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Kinetic Equations of Aggregation Processes in Disperse Systems with Allowance for Age-Dependent Clusters Properties

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The article presents the modifications of the two classical kinetic models of binary coagulation: the Smoluchowski equation and the Becker-Döring model. The main goal of these modifications is to submit approach for describing the influence of age-dependent properties of colliding clusters on the rate of aggregation process. The appropriate forms of generalized kinetic equations based both on the Smoluchowski equation and on the Becker-Döring model have been submitted and discussed.

1. Introduction

Contemporary chemical technologies often are aimed at production of materials with complex internal structure. For example, such materials have wide use in nano and smart-devices. Work of smart-devices with memory is characterized by dynamical formation of clusters of different orders. In order to create the methods for calculating intensity of transport phenomena in that case needs evaluation of the relaxation times and long-range interactions of structural components of a medium. Importance of this problem is redoubled by that resources for effective controlling such processes are limited, and it is important to calculate and select the best values of governing parameters.

Problems of modeling both high rate and nano-scale processes are in touch with deriving equations with retarded or divergent arguments that reflects the actual mechanism of transfer phenomena in the presence of memory phenomena (Blackman and Marshall, 1994). This approach allows considering the influence of relaxation times hierarchy on kinetics of aggregation process (Aldous, 1999). The main point of the classic Smoluchowski's and Becker-Döring equations is that speed of evolution of clusters concentration of given order depends on concentrations of the lowest orders clusters at the given moment (Ball, Carr & Penrose, 1986). Thus, according to the mentioned kinetic equations the rates of formation of new clusters are determined only by number of simultaneous collisions between clusters at present, i.e. it is supposed that formation of a new cluster at collision occurs instantly, and the properties of colliding clusters are dependent on theirs orders only (Wattis, 2006). However, in reality, the process of formation of any cluster does not occur instantly, and will be stretched in time (Boem, Poor & Grant, 1998).

So, one of the main, but practically non-discussed assumption which is intrinsic to the classic Smoluchowski and Becker-Döring equations, is that rate of evolution of clusters concentration of given order depends on concentrations of the lowest orders clusters at the given moment, and the kinetic properties of the clusters are proposed to be independent on their ages (Brener, 2006; 2011). However any given moment there exist a lot of clusters which have the same order but have different residential time in the disperse system.

In the paper we submit the modifications of Smoluchowski and Becker-Döring kinetic equations for particles coagulation with allowing for age-dependent clusters properties. These properties can change in time both for high-order clusters and for monomers. Some results of the theoretical analysis and numerical experiments according to the model are submitted too.

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2. General structure of modified kinetic equations

Let us construct the formal scheme for deriving kinetic equations describing the aggregation process with allowance for the different ages of clusters and possible changes in their properties in dependences on ages.

The discrete interpretation for evolution of the concentration of the clusters with given order i is shown in Figure 1.

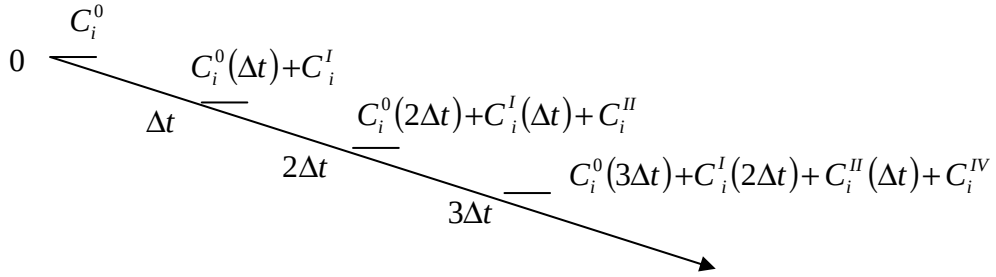

Figure 1: Discrete scheme for evolution of the clusters concentrations

Here C_i^0 is the concentration of clusters of i-th order at the initial moment; Δt is the time step; $C_i^0(\Delta t)$, $C_i^0(2\Delta t)$, $C_i^0(3\Delta t)$ are the concentrations of i-th order clusters which were arisen at the moment (0) and which have been observed at moments Δt, $2\Delta t$, $3\Delta t$; C_i^I, $C_i^I(\Delta t)$, $C_i^I(2\Delta t)$ are the similar denotations for i-th order clusters which were arisen at the moment (Δt) and which have observed at subsequent moments, and etc.

The above scheme gives grounds for the following modification of the Smoluchowski equation for binary coagulation (Davies, 1999, Brener, 2011)

$$\frac{dC_i}{dt}=\frac{1}{2}\sum_{j=1}^{i-1}\int_0^t\int_0^t N_{j,i-j}C_j(t_1)C_{i-j}(t_2)dt_1dt_2-\sum_{j=1}^{\infty}\int_0^t\int_0^t N_{i,j}C_i(t_1)C_j(t_2)dt_1dt_2, \tag{1}$$

Here the aggregation cores $N_{i,j}$ are functions of the delay times $\Delta t_1=(t-t_1)$ and $\Delta t_2=(t-t_2)$.

Let us present the aggregation cores in the form of product of two factors.

$$N_{i,j}=N_{i,j}^C N_{i,j}^A\ . \tag{2}$$

The first factor $N_{i,j}^C$ is the concentration-factor describing the contribution of clusters arisen at different moments in the appropriate concentrations, and the second factor $N_{i,j}^A$ is the age-factor accountable to dependence of clusters properties on their ages. Such form agrees with the probability view, namely with the product of appropriate factors of influence.

Let us consider further approach to calculate the factor $N_{i,j}^C$ in accordance with our previous works (Brener, 2011).

As it follows from Onsager and Casimir hypothesis the relaxation of fluctuations obeys the usual phenomenological macroscopic laws on average (Ernst, 1986). The linear relation between time-derivatives of fluctuations amplitude and amplitude itself follows from this hypothesis, as it is shown by S.R. de Groot (De Groot, Mazur, 2013). It was shown that this hypothesis didn't contradict the kinetic theory (Meakin, 1987). We suppose that simplest quasi-linear model equation for elements of the aggregation matrix on this approach reads (Brener, Balabekov & Kaugaeva, 2009)

$$r_i\frac{\partial N_{i,j}^C}{\partial s_1}+r_j\frac{\partial N_{i,j}^C}{\partial s_2}+\frac{f_{i,j}^0}{\tau_{i,j}}N_{i,j}^C=0\,. \tag{3}$$

In our case the characteristic times $\tau_{i,j}$ of the aggregation of i and j – mers play the role of relaxation times, $s_1 = t - t_1 \quad s_2 = t - t_2$.

In Eq (3) the coefficients r_i on a level with the relaxation time $\tau_{i,j}$ play a role of control parameters of a type of "inertness", the parameter f answers to the environment and particles characteristics.

Thus the aggregation matrix, satisfying Eq (3) and corresponding to the condition of fast relaxation in time $t >> \tau_{i,j}$, can be written as

$$N_{i,j}^{C} = \eta_{i,j}^{0} \exp\left(-\frac{f_{i,j}^{0}}{2\tau_{i,j}} \left(\frac{s_1}{r_i} + \frac{s_2}{r_j} \right) \right). \tag{4}$$

Thus, the master equation reads

$$\frac{dC_i}{dt} = \frac{1}{2} \sum_{1} \eta_{j,i-j} \exp(-(g_{j,i-j}^{(j)} + g_{j,i-j}^{(i-j)})t) I_1 I_2 - \sum_{2} \eta_{i,j} \exp(-(g_{i,j}^{(i)} + g_{i,j}^{(j)})t) I_3 I_4, \tag{5}$$

Here $g_{m,n}^{(i)} = \frac{a_{m,n}}{2r_i}$; $g_{m,n}^{(j)} = \frac{a_{m,n}}{2r_j}$; $a_{m,n} = \frac{f_{m,n}^{0}}{\tau_{m,n}}$;

$\sum_{1}$ means $\sum_{j=1}^{i-1}$; $\sum_{2}$ means $\sum_{j=1}^{\infty}$;

$$I_1 = \int_0^t \exp(g_{j,i-j}^{(i-j)} s) N_{i-j}^{A}(s) C_{i-j}(s) ds \,; I_2 = \int_0^t \exp(g_{j,i-j}^{(j)} s) N_{j}^{A}(s) C_{j}(s) ds \,;$$

$$I_3 = \int_0^t \exp(g_{i,j}^{(j)} s) N_{j}^{A}(s) C_{j}(s) ds \,; \; I_4 = \int_0^t \exp(g_{i,j}^{(i)} s) N_{i}^{A} C_{i}(s) ds \,.$$

Calculation of characteristic times depends, naturally, on the accepted mechanism of aggregation [3, 9, 10]. The certain ambiguity inherent to Eq (5) can be removed under deriving the generalized aggregation equation on the base of the Becker-Döring model (Doering, ben-Avraham, 1988, 1989)

$$\frac{dC_i}{dt} = J_{i-1}(t) - J_i(t), \quad (i \geq 2), \tag{6}$$

$$J_k(t) = a_k C_k(t) C_1(t) - b_{k+1} C_{k+1}(t). \tag{7}$$

Here

a_k is the forward rate coefficients of aggregating the r - order cluster with a monomer; b_k is the backward rate coefficients of the fragmentation of the r - order cluster by throwing off a monomer.

The generalized Becker-Döring kinetic equation can be written as

$$\frac{dC_i}{dt} = \int_0^t \int_0^t (a_{i-1} C_{i-1}(t_1) C_1(t_2) - b_i C_i(t_1)) dt_1 dt_2 - \int_0^t \int_0^t (a_i C_i(t_1) C_1(t_2) - b_{i+1} C_{i+1}(t_1)) dt_1 dt_2 . \tag{8}$$

It is known that the explicit solutions of the Smoluchowski equation have been obtained with the help of generating functions for only little number of certain special forms of aggregation cores (Wattis, 2006; Zahnov et al., 2011; Leyvraz, 2003).

The coefficients a_k and b_k can be just as (2) written in the multiplicative forms

$$a_k = a_k^C a_k^A ; \; b_k = b_k^C b_k^A , \tag{9}$$

where the factors in Eq (9) have the similar interpretations as the factors in form (2).
Certainly, the complete analysis of the general forms (5) and (8) is very complex problem.
Let us discuss below some ideas regarding the age-factors.

3. Concept for age-factors of aggregation cores

For modelling the aggregation cores depending on the cluster residential time (or age) the following heuristic considerations have been suggested.
Cluster aggregation activity depends on the number of active centres on its surface (Ben-Avraham & Havlin, 1982). In the case of a high-order fractal cluster, this surface has an intricate form and variable fractal dimension (Barabasi & Vicsek, 1991). If the process of aggregation stop, then the structuring of the cluster will be completed after some time, and the structure shape will be characterized by a minimum of free surface energy.
Thus, there can be noted the following key points for systematic describing the age-depending properties of clusters:
1. Drift to the steady state, i.e. to the state with minimum free surface energy (Alexander & Orbach, 1982).
2. Perturbations of the above drift at the moments of new clusters capture (Bunde et al., 1985).
The drift to the steady state in the case of the high-order cluster can take place both on the global cluster scale and on the local scales with generating of stable “islands” all over the cluster structure.
Formation of stable “islands” can be described as fading of local fluctuations (Bunde et al., 1985). The typical times of local stabilizations may be essentially less then global stabilization time. Moreover, it is the most probable that for high-order cluster the drift to the global steady state occurs through the set of local stabilizations chiefly, and the complete global stabilization time may be longer than process typical time.
However, if there is a periodic capture of new particles, then, the cluster "undergoes" a certain story between the times of captures. And at each moment of clusters collisions the structure will be newly perturbed.
This description is illustrated in Figure 2.

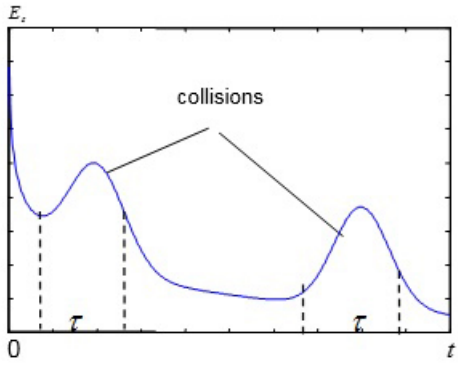

Figure 2: Characteristic plot of the time-dependent surface free energy of complex cluster

The question how properties of low-orders clusters, especially of monomers, can turn out depending on their ages should be considered separately. Indeed, in that case it is hardly correct to explain the age-dependence of properties with the help of the changeable internal structure of clusters. However, certain parameters (the surface charge of particles, particularly, which are defined as the result of interactions between clusters and environment) can change in time (Brener, 2011).
In this work, however, we will not further consider the above questions. In many processes the properties of monomers may be considered as independent on time (Duncan & Soheili, 2000). As for the high-order clusters, the main ideas for quantitative description of the age-factor may be deduced from tools of fractal theory (Herrmann & Stanley,1988). Namely, we offer to describe the age-factor through the relation between the full surface of fractal cluster and non-screened surface (Coniglio, Stanley, 1984) where the screen phenomenon is induced by increasing number of steady “islands” (Coniglio & Stanley,1984).
Thus, this evaluation reads

$$N_{i,j}^{A} = \tilde{N}_{i}^{A}\tilde{N}_{j}^{A} \sim i^{d_u^i} j^{d_u^j}. \quad (10)$$

Here d_u^i and d_u^j are the fractal dimensions of non-screened surfaces of the clusters of i-th and j-th orders (Cognilio, Stanley, 1984).

4. Some numerical results

We try to simplify the problem by using asymptotic behaviour of integrals in Eq (5). Namely, it is supposed that for small relaxation times (or big $a >> 1$) we can use Laplace method in the neighbourhood of the time point t. Thus, after certain rearrangements the following asymptotic equation has been obtained (Brener, 2011):

$$\varepsilon \frac{d^2 C_i}{d\theta^2} + \frac{dC_i}{d\theta} = 2\varepsilon^2 \sum_{1} N_{j,i-j}\left[C_j C_{i-j} - \varepsilon \frac{d}{d\theta}(C_j C_{i-j})\right] - 4\varepsilon^2 \sum_{2} N_{i,j}\left[C_i C_j - \varepsilon \frac{d}{d\theta}(C_i C_j)\right], \quad (11)$$

Here $\varepsilon = \tau_* / T$, $\theta = t/T$, τ_* is the characteristic time of collision, T is the typical process time.
It is interesting that preliminary estimation of the correctness of the above approximation looks as follows

$$\theta_{in} \sim -\varepsilon \ln \varepsilon . \quad (12)$$

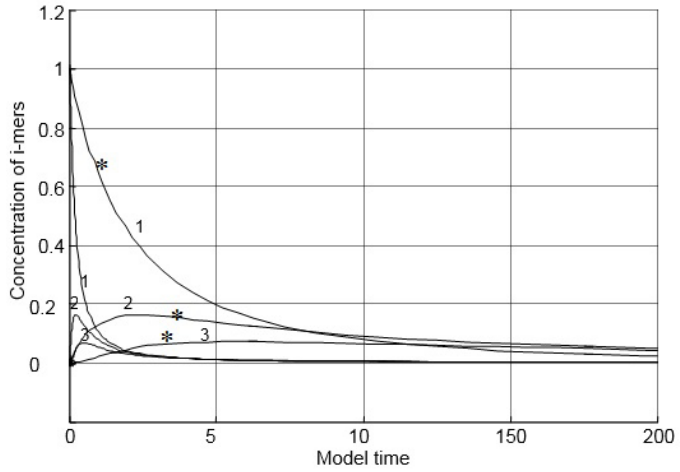

*Figure 3: Dependence of dimensionless concentration on model time for aggregation matrix. $N_{i,j}=1/\varepsilon$, $\varepsilon=1/10$. 1 – monomers, 2 – two-mers, 3 – three-mers. * - numerical solution by classical Smoluchowski equation, without special mark - numerical solution by modification (11) of Smoluchowski equation.*

Figure 3 depicts some results of experiments with reduced model (11).
The results of these experiments showed that essential qualitative differences from the decisions of the classical equation have observed on initial sites. It confirms evaluation (12).

5. Conclusions

In the paper the modifications of Smoluchowski and Becker-Döring kinetic equations for clusters aggregation with allowance for the age-dependent clusters properties have been submitted. The clusters properties can change in time both for high-order clusters and for monomers. The main submitted concept is that high-orders clusters properties can change in time due to changing the internal structure and the number of active surface centers, at the same time for monomers this phenomenon can be conditioned by changing properties of the environment. This approach allows considering the influence of relaxation times hierarchy on kinetics of

aggregation process. Some results of the theoretical analysis and numerical experiments according to the model are submitted.

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