Novel considerations on the scaling of rate kernels in the equations of cluster aggregation

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Novel considerations on the scaling of rate kernels in the equations of cluster aggregation

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Abstract. The paper deals with the problem of scaling under calculating the rate kernels in the Smoluchowski equation of binary aggregation. Compact overview and critical analysis of the practiced today approaches have been submitted. It is shown that the known methods do not take sufficient account of the role of cluster internal restructuring under self-organization phenomena and dependence of their outward aggregation activity on the prehistory of cluster formation and their fine structure. The novel considerations on these two classes of problems which can be useful for creating a more careful methodology have been submitted.

1. Introduction

In order to correctly calculating the intensity of heat and mass transfer processes in the design of production of materials with a complex internal structure, it is necessary to take into account relaxation times and the interaction of the structural components of the medium [1]. Similar problems also arise when modelling processes “with memory”. Dynamic structures interacting in systems change their characteristics in time, which must be taken into account in mathematical models of transport processes. The urgency of this problem is connected with the limited resources of effective control over such processes. It is important to correctly calculate and select the optimal values of the determining parameters [2].

All of the above is fully applicable to the processes of clusters aggregation in nano-dispersed media [3]. The history of researching and analyzing the Smoluchowski equation of the binary irreversible aggregation has been going on for over 100 years [4]. However, there is no reason to believe that this topic has been exhausted [5]. Although the suppositions leading to the derivation of the Smoluchowski kinetic equation are fairly transparent and basically follow the concept used for obtaining classical chemical kinetics equations, these equations lead to some fundamental problems due to the principal model nature of rate constants [6]. Namely, researches are still unable to close all problems in relation to the physical interpretation and correct description of the rate kernels in Smoluchowski equation for macroscopic scale clusters aggregation [7]. Currently, a fairly reasonable regime classification of the kinetics of aggregation into DLCA (diffusion-limited cluster aggregation) and RLCA (reaction-limited cluster aggregation) modes has been established, and the process can also occur in the area of mixed kinetics [8].

The analysis of various works shows that a certain scheme has now been established for the modeling of aggregation kernels, for example [9].

First, the kernels have been established in the form of an ansatz, which is a product of two factors [10]. The first factor rather conditionally describes the dependence of the total capture cross section of colliding clusters on their orders, and the second factor describes the dependence of cluster mobility, that is, the intensity of random drift before a collision, also in dependence on their orders [11]. It is without saying, the conditional diffusion coefficients of complex clusters, which are present in the second factor, cannot be generally identified with the molecular diffusion coefficients [12]. Second, the transition from DLCA to RLCA is considered by analyzing the hierarchy of the random drift and capture times, as well as by evaluating the corresponding probabilities of these stages of cluster aggregation in the collision process [13]. Third, the exponents included in the model ansatz equation are supposed to be associated with the fractal dimensions of complex high-order clusters, and they are selected from the results of computer simulations of random drift and collisions of particles over lattices of various configurations [14].

At the same time, the problems of dependence of fractal dimensions, as well as effective capture cross-sections on cluster orders and hierarchy of kinetic times, are not only poorly understood, but are not conceptually posed clearly. Besides, the known today models of aggregation do not take into account the influence of clusters age on their aggregation activity [15]. All this explains why the models currently used do not guarantee adequacy in describing real aggregation processes in polydispersed media [16].

The main goal of this paper is to give compact overview and critical analysis of the practiced today approaches and to present some novel considerations about the problems mentioned which can be relevant to create more physically reasonable and more flexible models that will be applied to technological design of the dispersive nano-systems.

2. Basic conceptual premises

2.1. Considerations on the role of cluster internal transformation and its age

The aggregation activity of a fractal cluster depends on the number of reactive centres on its surface. However, the surface can be of a complex form depending on the order of the cluster. If the process of adding new particles to a cluster of a certain order stopped, then after a while it could acquire a stable structure characterized by an absolute or local minimum of the free energy of the cluster surface, unless there are no interactions that can overcome the energy barrier of a given local extremum of surface energy [15].

The structure of cluster can be changed between collisions by the way of self-organization with creating certain patterns, up to the acquisition of a stable or metastable structure, which can be perturbed during the new collision. The self-organization of the cluster structure in accordance with the laws of thermodynamics is realized as a drift towards stable or metastable states. For a cluster of higher order, this self-organization can occur both on a global cluster scale and at local scales with the formation of stable screened domains closed for external reactivity.

The evolution of a cluster of a given order between successive collisions occurs in accordance with the inner kinetic equation, and manifests itself in a change in the properties of the cluster. The inner equation should describe the change in the parameters of the aggregation kernels depending on the age of the cluster of a given order. In other words, the internal kinetic equation describes the change in the surface density of reactive centres [17], or the fraction of the unscreened reactive surface of the cluster [18] as a function of the cluster lifetime of a given order, in contrast to the outward kinetic equation of aggregation describing the evolution of the concentrations of clusters of different orders [19].

The internal and external levels of kinetics can be combined by representing aggregation kernels as a product of two factors, one of which describes the change in the concentration of clusters of a given order taking into account their lifetimes distribution, and the second - the change in the properties of the cluster over time [15]. In order to realize such approach the method of the relaxation transfer kernels for deriving kinetic equations describing the clusters aggregation process with allowance for the possible changes in their properties depending on age seems quite reasonable.

The appropriate modified Smoluchowski equations read [20]

$$\frac{dC_I}{dt} = \frac{1}{2}\sum_{J=1}^{I-1}\int_0^t\int_0^t N_{J,I-J}C_J(t_1)C_{I-J}(t_2)dt_1dt_2 - \sum_{J=1}^{\infty}\int_0^t\int_0^t N_{I,J}C_I(t_1)C_J(t_2)dt_1dt_2\,. \quad (1)$$

Here C_I is the concentration of I - th order clusters, $N_{I,J}$ is the aggregation kernels, t is the time. Thus, in according to the submitted idea, the aggregation kernels are can be written in the form

$$N_{I,J} = N_{I,J}^{(in)} \cdot N_{I,J}^{(out)}\,. \quad (2)$$

The internal factor $N_{I,J}^{(in)}$ should be obtained by resolving some internal kinetic equation. The formation of stable (screened) domains can be described as reducing the local fluctuations. Each reduction means a transition to the new state with its own level of free surface energy of the cluster (figure 1). Figure 1 schematically depicts the formation of screened stable islands in the cluster global structure under realizing the transitions between the free energy levels of the cluster surface [15].

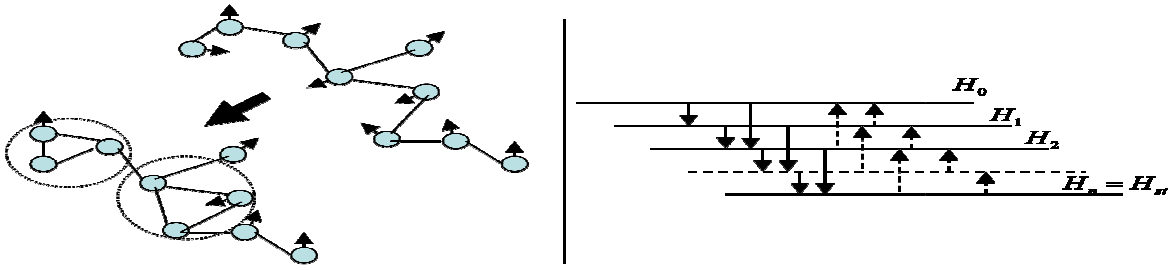

Figure 1. A discrete scheme for calculating the evolution of the concentration of clusters of a give order, taking into account the age distribution

In the process of aggregation, several characteristic times compete. They are: the diffusion drifts times of clusters before a collision, the relaxation times of collisions with possible aggregates formations or with subsequent separate drift of clusters after collision, and the relaxation times of the self-organization of the clusters structure. As it was already noted in the Introduction, some approximate analysis of the competition between times of random drift and collisions was carried out in several papers [13, 21].

Let us consider now the transition times from one cluster state to another, i.e. the characteristic times of transformations of the cluster structure between successive collisions with the appearance of screened “islands of stability”. These transformation times can be organized into the "restructuring times matrix" - τ_{ij}^{tr}, where τ_{lm}^{tr} is the characteristic time of the cluster transition from one state (l) to another (m). If the frequency of transitions between states is ω_{lm}^{tr}, then it is possible to define a matrix of probabilities of local transformations as

$$p_{lm}^{tr} = \tau_{lm}^{tr}\omega_{lm}^{tr}\,. \quad (3)$$

The ratio between frequencies of collisions and structural transformations of clusters in rarefied and dense dispersed systems will be, of course, different. However, for sufficiently rarefied disperse systems, namely for which the binary aggregation equations are valid, justice of Bogolyubov’s

analysis for the characteristic collision chain times in the Born-Bogolyubov-Kirkwood-Green-Ivon scheme (BBKGI) [22] can be allowed. This assumption reads

$$\tau_{lm}^{tr} << \tau_c << \tau_{dif} . \tag{4}$$

Then, if the cluster transformation process is irreversible, and transition times between various states are comparable, it can be assumed that the probabilities density of single (i.e., per one level) transitions between collisions does not much change [15].

Hence, for the probability density of a number of successive transitions, the Poisson law follows

$$p_k^{tr} = \frac{(\lambda t)^k}{k!} \exp(-\lambda t) . \tag{5}$$

In general setting, it will be necessary to use various schemes for deriving the internal kinetic equation and estimating the temporal distribution of the transition chain probability based on the transition probability matrix. Since the kinetic equation describing the evolution of cluster states in the general case should give relaxation to an equilibrium state, it will probably be possible to use an equation of the Crook – Bhatnagar – Gross type [23] as an acceptable mathematical model.

2.2. Considerations on the influence of clusters outward reactivity on rate kernels

Most often found in modern works, the ansatz for modelling aggregation kernels in the case of DLCA has the following structure [21]

$$N_{I,J} = k_{11}\left(R_I + R_J\right)\left(D_I + D_J\right). \tag{6}$$

Here R_I is the conditional radius, and D_I is the conditional diffusion coefficient (mobility) of the fractal cluster of *I*-th order. This ansatz goes back to the works by Smoluchowski. The first factor is a conditional cross section of collision and capture, and the second factor is intended to describe the mobility of clusters [24].

Usually, from considerations of symmetric scaling, the conditional radius and the conditional diffusion coefficient in the ansatz (6) are written as

$$R_I = I^{\mu}, \; D_I = I^{\nu} . \tag{7}$$

Exponents μ and ν are represented as functions of the fractal dimensions of clusters. However, it is curious that the same authors in different works use exponents expressed in different dimensions without additional comments.

For example, in works by Odriozola with coauthors the following expressions are used [21, 13]: $\mu = 1/d_f$, $\nu = -1/d_h$, and $\mu = 1/d_f$, $\nu = -1/d_f$. Here d_f is the geometric fractal dimension of the cluster, and d_h is the hydrodynamic fractal dimension. Such uncertainty is found in a number of other works too [4].

It can be concluded, such uncertainty is due to too rough schematic character of expression (6), which completely ignores the fine structure both of a complex fractal cluster and its surface. Besides, it is difficult to find a convincing rationale for the use of identical fractal dimensions for clusters of different orders [25].

Further, the several initial positions are proposed, on the basis of which a kinetic equation for the calculation of aggregation kernels taking into account the external aggregative activity of colliding clusters of various orders changing in the process of collisions can be probably constructed.

1. Scales of "reactive dots and spots" and their distribution over the fractal cluster surface control the aggregation activity. And these factors depend on the cluster order.

2. The reactive fosses can serve as potential pitfalls for clusters that have appropriate orders, but they cannot provide reliable capture of clusters with an order corresponding to a size exceeding the maximum characteristic size of the fosses. It can be assumed that although such a capture is still possible, it does not lead to the creation of a stable cluster. However, if the cluster that has been formed will not be destroyed for some time, it can acquire a stable form by restructuring.

3. The bond strength of clusters in the process of collision is determined by several factors, and one of the mostly influent factor is the correlation between the characteristic sizes of the larger cluster (in other words, of the cluster of a larger order) and the sizes of its traps on the active surface. These sizes determine the probability of possible orders of clusters that could be captured in the collision.

4. Another one factor that plays an important role in the offered model is the correlation between common surfaces (and masses) of collided clusters and active surfaces of the capture. It is important also to differ the situations when aggregation is controlled by central or surface forces.

5. The adhesion strength of clusters is supposed to be determined by the number of occupied reactive centers according to the scheme "center to center".

6. As a result, the characteristic engagement time depends on orders of the clusters and the density of active centers on the engagement surface.

Some helpful calculations for the implementation of the above points in the form of mathematical model can be found in a number of rather old works [18, 26]. In the analysis of the penetration and invagination processes occurring during the formation of a new cluster as a result of aggregation of clusters of various orders, it can be concluded that its fractal dimension and surface reactivity will be depend not only on the complete cluster order but on the prehistory of its formation too.

This background can influence the properties of a cluster not only through its age, as it is shown in Section *2.1*, but also due to that that clusters having the same order and even the same age can be formed from clusters of different orders during aggregation.

Let us the cluster of *I*-th order is formed from k clusters of different orders:

$$I = J_0 + \sum_{s=1}^{k} J_s \,. \tag{8}$$

Here J_0 is the order of an initial cluster playing the role of nucleus or germ [27].

The estimate for the fractal dimension of the active unscreened surface can be obtained by counting the active centers arising after the capture and penetration of a new cluster into another cluster [26].

Moreover, during the formation of aggregates from clusters of different orders, spatially non-isomorphic clusters with the same order may appear. Figure 2 depicts this aspect in conditional form as the construction of non-isomorphic graphs. Clusters of the same orders but with non-isomorphic structures may have different density of reactive centers, and different characteristic radiuses.

The number of arising centers N_a can be evaluated as follows

$$N_a \sim R^{d_f - 1} \cdot \lambda \,, \tag{9}$$

where R is the characteristic radius of the cluster-recipient, λ is the characteristic penetration depth for the captured cluster [18].

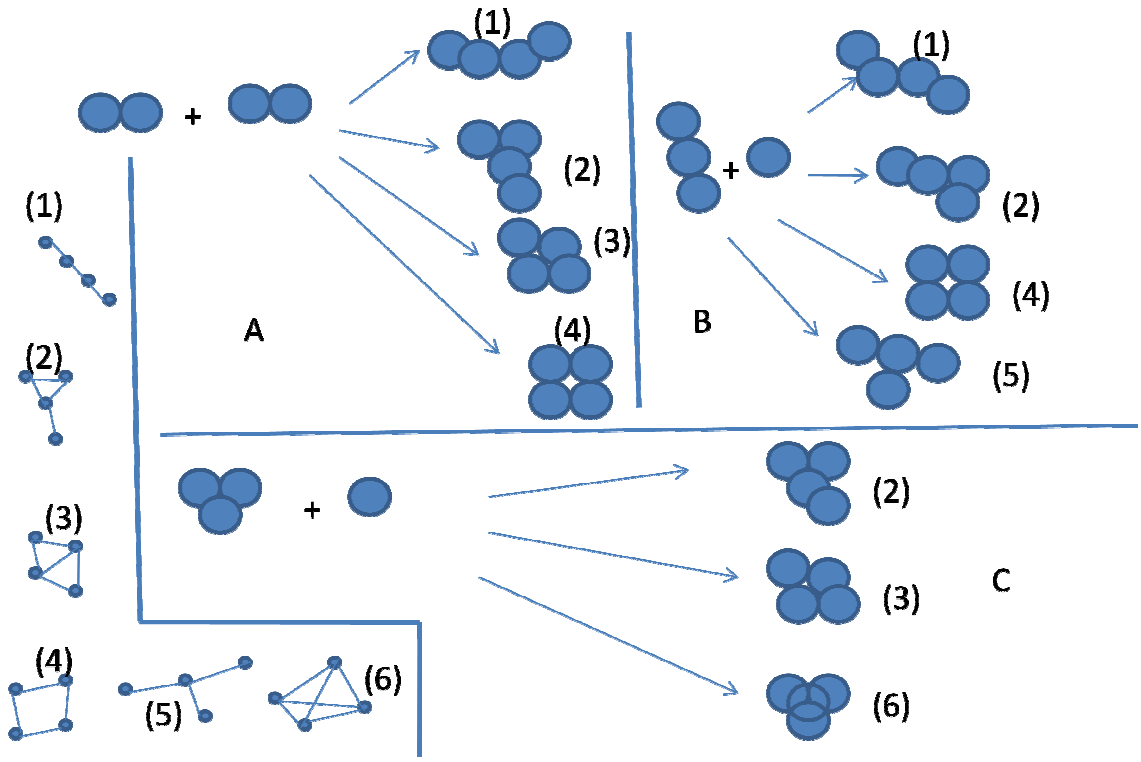

Figure 2. Various non-isomorphic structures of clusters of conditionally fourth order that may occur during the aggregation of two clusters.

The process is considered in the natural physical 3D space. With the help of penetration theory methods, the following recurrent estimate of the change in the fractal dimension of the active surface when a new cluster is captured has been obtained [18]

$$d_{f(s+1)} \sim d_{f(s)} + \frac{3 - d_{f(s)}}{d_s}. \tag{10}$$

Here $d_{f(s)}$ is the fractal dimension of the cluster-recipient after a collision with number *s,* and d_s is the fractal dimension of the captured cluster. A correct methodology for calculating the aggregation kernels should be developed on the base of estimates (8), (9), (10).

3. Conclusions

It can be concluded that two important aspects while calculating and scaling the rate kernels in the Smoluchowski equation of binary aggregation are still poorly understood. They are: the role of clusters internal transformations and their fine structure as well as the change in their aggregation activity due to the prehistory of formation. In order to resolve these problems the aggregation kernels are proposed to be presented as a product of two factors, one of which describes the change in the concentration of clusters of a given order taking into account their lifetimes distribution, and the second - the change in the properties of the cluster over time has been presented.

As for the first factor, since the kinetic equation describing the evolution of cluster states in the general case should give relaxation to an equilibrium state, the use of an equation of the Crook – Bhatnagar – Gross type is promising for creating an accurate model. It can be concluded that correct model for accounting the second factor should be developed with the help of penetration theory

methods, and preliminary recurrent estimate of the change in the fractal dimension of the active surface when a new cluster is captured has been obtained.

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