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Kinetics of Aggregation in Media with Memory

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***Abstract*—**In the paper we submit the non-local modification of kinetic Smoluchowski equation for binary aggregation applying to dispersed media having memory. Our supposition consists in that that intensity of evolution of clusters is supposed to be a function of the product of concentrations of the lowest orders clusters at different moments. The new form of kinetic equation for aggregation is derived on the base of the transfer kernels approach. This approach allows considering the influence of relaxation times hierarchy on kinetics of aggregation process in media with memory.

***Keywords*—**Binary aggregation, Media with memory, Non-local model, Relaxation times

I. Introduction

CONTEMPORARY chemical technologies often are aimed at production of materials with complex internal structure. Personally, 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.

So, creation of methods for calculating intensity of transport phenomena in that case needs appreciation of the relaxation times and long-range interaction of structural components of a medium [1–3]. Importance of this problem is redoubled by that resources of effective controlling such processes are limited, and it is important to calculate correctly and select the best values of governing parameters. Problems of modeling both high rate and nano-scale processes are in touch with construction of equations with retarded or divergent arguments that reflects the actual mechanism of transfer phenomena in the media having memory [2, 3].

The main point of the classic Smoluchowski's equation is that speed of evolution of clusters concentration of given order depends on concentrations of the lowest orders clusters at the fixed moment [1, 2]. Thus, according to the Smoluchowski's equation the speed of formation of new clusters is determined only by number of simultaneous collisions between clusters at present, i.e. it is necessary that formation of a new cluster at collision occurs instantly. However, in reality, the process of formation of any cluster does not occur instantly, and will be stretched in time [3, 4, 5]. The control parameter in a situation of time non-locality should be the relaxation time, i.e. the time for overcoming power barrier under cluster formation [3]. And so, in our opinion, it makes sense to modify the kinetic equation of the aggregation with allowing for the delay when defining the speed of irreversible formation of the cluster. This factor can be considered as original memory of the system.

So, it is necessary to take into account concentrations of clusters of the lowest orders not only at present, but also during the previous moments. this process goes continuously, thus we offer to consider the concentrations of clusters participating in interaction during the previous moments and to account the relaxation of their influence depending on remoteness of time of formation of these clusters from the given moment.

The methodology of the account of continuous sequence of previous states under deriving the integro-differential kinetic equations has been created by V. Volterra in his work [6].

This paper deals with the non-local modification of the Smoluchowski's equation based on the scheme of the transfer kernels approach [7, 8, 9].

II. Mathematical Model

The non-local modification of the Smoluchowski's equation for aggregation in dispersed systems reads [8]:

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

C_i denotes the concentration of i-mers, and aggregation kernels $N_{i,j}$ are functions of the delay times $(t-t_1)$ and $(t-t_2)$.

In our case the characteristic times $\tau_{i,j}$ of the aggregation of i and $j-$mers play the role of relaxation times. Calculation of characteristic times depends, naturally, on the accepted mechanism of aggregation [3, 9, 10].

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 [11-14].

Rudyak showed that this hypothesis didn't contradict the kinetic theory [7]. We suppose that simplest quasi-linear model equation for elements of the aggregation matrix on this approach reads [8, 9].

$$r_i\frac{\partial N_{i,j}}{\partial s_1} + r_j\frac{\partial N_{i,j}}{\partial s_2} + \frac{f^0_{i,j}}{\tau_{i,j}}N_{i,j} = 0, \quad (2)$$

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where $s_1 = t - t_1 \quad s_2 = t - t_2$.

In equation (2) the coefficients r_i on a level with relaxation time $\tau_{i,j}$ play a part of control parameters of clusters "inertness", the parameter f answers for media and particles characteristics.

Thus the aggregation matrix, satisfying (2) and coming up to the condition of fast relaxation in time $t >> \tau_{i,j}$, can be written as

$$N_{i,j} = \eta^0_{i,j} \exp\left(-\frac{f^0_{i,j}}{2\tau_{i,j}} \left(\frac{s_1}{r_i} + \frac{s_2}{r_j} \right) \right) \tag{3}$$

The master equation reads

$$\frac{dC_i}{dt} = \frac{1}{2} \sum_1 \eta_{j,i-j} \exp(-(g^{(j)}_{j,i-j} + g^{(i-j)}_{j,i-j})t) I_1 I_2 - \sum_2 \eta_{i,j} \exp(-(g^{(i)}_{i,j} + g^{(j)}_{i,j})t) I_3 I_4 \tag{4}$$

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

$\sum_1$ means $\sum_{j=1}^{i-1}$; $\sum_2$ means $\sum_{j=1}^{\infty}$;

$$I_1 = \int_0^t \exp(g^{(i-j)}_{j,i-j} s) C_{i-j}(s) ds; \; I_2 = \int_0^t \exp(g^{(j)}_{j,i-j} s) C_j(s) ds$$

$$I_3 = \int_0^t \exp(g^{(j)}_{i,j} s) C_j(s) ds \; ; \; I_4 = \int_0^t \exp(g^{(i)}_{i,j} s) C_i(s) ds .$$

We consider here the simplified model with $r_i = r_j = 1$ and $\frac{f^0_{i,j}}{\tau_{i,j}} \equiv a_{i,j} = a = const$.

Thus we obtain

$$\frac{dC_i}{dt} = \frac{1}{2} \exp(-at) \sum_1 \eta_{j,i-j} I_1 I_2 - \exp(-at) I_3 \sum_2 \eta_{i,j} I_2 \tag{5}$$

Here $I_1 = \int_0^t \exp(as/2) C_{i-j}(s) ds$;

$$I_2 = \int_0^t \exp(as/2) C_j(s) ds \; ; \; I_3 = \int_0^t \exp(as/2) C_i(s) ds .$$

We try to simplify the problem by using asymptotic behavior of integrals in (5).

Namely, it is supposed that for small relaxation times (or big $a >> 1$) we can use Laplace method in the neighborhood of the time point t. But immediate substitution of the integrals expansions into (5) requires multiplication of asymptotic sequences. Such procedure may lead to utter loss of checking orders of approximation.

In order to prevent it we rearrange the equations to the form that is free from a product of integrals:

$$\frac{d^2C_i}{dt^2} + a\frac{dC_i}{dt} = \frac{1}{2} \exp\left(-\frac{at}{2}\right) \sum_1 \eta_{j,i-j} (C_j I_1 + C_{i-j} I_2) - \exp\left(-\frac{at}{2}\right) \left[C_i \sum_2 \eta_{i,j} I_2 + I_3 \sum_2 \eta_{i,j} C_j \right] \tag{6}$$

Let's assume $1/a = \tau_*$.

The parameter τ_* has a time dimension. So, let T be the characteristic time of the process. Introducing the small parameter $\varepsilon = \tau_* / T$ we can pass to the dimensionless time $\theta = t/T$ and dimensionless aggregation kernels $\overline{\eta}_{i,j} = T^3 \eta_{i,j}$.

Using then Laplace method we obtain [15]:

$$\varepsilon \frac{d^2C_i}{d\theta^2} + \frac{dC_i}{d\theta} = 2\varepsilon^2 \sum_1 \overline{\eta}_{j,i-j} \left[C_j C_{i-j} - \varepsilon \frac{d}{d\theta}(C_j C_{i-j}) \right] - 4\varepsilon^2 \sum_2 \overline{\eta}_{i,j} \left[C_i C_j - \varepsilon \frac{d}{d\theta}(C_i C_j) \right] + \Phi_0 \tag{7}$$

Here Φ_0 reads

$$\Phi_0 = -\varepsilon^2 \exp\left(-\frac{\theta}{2\varepsilon}\right) \sum_1 \overline{\eta}_{j,i-j} \left[C_j \left(C_{i-j}(0) - 2\varepsilon \frac{dC_{i-j}(0)}{d\theta} \right) + C_{i-j} \left(C_j(0) - 2\varepsilon \frac{dC_j(0)}{d\theta} \right) \right] + 2\varepsilon^2 \exp\left(-\frac{\theta}{2\varepsilon}\right) \sum_2 \overline{\eta}_{i,j} \left[C_i \left(C_j(0) - 2\varepsilon \frac{dC_j(0)}{d\theta} \right) - C_j \left(C_i(0) - 2\varepsilon \frac{dC_i(0)}{d\theta} \right) \right] \tag{8}$$

The interesting peculiarity of expression (8) is that (8) contains factor $-\varepsilon^2 \exp\left(-\frac{\theta}{2\varepsilon}\right)$. However its order can be comparable with ε^2 at sufficiently small times. For estimating this period we will consider the inequality.

$$\varepsilon^2 \exp\left(-\frac{\theta}{2\varepsilon}\right) >> \varepsilon^3. \quad (9)$$

The preliminary estimation of this period we can submit as follows.

$$\theta_{in} \sim -\varepsilon \ln \varepsilon. \quad (10)$$

Fig. 1 depicts the characteristic plot of dependence (10).

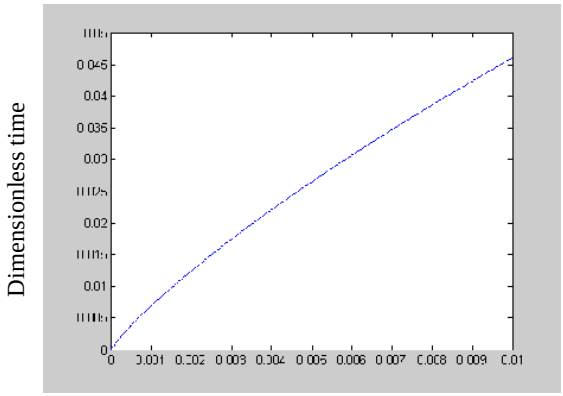

Fig. 1 Initial dimensionless delay time as function of the parameter ε

The detailed theoretical analysis of the obtained equations demands, of course, close examination of various parities of coefficients and initial derivatives by orders. However, in all cases we will obtain singularly perturbed kinetic equations which can demonstrate great diversity in behavior of solutions [16, 17].

III. Numerical Experiment And Conclusion

The initial conditions for derived kinetic equations can be set up from physical considerations. For example, we can consider formation of a new dispersed phase as a result of chemical reaction or phase transition with known intensity [3, 10, 17]. It is important that the numerical experiment should be carefully performed so that received results could be interpreted correctly. And it is especially important, considering possible variety of behavior of decisions of the basic kinetic equation. However, it wasn't the purpose in the given message.

Here the trial numerical experiment has been carried out on the basis of the reduced equation. Firstly we calculated the initial time-derivatives of clusters concentration using the first-order equation, and then we considered the calculated value as the second initial condition for the second-order equation. Besides, we didn't consider the infinite chain of the kinetic equations, and values of elements of aggregation matrixes were accepted to be equal to zero at the orders more than 6.

The comparison between the numerical results obtained using the classical Smoluchowski equation and our models (7), (8) is shown in Figures 2, 3, 4.

Results of numerical experiments confirm as a whole estimation (10). The results of these experiments have not shown essential qualitative differences from decisions of the classical equation though numerical differences on initial sites are appreciable. The visible difference between solutions of equations (7) in its reduced form and model (7), (8) can be observed at the initial period θ_{in} (see (10)):

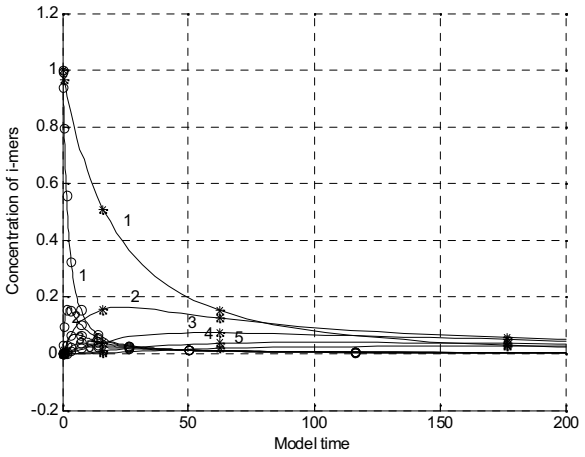

Fig. 2 Dependence of dimensionless concentration on model time for aggregation matrix Ni,j=1/ε, ε=0.1. 1 – monomer, 2 – two-mers, 3 – three-mers, 4 – four-mers, 5 – five-mers
* - numerical solution by classical Smoluchowski equation,
o-numerical solution by our non-local modification of Smoluchowski equation

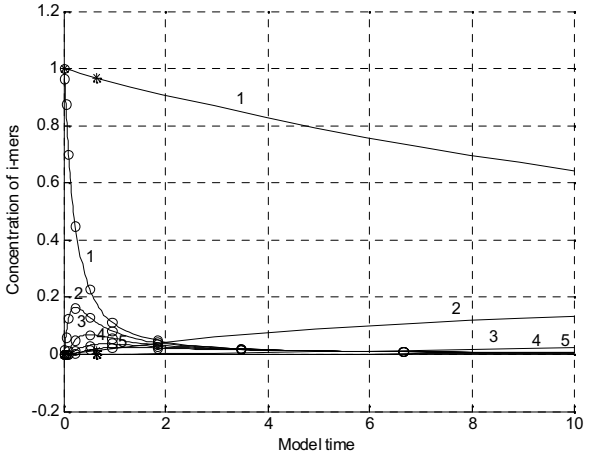

Fig. 3 Dependence of dimensionless concentration on model time for aggregation matrix $N_{i,j}=1/\varepsilon^2$, $\varepsilon=0.01$. 1 – monomer, 2 – two-mers, 3 – three-mers, 4 – four-mers, 5 – five-mers.
* - numerical solution by classical Smoluchowski equation,
o - numerical solution by our non-local modification of Smoluchowski equation

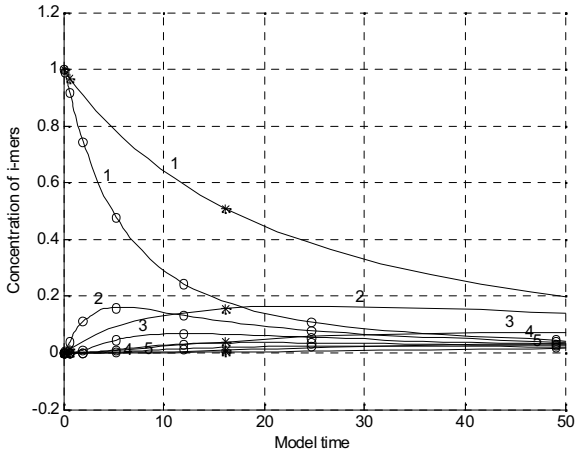

Fig. 4 Dependence of dimensionless concentration on model time for aggregation matrix. $N_{i,j}=1$, $\varepsilon=0.2$. 1 – monomer, 2 – two-mers, 3 – three-mers, 4 – four-mers, 5 – five-mers.
* - numerical solution by classical Smoluchowski equation,
o - numerical solution by our non-local modification of Smoluchowski equation

Note that depending on the specific correlation between values of the relaxation time and aggregation kernels we consider three different types of the aggregation process.

They are the fast, moderate and slow aggregations:

$$\eta_{i,j} = O\left(1/\tau_*^2\right), \quad \eta_{i,j} = O\left(1/\tau_*\right), \quad \eta_{i,j} = O(1) \tag{11}$$

As a result we can conclude that taking into account the memory phenomena in smart media under processes of cluster aggregation of different orders changes the form of the kinetic equation of aggregation, which had been neglected in the known aggregation models [16, 18].

This fact manifests itself most considerably at the initial moment, when the kinetic equation needs to be considered in its complete form (7, 8).

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