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Model of Many-Particle Aggregation in Dense Particle Systems

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The paper deals with the problem of describing many-particle aggregation in dense dispersed system without any limitation for the number of colliding clusters. The ranges of applicability of the binary model of aggregation and the known models of many-particle aggregation have been analyzed. The models for generalizing the discrete binary aggregation Smoluchowski's equation as well as the new version of the Becker - Döring kinetic equation adapted to a situation when many-body interactions are taken into account have been submitted.

1. Introduction

Well-known works (Skellam, 1951; Murray, 1989; Cohen and Murray, 1981; Levin and Segel, 1985; Mogliner, Edelstein-Keshet, 1999) describe continuum models for swarming behavior of biochemical systems. The models consist of integro-differential advection-diffusion equations, with convolution terms that describe also long range attraction and repulsion. The other approach to aggregation processes complies with a mean field description on the base of Smoluchowski's coagulation equation, which can be used in the discrete or continuum forms (Li and Logan, 1997; Logan, 2012; Menon and Pego, 2004). At the same time the Smoluchowski's equation as well as the known Becker - Döring model describe binary coagulation, and this limitation is not quite proper to the nature of the swarming process (Doering and ben-Abraham, 1988, 1989; Duncan, Soheili, 2000; Ball et al., 1986).
The so called many-body Smoluchowski's coagulation equation is a continuum model, and this limitation does not allow to describe the aggregation mechanism with more details (Aldous, 1999; Blackman and Marshall, 1994; Boehm et al., 1998).
So it is very relevant to discuss the models for generalizing the Smoluchowski's equation for discrete binary aggregation as well as the Becker - Döring kinetic equation to a situation where many-body clusters interactions (i.e. interactions which multiplicity is more than two) culminating in the formation of clusters of higher orders are taken into account. The probability of such collisions resulted in the formation of aggregates of particles is assumed to be dependent on the ratio of orders of interacting clusters (Ernst, 1986; Fadda et al., 2009).
There are two main issues here. First, it is important to assess and compare the probability of binary and multiple collisions in the time dynamics. Secondly, it is interesting to obtain estimates for the orders of coagulation kernels, depending on the orders of interacting clusters in the formation of aggregates as a result of multiple collisions (Barabasi et al., 1991; Bellomo, 1985; Di Perma and Lions, 1988, Pen'kov, 1992).
In our paper we try to justify the hypothesis that under the interaction between clusters with high-different orders, the probability of formation of the high-order cluster as a result of a many-particle aggregation can be comparable in value with the probability of a binary aggregation of clusters with close orders. On the base of these suppositions the discrete kinetic equations of many-particle aggregation in dense disperse systems have been submitted. We present also an integro-differential modification of the model with allowing for the systems with memory. This transition has been carried out with the help of relaxation transfer kernels methodology. Therefore, the goals of this paper are analysis of the range of applicability of the binary model of aggregation, analysis of the known models of many-particle aggregation and

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presentation of the original generalized kinetic equation based on the Becker-Döring model which is adapted to describing the many-particle aggregation in dense systems.

2. Analysis of suppositions

The Smoluchowski equation for binary coagulation reads

$$\frac{dC_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} N_{i-j,j} C_{i-j} C_j - C_i \sum_{j=1}^{\infty} N_{i,j} C_j \tag{1}$$

Here C_i is a concentration of i-mers, $N_{i,j}$ is a coagulation kernel and t is time. For $i=1$ the first sum in (1) is absent.

Usually, it is considered that the probability of the multiple collisions is much smaller than the probability of binary collisions (Li and Logan, 1997). It means the solutions of Eq. (1) must be agreed with the hypothesis about dominating the contribution of binary collisions in the kinetics of the aggregation process at any time.

In order to show that it is not doubt only on the long time description, let us explore how various products of the relative concentrations of the clusters change in time according to the Smoluchowski equation under the different types of coagulation kernels.

Let us assume mono-disperse initial conditions (Wattis, 2006)

$$C_r(0) = 0 \text{ for } r > 1 \text{ and } C_1(0) = 1. \tag{2}$$

The form of coagulation kernels depends on the accepted model. The constant kernels can be accepted for Brownian coagulation, the additive kernels are admissible for gravitational coagulation, and the product kernels can be used for describing the polymerisation process.

In the case of the constant kernels $N_{i,j}=1$ the problem (1), (2) has the explicit solution (Wattis, 2006)

$$C_r(t) = \frac{4}{(t+2)^2}\left(\frac{t}{t+2}\right)^{r-1}. \tag{3}$$

Using the solution (3) we will evaluate the time period for which the following inequality can be fulfilled

$$C_r C_s \le \alpha \prod_{\sum p_i = r+s} C_{p_i} \tag{4}$$

where α is a certain fixed coefficient.

So we obtain

$$0 < t \le \sqrt{1+4\alpha^{1/(N-2)}} - 1 \tag{5}$$

where N is the number of factors on the right side of (4).

Particularly, if $\alpha = 10$ and $N = 3$, the contributions of binary and triple collisions may be of comparable orders at the initial time period. For some other cases in which the problem has explicit solutions, namely for the additive kernels $N_{i,j} = \frac{1}{2}(r+s)$ and for the product kernels $N_{i,j} = rs$, the analogous results were obtained, i.e. there exists the initial period when the contributions of binary and multiple collisions may be comparable. However, as the multiple collisions are not considered in the bounds of Eq (1) the obtained explicit solutions are at the variance with accepted physical suppositions at certain time periods.

Moreover, imposing the dynamic scaling idea (Leyvraz, 2003), it can be concluded that such situation will be observed for all types of coagulation kernels obeying the homogeneity conditions (Wattis, 2006).

Thus, the general form of the dynamical scaling solution of Eq (1) with initial conditions (2) reads (Wattis, 2006)

$$C_r(t) \sim \frac{1}{s(t)^{\tau}} g\left(\frac{r}{s(t)}\right), \tag{6}$$

where g is a certain smooth function, $s(t)$ is a typical cluster size, τ is a control parameter.

Let us consider the ratio between $C_r C_p$ and $C_r C_{p/2} C_{p/2}$

$$\Lambda_p = \frac{1}{s(t)^{\tau}} g^2\left(p/2s(t)\right) \Big/ g\left(p/s(t)\right) \tag{7}$$

Owing to the conditions (2) there exists the initial period when the concentrations of clusters of low orders are essentially more than concentrations of clusters of higher orders (Brener, 2009) So, for any p the certain initial period T_p when $\Lambda_p \sim O(1)$ will be observed.

Another important aspect while evaluating the multiplicity of particle collisions is a specific time interval, during which one collision terminates. Then the number of collisions terminating during this relaxation time can be identified as a multiplicity of collisions. The kinetic equation for binary aggregation in the dispersed system with allowing for the relaxation time of collisions can be written as follows (Brener, 2011; Brener et al., 2009)

$$\frac{dC_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \int_0^t \int_0^t N_{j,i-j} C_j(t_1) C_{i-j}(t_2) dt_1 dt_2 - \sum_{j=1}^{\infty} \int_0^t \int_0^t N_{i,j} C_i(t_1) C_j(t_2) dt_1 dt_2, \tag{8}$$

where $N_{i,j}$ are functions of the delay times $(t-t_1)$ and $(t-t_2)$ (Brener, 2011). If a typical multiplicity of collisions is denoted as k, then $\theta_{in} = 1/k$ is a dimensionless time-scale of one collision. Using the relaxation transfer kernels approach (Brener, 2006; Brener, 2011) the following estimation for θ_{in} was obtained

$$\theta_{in} \sim -\left(\tau_{i,j}/T\right) \ln\left(\tau_{i,j}/T\right). \tag{9}$$

Here $\tau_{i,j}$ is the relaxation time of aggregation process for two clusters. The relaxation time $\tau_{i,j}$ can be calculated from physical meanings (Brener, 2011), and parameter T is the characteristic process time (for example, residential time of components in an apparatus).

The account of collisions multiplicity is especially reasonable for real industrial bio-technological apparatuses with dense chemical or bio-chemical disperse systems which are possessed of sources of low orders clusters (Friedlander, 2000; Davies et al., 1999). In fact, for the situations, considered above, a total concentration of various orders clusters in the disperse system monotonously decreases in time and tends to zero (Wattis, 2006). Because of that phenomenon the probability of multiple collisions also decreases rather quickly. But if the system contains a positive source of monomers with intensity ω^2, the new kinetic equation for $i = 1$ can be written as

$$\frac{dC_1}{dt} = -C_1 \sum_{j=1}^{\infty} N_{i,j} C_j + \omega^2 / 2. \tag{10}$$

System (1), (10) with initial conditions (2) and constant coagulation kernels was solved with the help of the generating functions method. Here the complete solution is not adduced because of its bulky appearance. The evolution of total concentration of various orders clusters $M_0(t)$ according to this model reads

$$M_0(t) = \left[\omega(\omega+1)\exp(t) - \omega(\omega-1)\right] / \left[(\omega+1)\exp(t) + (\omega-1)\right]. \quad (11)$$

Function (11) monotonously increases for $\omega > 1$ end tends to ω . It leads to the system remains dense, and the probability of multiple collisions may be not too small.

3. Kinetic equations of many-particle aggregation

The formal generalization of Smoluchowski equation as applied to the *n*-particle collisions reads (Krapivski, 1991; Krivitski, 1995)

$$\frac{dC_i}{dt} = \frac{1}{n!} \sum_{j_1+j_2+\cdots+j_n=i} N(j_1, j_2, ..., j_n) C_{j_1} C_{j_2} \cdots C_{j_n} - \frac{C_i}{(n-1)!} \sum_{j_1, j_2, \ldots j_{n-1}=1}^{\infty} N(i, j_1, j_2, ..., j_{n-1}) C_{j_1} C_{j_2} ... C_{j_{n-1}} \quad (12)$$

The explicit solutions of Eq (12) can be obtained with the help of generating functions for the certain special forms of aggregation kernels (Wattis, 2006; Zahnov et al., 2011; Leyvraz, 2003).
However, this form is not most general, as the total number of colliding particles is restricted without any well-founded estimates of the limit. The more thorough mathematical investigation of the coagulation processes in dense systems with allowing for many-particle collisions was carried out by Pen'kov (Pen'kov, 1992). At the same time the main conclusions of this work have limited practical significance as they were obtained on quasi-linear approximation. Besides, the problem of upper limits of the number of colliding particles is not clarified too.
For correct description of the transition procedure from discrete collisions to the swarming process in dense system the kinetic equation should account multiple collisions without any beforehand set limits of the number of colliding particles. The appropriate original models are submitted below.
The first model is a modification of the Smoluchowski equation that covers the case of multiple collisions. This model can be written as

$$\frac{dC_i}{dt} = \sum_{n=2}^{i} A_n - C_i \sum_{n=2}^{\infty} B_n \ , \quad (13)$$

where

$$A_n = \frac{1}{n!} \sum_{j_1+j_2+\cdots+j_n=i} N(j_1, j_2, ..., j_n) C_{j_1} C_{j_2} \cdots C_{j_n} \ ; \quad (14)$$

$$B_n = -\frac{1}{(n-1)!} \sum_{j_1, j_2, \ldots j_{n-1}=1}^{\infty} N(i, j_1, j_2, ..., j_{n-1}) C_{j_1} C_{j_2} ... C_{j_{n-1}} \ . \quad (15)$$

Every of inner sums A_n consists of $\mathrm{P}_n(i)$ summands, where $\mathrm{P}_n(i)$ is the number of every possible different partitions of the integer i on n summands. Unfortunately, the strong analysis of the model () becomes especially complex since though the upper limit in the first sum in Eq (13) is clearly defined, but $\mathrm{P}_n(i)$ can not be indicated with a simple formula. The method for calculating $\mathrm{P}_n(i)$ is known (Andrews, 1976), but it entails bulk mathematical procedures and hardly suitable for engineering practice. At the same time the computer simulation of aggregation processes on the base of model (13-15) would be interesting.
The obstacle inherent to Eq (13) can be removed under deriving the generalized aggregation equation on the base of the Becker-Döring model (Doering and ben-Abraham, 1988, 1989, Wattis, 2006). Thus, the second original generalized kinetic equation which is submitted for discussion in this work reads

$$\frac{dC_i}{dt} = \sum_{k=1}^{i-1} \left(a_{(i-k),k} C_{i-k} (C_1)^k - b_{i,k} C_i \right) - \sum_{k=1}^{\infty} \left(a_{(i+k),k} C_i (C_1)^k - b_{(i+k),k} C_{i+k} \right). \quad (16)$$

Here $a_{r,k}$ is the forward rate of aggregating the r - order cluster with k monomers; $b_{r,k}$ is the backward rate of the fragmentation of the r - order cluster by throwing off k monomers;
The main question that is intrinsic to all considered aggregation models is how the value of coagulation kernels depends on the orders of interacting clusters. As to the generalized Smoluchowski equation this question looks very complex (Yu Jiang and Hugang, 1988; 1989). For the n-particle coagulation the intensity of the clusters merger can be determined by the formula (Yu Jiang and Hu Gang, 1989)

$$N(j_1, j_2, ...j_n) = s_{j_1} s_{j_2} ... s_{j_n} . \tag{17}$$

$$s_j = j^{\omega_j} , \tag{18}$$

where $\omega_j \le 1$ is a geometric factor characterizing the surface of a j-mer. For compact cluster we can evaluate $\omega \sim 2/3$ but for a fractal cluster the degree ω should be defined from the cluster fractal dimension.
For the multiple aggregation process according to the modified Becker-Döring model (Eq (16) we offer the new estimation. In that case the situation looks somewhat easier. Namely, it is reasonable to introduce a certain limit number k^* (collision multiplicity) of monomers which can be captured by the surface of big r - mer. This limit can be estimated through the number of active reaction centres on a surface of high-order cluster (Slemrod, 1990; Spicer and Pratsinis, 1996).
Therefore, we obtain

$$a_{r,k} \sim \beta r^{\omega} \sigma^{\mu\left(k-k^*\right)}, \tag{19}$$

$$k_{\max} = k^* \sim \delta r^{\omega}, \tag{20}$$

where β is collision efficiency, σ is a cross section of particle capture, $\mu < 0$ and δ are certain coefficients dependent on media properties.
In contradistinction to the mentioned above approaches the approach based on Eq. (16) and relations (19), (20) allows to use the well-founded physical methods for evaluating collisions multiplicity and calculating the coagulation kernels (Flory, 1953, Spicer and Pratsinis, 1996).
Details of gelation process according to the submitted model need special investigations (Zahnov et al., 2011).

4. Conclusions

The article presents analysis of possible approaches to modelling a many-particle aggregation in dense disperse systems. It is shown that the account of many-particle collisions may be important at the initial period of the process and in the case where there are sources of low-orders clusters in the system. In particular, it is shown that the contributions of many-particle collisions may be of comparable orders at the initial time period in the case of constant coagulation kernels. The correct forms of generalized kinetic equations based both on the Smoluchowski equation and on the Becker-Döring model have been submitted and discussed. It can be concluded that generalized Becker-Döring model is preferable for describing many-particle aggregation processes. The main arguments are that for Becker-Döring model adapted to many-particle collisions the uncertainty in number of summands can be avoided and the way to calculating the coagulations kernels become more clear.

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