom of 25,000, which allows considering the single nucleates. It is clearly seen a high proportion of almost spherical particles that arise during the intense many-particle collisions (Brener, 2014). Particles of more complex shapes correspond to clusters arisen for a more long time by the way of mostly binary collisions.

Figure 2D corresponds to supersaturation of 1.4, but the picture was taken with the zoom in 5000. It is evident that even at the micro level the degree of heterogeneity of the dispersion is large.

Studies clearly indicate that provided a large initial supersaturation when the rapid formation of a large number of nuclei (monomers) of the disperse phase per unit volume of the apparatus is observed, the contribution of many-body collisions is also large (Brener, 2014). This is clearly seen in the figures taken at high magnification. Namely, large clusters of the particles are composed of many small nuclei, moreover the large globular clusters grow quite round, which is only possible with a simultaneous merger of many small particles across the surface of the larger clusters. Then, after a sharp decrease in the vapour concentration the aggregation process becomes limited by diffusion resistance in the gas phase (Happel and Brenner, 2012). Because of this the intensity of the aggregation process drops sharply, and, in terms of our model, this leads to a sharp decrease in the values of coagulation kernels. As a result the dispersion with sufficiently homogeneous fractional composition can be obtained. Under the low initial supersaturation the aggregation process is "blurred" over time, since its rate is determined mainly by binary collisions. Such regime of the

process is accompanied by competition between diffusion rate and the aggregation kinetics (Kaschiev, 2000). Therefore, the fractional composition of the dispersion becomes very heterogeneous. Of course, we must bear in mind that in the described experiments a solid phase formation occurred on the solid substrate. The kinetics of this process has certain differences from the kinetics of the desublimation in the volume of an apparatus (Sonntag et al., 2012). Nevertheless, it can be supposed that the proposed interpretation is still valid as these differences are relevant only to the short stage of initial nucleation (Voloschuk and Sedunov, 1975).

4. Conclusions

The submitted simplified approach for accounting the influence of the clusters orders and their ages on the aggregation activity allows offering the control parameters which are likely to be useful for defining optimal technological regimes of producing the dispersions with needed characteristics of fractional composition. The results of the study demonstrate a possibility to get the satisfactory interpretation of the experimentally observed regularities of nucleation-coagulation processes with the help of the submitted model approach. However, this problem should be investigated more deeply.

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