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# ANALYSIS OF MATHEMATICAL MODELS OF TECHNOLOGICAL SYSTEMS WITH CLUSTERING OR AGGREGATION

**Abstract.** A critical analysis of the main widely used aggregation models based on the Smoluchowski kinetic equations has been carried out. It is shown that these models have a drawback that the rate of evolution of the clusters concentration with given orders is assumed to be dependent immediately on the concentrations of clusters of lower orders at the same moment. Some prospective ways for overcoming the shortcomings of known models noted in the analysis have been proposed, and new equations have been derived.

**Keywords:** clustering, aggregation, kinetic equation, dispersed phase, modification, modeling, equations.

**Introduction.**Technological systems where physical and chemical transformations are accompanied by aggregation process of an internal phase and clustering with a complex internal structure are widely used in the chemical, pharmaceutical, metallurgical and other industries. Therefore, the problems of modeling and calculating of such systems attract great attention of researchers. However, despite a significant number of works, many problems remain poorly studied, and the common models of the clustering processes of internal phases in complex physical and chemical systems have a number of shortcomings deteriorating their practical value.

In this paper is given a brief review of the main commonly used aggregation models on the basis of Smoluchowski kinetic equations [1,2]. Some ways which are in the authors' opinion prospective ways of overcoming the shortcomings of known models noted during the analysis are also proposed.

**Smoluchowski equation and its features.** The growth of the cluster according to the Smoluchowski model takes place on the basis of attachment of primary particles and secondary crystals to it which enter the cluster surface through a diffusion mechanism. Whereby the growth of the cluster is described as the movement of the reacting zone, i.e. a region where new particles join the cluster. The particle trajectories start outside the region occupied by the cluster, and end at the moment the particle is in contact with the cluster. This process can also be described as a random walk using the Smoluchowski equation of the following form:

$$\frac{dn_k(t)}{dt} = \frac{1}{2}\sum_{i+i+j=k}\Phi_{ij}C_i(t)C_j(t) - n_k(t)\sum_{j=1}^{\infty}\Phi_{jk}C_j(t). \qquad (1)$$

Where $C_k(t)$- density of $k$ –partial clusters.

The kernel $\Phi_{ij}$ of system of equations (1) takes into account the dependence of the collision cross section on the dimensions and mobility of clusters. Such an approach can be successfully applied to problems where there are sources and sinks that correspond to the presence of an external field in the point of neighborhood of equilibrium phase transition [2, 3].

A certain internal contradiction inherent in the kinetic equations of aggregation on the basis of the Smoluchowski binary coagulation model is that the rate of evolution of the concentration of clusters of a certain order is assumed to be dependent on the concentrations of clusters of lower orders at the same

time. It actually means the instantaneous formation of a cluster when its constituents physically interact between each other. At the same time, the relaxation time of the process is calculated on the basis of particular models that develop the physical mechanism of the aggregation process (for example, DLFO). In addition specificities of the mechanism are usually become apparent only as to the method of calculation of coagulation kernels without changing the kinetic equation form. This approach does not allow to calculate the evolution of the system with incomplete information on the initial concentrations of clusters, and also take into account the memory effects in the system.

This contradiction can be eliminated only by modifying the kinetic equation form of aggregation itself, taking into account the relaxation times. Moreover, we proceed from the premise that the kinetic equation form can nevertheless be considered indirectly to the specifics of the physical nature and mechanism of the aggregation process if it is assumed that the main path of the influence of this specificity on the kinetic equation itself is the formation of a hierarchy of relaxation times. The derivation of the classical Fokker-Planck equation can be mentioned as an example of such approach [3].

The need to take into account the relaxation phenomena in the derivation of the kinetic equations of aggregation was noted by many researchers [4,5].

Consider for example the formation of rain drops in the atmosphere. At the initial moment of the formation of a drop, it is characterized by a certain initial size of the primary embryo, which we will consider as a cluster of the first order. Then the drops are combined with each other and become larger.

In order to describe the kinetics of the aggregation process, we need to know, first, what is the concentration of such drops (first order, second order), i.e. primary drops, combined in two, three drops etc. We need to know how fast the drops of different orders will be combined with each other. The kinetic coefficients required for such a description depend for example on the electric charge carried by the drops. And the electric charge depends on how long the drop is in the atmosphere. Herein lies the impact of the background of the process.

If the drops have different backgrounds, they will differently aggregate. We can not know all this information. But we can estimate the characteristic time during which this electric charge varies by a definite quantity. And with the help of the knowledge of this relaxation time, the influence of unknown in details background on the kinetics of the process can be estimated.

one can make an assessment of how the entire prehistory, which is not known in detail, will affect the kinetics of the process.

All this is fully applicable to the description of aggregation processes in systems with chemical sources of a dispersed phase [6].

Earlier, the papers [4-6] considered the problems of modeling of heat and mass exchange processes based on the methodology of relaxation transfer kernels. Here the derivation of nonlocal kinetic equations of aggregation in homogeneous disperse systems on the basis of the same methodology is proposed for discussion. For binary coagulation is used the Smoluchowski equation as the base model [2].

This is about temporal nonlocality, i.e. about the delay of the process taking into account the hierarchy of relaxation times. The choice of the model equation in this case is a technical issue. Other models can be also used [7,8]. More importantly, the application of the methodology of relaxation transfer kernels [6] for the modification of the kinetic equations is more formal than for the transfer equations. Thisapproachis controversial, ofcourse.

Another aspect of the problem is related to the fact that the Smoluchowski kinetic equation is written for a medium that is assumed to be absolutely homogeneous with respect to the volume concentration of clusters of different orders. The same assumption is made in the new model.

**Modified Smoluchowski equation.** Let's consider the modification of the Smoluchowski equation with the time lag of aggregation, which is intended to describe the effect of the characteristic time of formation of the aggregate on the kinetics of the process [6].

In our situation, the role of relaxation times is played by the characteristic times $\tau_{i,j}$ of aggregations $i-$ and $j-$. Then the following nonlocal modification of Smoluchowski equation is proposed for the aggregation process in a polydisperse system [6, 7]:

$$\frac{\partial C_i}{\partial t} = \frac{1}{2}\sum_{j=1}^{i-1}\int dt_1 \Phi_{i-j,j}(t,t_1) C_{i-j}(t_1) C_j(t_1) - \sum_{j=1}^{\infty}\int dt_1 \Phi_{i,j}(t,t_1) C_i(t_1) C_j(t_1) \tag{2}$$

The model equations for the elements of the coagulation matrix are as follows [6]:

$$\frac{\partial}{\partial t}\Phi_{i,j} + \frac{\Phi_{i,j}}{\tau_{i,j}} f^0_{i,j} = 0 \ . \tag{3}$$

Then the integro-differential equations take the following form:

$$\begin{aligned}\frac{\partial C_i}{\partial t} = \frac{1}{2}\sum_{j=1}^{i-1}\int dt_1 \Phi^0_{i-j,j} \exp\left(-\frac{f^0_{i-j,j}}{\tau_{i-j,j}}(t-t_1)\right) C_{i-j}(t_1) C_j(t_1) - \\ \sum_{j=1}^{\infty}\int dt_1 \Phi^0_{i,j} \exp\left(-\frac{f^0_{i,j}}{\tau_{i,j}}(t-t_1)\right) C_i(t_1) C_j(t_1)\end{aligned} \tag{4}$$

For the case of an isotropic and homogeneous medium, relations (4) can be regarded as ordinary differential equations

The time derivatives of the cumulative elements have the following form

$$\Phi^0_{i,j} C_i(t) C_j(t) - \frac{f^0_{i,j}}{\tau_{i,j}} \Phi^0_{i,j} \int_0^t dt_1 C_i(t_1) C_j(t_1) \exp\left(-\frac{f^0_{i,j}}{\tau_{i,j}}(t-t_1)\right). \tag{5}$$

Then the equation can be changed to the following form:

$$\begin{aligned}\frac{d^2 C_i}{dt^2} = \frac{1}{2}\sum_{j=1}^{i-1}\Phi^0_{i-j,j} C_{i-j}(t) C_j(t) - \sum_{j=1}^{\infty}\Phi^0_{i,j} C_i(t) C_j(t) - \\ -\frac{1}{2}\sum_{j=1}^{i-1}\frac{f^0_{i-j,j}}{\tau_{i-j,j}}\int dt_1 \Phi^0_{i-j,j} \exp\left(-\frac{f^0_{i-j,j}}{\tau_{i-j,j}}(t-t_1)\right) C_{i-j}(t_1) C_j(t_1) + \\ +\sum_{j=1}^{\infty}\frac{f^0_{i,j}}{\tau_{i,j}}\int dt_1 \Phi^0_{i,j} \exp\left(-\frac{f^0_{i,j}}{\tau_{i,j}}(t-t_1)\right) C_i(t_1) C_j(t_1)\end{aligned} \tag{6}$$

Let's take derivative with time once again:

$$\begin{aligned}\frac{d^3 C_i}{dt^3} = \frac{d}{dt}\left(\frac{1}{2}\sum_{j=1}^{i-1}\Phi^0_{i-j,j} C_{i-j}(t) C_j(t) - \sum_{j=1}^{\infty}\Phi^0_{i,j} C_i(t) C_j(t)\right) - \\ -\frac{1}{2}\sum_{j=1}^{i-1}\frac{f^0_{i-j,j}}{\tau_{i-j,j}}\Phi^0_{i-j,j} C_{i-j}(t) C_j(t) + \\ +\frac{1}{2}\sum_{j=1}^{i-1}\left(\frac{f^0_{i-j,j}}{\tau_{i-j,j}}\right)^2\int dt_1 \Phi^0_{i-j,j} \exp\left(-\frac{f^0_{i-j,j}}{\tau_{i-j,j}}(t-t_1)\right) C_{i-j}(t_1) C_j(t_1) + \\ +\sum_{j=1}^{\infty}\frac{f^0_{i,j}}{\tau_{i,j}}\Phi^0_{i,j} C_i(t) C_j(t) - \\ -\sum_{j=1}^{\infty}\left(\frac{f^0_{i,j}}{\tau_{i,j}}\right)^2\int dt_1 \Phi^0_{i,j} \exp\left(-\frac{f^0_{i,j}}{\tau_{i,j}}(t-t_1)\right) C_i(t_1) C_j(t_1)\end{aligned} \tag{7}$$

Carrying out separate average over groups of indices for elements describing formation and destruction of $i$ -, we have the system of equations

$$\frac{d^3C_i}{dt^3}=\frac{d}{dt}(\frac{1}{2}\sum_{j=1}^{i-1}\Phi^0_{i-j,j}C_{i-j}(t)C_j(t)-\sum_{j=1}^{\infty}\Phi^0_{i,j}C_i(t)C_j(t))-$$
$$-\frac{1}{2}A_1\sum_{j=1}^{i-1}\Phi^0_{i-j,j}C_{i-j}(t)C_j(t)+$$
$$+\frac{1}{2}B_1^2\sum_{j=1}^{i-1}\int dt_1\Phi^0_{i-j,j}\exp\left(-\frac{f^0_{i-j,j}}{\tau_{i-j,j}}(t-t_1)\right)C_{i-j}(t_1)C_j(t_1)+ \quad (8)$$
$$+A_2\sum_{j=1}^{\infty}\Phi^0_{i,j}C_i(t)C_j(t)-$$
$$-B_2^2\sum_{j=1}^{\infty}\int dt_1\Phi^0_{i,j}\exp\left(-\frac{f^0_{i,j}}{\tau_{i,j}}(t-t_1)\right)C_i(t_1)C_j(t_1)$$

More compact view of the system is taken after changing

$$\frac{d^3C_i}{dt^3}+(B_1+B_2)\frac{d^2C_i}{dt^2}+B_1B_2\frac{dC_i}{dt}=$$
$$=(B_1+B_2+\frac{d}{dt})(\frac{1}{2}\sum_{j=1}^{i-1}\Phi^0_{i-j,j}C_{i-j}(t)C_j(t)-\sum_{j=1}^{\infty}\Phi^0_{i,j}C_i(t)C_j(t))- \quad (9)$$
$$-\frac{1}{2}A_1\sum_{j=1}^{i-1}\Phi^0_{i-j,j}C_{i-j}(t)C_j(t)+A_2\sum_{j=1}^{\infty}\Phi^0_{i,j}C_i(t)C_j(t)$$

A special feature of equation (9) is the existence of solutions describing the passage of disturbance with finite velocity [8]. The further development of the proposed model may consist in taking into account the difference in the characteristic times of coagulation in the aggregation of globules of different orders.

At the same time, the analysis of the obtained equation shows that the use of the local form of Smoluchowski equations with aggregation matrices subject to equations of the form (3) is completely correct for small parameter point because a correction to the local form has at least a second order of smallness [7].

**Conclusion.** The article gives a brief critical analysis of models of dispersed phase aggregation in physical and chemical systems. The need to take into account the relaxation phenomena is shown and techniques of derivation of the kinetic equations of aggregation with phenomena of time lag in the formation of aggregated clusters of disperse phase is outlined. This methodology can be used for modeling of dynamic processes in memory systems based on nonlocal transfer equations.

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