Competing role of catalysis-coagulation and catalysis-fragmentation in kinetic aggregation behaviours*

Li Xiao-Dong(李晓东), Lin Zhen-Quan(林振权)†, Song Mei-Xia(宋美霞), and Ke Jian-Hong(柯见洪)

Department of Physics, Wenzhou University, Wenzhou 325035*, China*

(Received 20 March 2010; revised manuscript received 3 August 2010)

We propose a kinetic aggregation model where species A aggregates evolve by the catalysis-coagulation and the catalysis-fragmentation, while the catalyst aggregates of the same species B or C perform self-coagulation processes. By means of the generalized Smoluchowski rate equation based on the mean-field assumption, we study the kinetic behaviours of the system with the catalysis-coagulation rate kernel $K(i,j;l) \propto l^{\nu}$ and the catalysis-fragmentation rate kernel $F(i,j;l) \propto l^{\mu}$, where l is the size of the catalyst aggregate, and ν and μ are two parameters reflecting the dependence of the catalysis reaction on the size of the catalyst aggregate. The relation between the values of parameters ν and μ reflects the competing roles between the two catalysis processes in the kinetic evolution of species A. It is found that the competing roles of the catalysis-coagulation and catalysis-fragmentation in the kinetic aggregation behaviours are not determined simply by the relation between the two parameters ν and μ, but also depend on the values of these two parameters. When $\nu > \mu$ and $\nu \geq 0$, the kinetic evolution of species A is dominated by the catalysis-coagulation and its aggregate size distribution $a_k(t)$ obeys the conventional or generalized scaling law; when $\nu < \mu$ and $\nu \geq 0$ or $\nu < 0$ but $\mu \geq 0$, the catalysis-fragmentation process may play a dominating role and $a_k(t)$ approaches the scale-free form; and in other cases, a balance is established between the two competing processes at large times and $a_k(t)$ obeys a modified scaling law.

Keywords: kinetic aggregation behaviour, catalysis-coagulation, catalysis-fragmentation, rate equations

PACC: 8220M, 6810J, 8230

1. Introduction

Aggregation growth phenomena are popular and important in a wide variety of fields in nature. For example, aggregation underlies the evolution of planetary systems in astrophysics, cloud formation and dust accumulation in atmospheric sciences,[1−3] as well as polymer and gel formation in chemical physics.[4−6] The irreversible aggregation of clusters is an important aggregation process, for which much research effort has been made and a considerable understanding of the evolution behaviours of various aggregation processes has been achieved.[7] This binary coalescence process was then generalized to multi-aggregate (or n-polymer) stochastic aggregation, and then aggregation processes through aggregation–annihilation mechanisms were proposed.[8−13] On the other hand, the reversible aggregation of aggregates is also an important phenomenon occurring in a variety of situations and has aroused the great interest.[14,15] It was found that the size distribution of aggregates may approach a steady state in the long-time limit.[16] In recent years, considerable interest has been aroused in a variety of aggregations and other reaction mechanisms.[17−21] These different mechanisms provide a good description for the evolution of aggregation, and the results show that these mechanisms give rise to many abundant kinetic behaviours.

However, most of these studies focused only on aggregation models with the self-coagulation of aggregates of the same species and self-fragmentation processes. In addition, there also exist some other growth mechanisms in physics and social science. For example, in the case in which the aggregates are chemically stable and cannot aggregate by themselves under normal physical condition, one may add a certain catalyst to make the aggregation possible. Burlatsky and Ovchinnikov,[22] Burlatsky and Moreau,[23] and Oshanin *et al.*[24] proposed a three-molecule catalytically activated reaction model (CARM), in which the

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10875086 and 10775104).

†Corresponding author. E-mail: zqlin@wzu.edu.cn; linzhenquan@yahoo.com.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

elementary reaction step is $A + B + C \rightarrow$ product (where A and B represent two different types of stable species and C denotes a catalytic substance), and they incisively analysed its kinetics by extending the Smoluchowski approach.

In our previous work, Ke and Lin[25,26] have introduced several catalysis-driven aggregation models and studied their kinetic behaviours based on the CARM. In those models, the first elementary reaction step is a reversible reaction, $A_i + B_l \rightleftarrows A_iB_l$, and the second step is an irreversible reaction, $A_iB_l + A_j \rightarrow A_{i+j} + B_l^*$, where A is a kind of chemically stable species that cannot coalesce by itself, B is a catalyst, and B^* is the product of the catalyst. They assumed that the reversible reaction reached its steady state in no time. Thus, the catalytic reaction is controlled by the second step. The catalytic reaction then is $A_i + A_j + B_l \xrightarrow{K(i;j)} A_{i+j} + B_l^*$. These processes exhibit much more abundant kinetic behaviours than those in single aggregation by itself. After that, Ke *et al.*[27] also studied several aggregation models with catalysis-driven fragmentation, in which two aggregates of the same species A bond spontaneously formed a large aggregate while larger A aggregates broke up only with the help of catalyst B. The aggregation reaction is $A_i + A_j \xrightarrow{K_A(i;j)} A_{i+j}$ and $A_{i+j} + B_l \xrightarrow{J_A(i;j)} A_i + A_j + B_l$. It is found that for some situations, the catalyst aggregates may aggregate by themselves. This is assumed to proceed in the reaction scheme $B_i + B_j \xrightarrow{K_B(i;j)} B_{i+j}$. The results show that kinetics of the aggregation process depends strongly on whether the catalyst aggregates by itself.

In other cases, the reactions of catalysis-aggregation and catalysis-fragmentation will coexist in the same system and drive the system to reach a steady state or give birth to many interesting results. For example, in the macromolecule chemistry,[28] the aggregation or fragmentation of some high polymers cannot take place by itself, it needs some catalyzer to catalyze or control the reaction, while the aggregation of catalyzer will also affect the aggregation rate of catalyzed aggregation. On the other hand, since some parts of the catalyst may aggregate by themselves, this growth phenomenon will reduce the size and the total quantity of catalyze so that the catalyst may lose or weak its catalytic ability sometimes, the aggregation or fragmentation rate of the aggregates will slow down or speed up. So the rate of the aggregation reaction is dependent on the details (including the concentration and the catalytic ability) of the catalyst. All these different mechanisms unfold a lot of rich kinetic behaviours of the aggregation system.

Motivated by these studies, we propose a catalysis-driven reversible aggregation model. In this model, there are three distinct species of aggregates in the system, i.e., A, B, and C. Aggregates of species A are chemically stable and cannot aggregate by themselves. However, two aggregates of species A can coagulate with the help of an aggregate of species B, and an larger aggregate of species A can fragmentate with the help of an aggregate of species C. These two reactions are catalysis-coagulation and the catalysis-fragmentation, respectively. The whole catalytic reactions then are $A_i + A_j + B_l \xrightarrow{K(i,j;l)} A_{i+j} + B_l$ and $A_{i+j} + C_l \xrightarrow{F(i,j;l)} A_i + A_j + C_l$, where A_i denotes an aggregate that consists of i monomers of species A; $K(i,j;l)$ is the rate kernel of the coagulation between the aggregates A_i and A_j; $F(i,j;l)$ is the rate kernel of the reverse process in which the aggregate A_{i+j} breaks into two smaller aggregates A_i and A_j. The catalyst aggregates may coagulate by themselves: $B_i + B_j \xrightarrow{I(i,j)} B_{i+j}$ and $C_i + C_j \xrightarrow{J(i,j)} C_{i+j}$, where $I(i,j)$ and $J(i,j)$ are the self-coagulation rate kernels of species B and C, respectively.

The theoretical approach to reversible aggregation processes can be preformed in the mean-field limit. The mean-field assumption neglects the spatial fluctuation of the reactant densities and is applied to the case in which the spatial dimension d of the system is greater than or equal to a critical dimension d_c. However, for the case of $d < d_c$, the fluctuation in the density of reactants may lead to a dimension-dependent kinetic behaviour in long-time limit and some more sophisticated methods to investigate the kinetics of such low-dimensional systems are required.[6,29,30] It is found that for an irreversible aggregation system $d_c = 2$.[6] On the other hand, Family *et al.*[30] verified that for the general reversible case the mean-field results are valid in the $d_c \geqslant 1$ case. Since our model interpolates between the irreversible and the reversible aggregation processes, it is reasonable to consider the critical dimension d_c of our system to be less than 2. For simplicity, we assume that the dimension of our system is greater than or equal to 2 and the mean-field approach is thus valid. The results show that the evolution behaviours of species A depend crucially on the competition between the catalysis-coagulation and the catalysis-fragmentation.

The rest of this paper is organized as follows. In Section 2, we introduce a model of aggregation growth with competition between the catalysis-driven fragmentation and the catalysis-driven aggregation processes in the reversible aggregation, and describe the outline of the generalized Smoluchowski's rate equation approach to the study of the kinetic evolution behaviours of the aggregate size distributions. In Section 3, we study the kinetics of the system in various cases with different values of the parameters ν and μ reflecting the competition between the catalysis-coagulation and the catalysis-fragmentation. Finally, a brief summary is given in Section 4.

2. Aggregation model with catalysis-coagulation and catalysis-fragmentation

The investigation into the kinetic behaviours of the aggregation process focuses mainly on the evolution of the concentrations of the aggregates. Here they are the aggregate size distributions, $a_k(t)$, $b_k(t)$ and $c_k(t)$ of species A, B and C, respectively. The aggregate size distribution $a_k(t)$ denotes the concentration or the number of aggregates A_k, and so do the aggregate size distributions $b_k(t)$ and $c_k(t)$. The theoretical approach to the investigation of the kinetics of the aggregation process can be based on the rate equations in the mean-field frame on the assumption that the reaction proceeds at a rate proportional to the reactant concentrations. We generalize the rate equation for the catalysis-driven aggregation process, and write the corresponding rate equations for our system as follows:

$$\begin{aligned}\frac{\mathrm{d}a_k(t)}{\mathrm{d}t} = & \frac{1}{2}\sum_{i+j=k}^{\infty}\sum_{l=1}^{\infty}K(i,j;l)a_ia_jb_l \\ & -\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}K(k,j;l)a_ka_jb_l \\ & -\frac{1}{2}\sum_{i+j=k}^{\infty}\sum_{l=1}^{\infty}F(i,j;l)a_{i+j}c_l \\ & +\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}F(k,j;l)a_{k+j}c_l, \qquad (1)\end{aligned}$$

$$\frac{\mathrm{d}b_k(t)}{\mathrm{d}t} = \frac{1}{2}\sum_{i+j=k}^{\infty}I(i,j)b_ib_j - \sum_{j=1}^{\infty}I(k,j)b_kb_j, \qquad (2)$$

$$\frac{\mathrm{d}c_k(t)}{\mathrm{d}t} = \frac{1}{2}\sum_{i+j=k}^{\infty}J(i,j)c_ic_j - \sum_{j=1}^{\infty}J(k,j)c_kc_j. \qquad (3)$$

In Eq. (1), the first and the fourth terms on the right-hand side account for the gains in $a_k(t)$ due to the reaction channels $A_i + A_j + B_l \xrightarrow{K(i,j;l)} A_{i+j} + B_l$ and $A_{k+j} + C_l \xrightarrow{F(k,j;l)} A_k + A_j + C_l$. The second and the third terms account for the losses in $a_k(t)$ due to the reaction channels $A_k + A_j + B_l \xrightarrow{K(k,j;l)} A_{k+j} + B_l$ and $A_k + C_l \xrightarrow{F(i,j;l)} A_i + A_j + C_l$. In Eq. (2) [similarly in Eq. (3)], the first term accounts for the gain in $b_k(t)$ due to the aggregation $B_i + B_j \xrightarrow{I(i,j)} B_{i+j}$ and the second term accounts for the loss in $b_k(t)$ due to the migration $B_k + B_j \xrightarrow{I(k,j)} B_{k+j}$.

As we aim to investigate the dependence of the kinetics of our system on the competition between the catalysis-coagulation and the catalysis-fragmentation, we only consider all the aggregates to be one-dimensional chains and assume the rate kernel to depend only on the size of the catalyst aggregate, and the rate kernels of the catalysis-coagulation and the catalysis-fragmentation to be $K(i,j;l) = Kl^{\nu}$ and $F(i,j;l) = Fl^{\mu}$, respectively, where K and F are two proportional constants, and ν and μ are two parameters which represent the catalytic abilities of the catalyst aggregates of B and C species, respectively. For the cases where both species A and B (or C) are polymers and the bonding between any two polymers takes place only at their surfaces, one may consider $K(i,j;l) = S_l$, where S_l represents the effective catalytic surface area of an aggregate of B species of size l. For large l, $S_l \sim l^{\nu}$ (where ν denotes a geometric index characterizing the catalytic surface of an l-mer, e.g., for compact clusters $\nu = 2/3$),[31] and it is found that $0 \leq \nu \leq 1$. For some other situations, the aggregation of the aggregates does not depend merely on their geometric surfaces and thus the rate exponent ν may not have the above-mentioned constraint. For example, in economic and social systems (see Ref. [32] and references therein), there exists collaboration (here $\nu > 1$) or hostile (here $\nu < 0$) between two generalized 'aggregates' (e.g., population aggregates), so we consider the general situation that $-\infty < \nu < \infty$ and $-\infty < \mu < \infty$. On the same consideration, the catalyst aggregates are one-dimensional chains, so we assume that the rate kernels of the self-coagulations of the catalyst aggregates of species B and C are $I(i,j) = I$ and $J(i,j) = J$, respectively. Further more, we consider the simplest but important case in

which there only exist monomer aggregates of species A, B and C at $t = 0$ and their concentrations are equal to A_0, B_0 and C_0, respectively. Then the initial conditions for the aggregate size distributions of the three species are $a_k(0) = A_0\delta_{k1}$, $b_k(0) = B_0\delta_{k1}$ and $c_k(0) = C_0\delta_{k1}$, respectively.

The ν-th moment of the aggregate size distribution $a_k(t)$ of species A can be expressed as $M_\nu^A(t) = \sum_{k=1}^{\infty} k^\nu a_k(t)$. Especially, the first two moments $M_0^A(t) = \sum_{k=1}^{\infty} a_k(t)$ and $M_1^A(t) = \sum_{k=1}^{\infty} k a_k(t)$ are the total aggregate number and the total mass of species A, respectively. And the ν-th moments of the aggregate size distributions $b_k(t)$ and $c_k(t)$ have similar expressions.

Using the above expressions of the moments of the aggregate size distributions, the above equations (1)–(3) can be rewritten in the following forms:

$$\frac{\mathrm{d}a_k(t)}{\mathrm{d}t} = \frac{K}{2}\left(\sum_{i+j=k}^{\infty} a_i a_j - 2a_k M_0^A\right) M_\nu^B - \frac{F}{2}\left(\sum_{i+j=k}^{\infty} a_{i+j} - 2\sum_{j=1}^{\infty} a_{k+j}\right) M_\mu^C, \quad (4)$$

$$\frac{\mathrm{d}b_k(t)}{\mathrm{d}t} = \frac{I}{2}\sum_{i+j=k}^{\infty} b_i b_j - I b_k M_0^B, \quad (5)$$

$$\frac{\mathrm{d}c_k(t)}{\mathrm{d}t} = \frac{J}{2}\sum_{i+j=k}^{\infty} c_i c_j - J c_k M_0^C. \quad (6)$$

Several methods to solve the rate equations in different aggregation processes have been developed. In aggregation–annihilation processes,[12,13] the rate equations were solved with the help of a special ansatz $a_k(t) = A(t)[a(t)]^{k-1}$, and by the generating function method as well. Recently, Lin *et al.*[33] and Wang *et al.*[34] gave a thorough discussion of the applicability of this ansatz. Here we find that our current rate equations $(4)-(6)$ can be solved with the help of the ansatz

$$a_k(t) = A(t)[a(t)]^{k-1},$$
$$b_k(t) = B(t)[b(t)]^{k-1},$$
$$c_k(t) = C(t)[c(t)]^{k-1}. \quad (7)$$

In the previous studies of the catalysis-driven aggregation processes,[25,26] equations (5) and (6) have been exactly solved with the help of the ansatz under the same initial conditions, the accurate solutions to the aggregate size distributions of species B and species C are

$$b_k(t) = \frac{4B_0}{(2+IB_0t)^2}\left(1 - \frac{2}{2+IB_0t}\right)^{k-1}, \quad (8)$$

$$c_k(t) = \frac{4C_0}{(2+JC_0t)^2}\left(1 - \frac{2}{2+JC_0t}\right)^{k-1}. \quad (9)$$

In the region of $t \gg 1$ and $k \gg 1$, equations (8) and (9) can be asymptotically rewritten as

$$b_k(t) \simeq 4I^{-2}B_0^{-1}t^{-2}\exp(-x),$$
$$c_k(t) \simeq 4J^{-2}C_0^{-1}t^{-2}\exp(-y), \quad (10)$$

where $x = (2/IB_0)kt^{-1}$, $y = (2/JC_0)kt^{-1}$.

The aggregate size distribution of species B satisfies the conventional scaling law in the long-time limit,[12,13]

$$b_k(t) \simeq t^{-w}\Phi[-k/S_B(t)],\ S_B(t) \propto t^z, \quad (11)$$

where the scaling function is $\Phi(x) = \exp(-x)$ and scaling parameters are $w = 2$ and $z = 1$; $S_B(t) = (IB_0/2)t$ is the characteristic size of aggregates, which plays a role similar to that of the correlation length in critical phenomena. And the aggregate size distribution of species C satisfies a similar conventional scaling law in the long-time limit.

In the long-time limit, we determine the moments of species B and species C in several cases with different parameters,[26] respectively,

$$M_\nu^B(t) = \sum_{l=1}^{\infty} l^\nu b_l(t) \simeq \begin{cases} C_1 t^{\nu-1} & \text{for } \nu > -1, \\ 4I^{-2}B_0^{-1}\ln(IB_0t)t^{-2} & \text{for } \nu = -1, \\ C_2 t^{-2} & \text{for } \nu < -1, \end{cases} \quad (12)$$

$$M_\mu^C(t) = \sum_{l=1}^{\infty} l^\mu c_l(t) \simeq \begin{cases} C_3 t^{\mu-1} & \text{for } \mu > -1, \\ 4J^{-2}C_0^{-1}\ln(JC_0t)t^{-2} & \text{for } \mu = -1, \\ C_4 t^{-2} & \text{for } \mu < -1, \end{cases} \quad (13)$$

where $C_1 = \Gamma(1+\nu)B_0^{\nu}I^{\nu-1}$, $C_2 = 4I^{-2}B_0^{-1}\sum_{l=1}^{\infty} l^{\nu}$, $C_3 = \Gamma(1+\mu)C_0^{\mu}J^{\mu-1}$, $C_4 = 4J^{-2}C_0^{-1}\sum_{l=1}^{\infty} l^{\mu}$ and $\sum_{l=1}^{\infty} l^{\mu}$ is the Riemann zeta function.

Then we investigate the evolution behaviour of species A in several different cases. Substituting ansatz (7) into rate equation (4), we can transform Eq. (4) into the following differential equations:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{K}{2}AM_{\nu}^{B} - \frac{F}{2}aM_{\mu}^{C}, \tag{14}$$

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -\frac{KA^2}{1-a}M_{\nu}^{B} + \frac{FAa}{1-a}M_{\mu}^{C}. \tag{15}$$

The monodisperse initial conditions are transformed correspondingly on the ansatz into

$$\begin{aligned} &a = b = c = 0, \quad A(0) = A_0, \\ &B(0) = B_0, \quad C(0) = C_0, \quad \text{at } t = 0. \end{aligned} \tag{16}$$

On ansatz (7), the first two moments of the aggregate size distribution $a_k(t)$ can be expressed as

$$\begin{aligned} M_0^A(t) &= \sum_{k=1}^{\infty} a_k(t) \\ &= A(t)\sum_{k=1}^{\infty} a^{k-1}(t) \\ &= \frac{A(t)}{1-a(t)}, \end{aligned} \tag{17}$$

$$\begin{aligned} M_1^A(t) &= \sum_{k=1}^{\infty} ka_k(t) \\ &= A(t)\sum_{k=1}^{\infty} ka^{k-1}(t) \\ &= \frac{A(t)}{[1-a(t)]^2}. \end{aligned} \tag{18}$$

Using these moment expressions, equations (14) and (15) can be rewritten as

$$\frac{1}{1-a}\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{K}{2}M_0^A M_{\nu}^B - \frac{F}{2}\frac{a}{A}M_0^A M_{\mu}^C, \tag{19}$$

$$\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}t} = -KM_0^A M_{\nu}^B + F\frac{a}{A}M_0^A M_{\mu}^C. \tag{20}$$

From these equations, the equation for the total aggregate mass M_1^A can be derived as follows:

$$\frac{\mathrm{d}\ln M_1^A}{\mathrm{d}t} = \frac{2}{1-a}\frac{\mathrm{d}a}{\mathrm{d}t} + \frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}t} = 0. \tag{21}$$

It implies that the total mass of species A keeps conserved in the whole process, $M_1^A = A_0$, which accords with the fact that in the present process species performs only the coagulation and fragmentation. The total mass $M_1^A = A_0$ gives the relation $A = A_0(1-a)^2$. Inserting this relation into Eq. (14), we can obtain

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{K}{2}A_0(1-a)^2M_{\nu}^B - \frac{F}{2}aM_{\mu}^C. \tag{22}$$

Introducing a new time variable, $T(t) \equiv (K/2)\int_0^t M_{\nu}^B(t')\mathrm{d}t'$, we recast Eq. (22) into the following differential equation:

$$\frac{\mathrm{d}a}{\mathrm{d}T} = A_0(1-a)^2 - \frac{F}{K}\frac{M_{\mu}^C}{M_{\nu}^B}a. \tag{23}$$

In the next section, we will study the evolution behaviours of species A in various cases with different rate kernel parameters ν and μ, which reflect the competition between the catalysis-coagulation and the catalysis-fragmentation.

3. The kinetic aggregation behaviours through catalysis-coagulation and catalysis-fragmentation

3.1. Case of $\nu = \mu = 1$

First, we investigate the simplest case with catalysis reaction rate kernel parameters $\nu = 1$ and $\mu = 1$, i.e., either of the rate kernels $K(i,j;l) = Kl$ and $F(i,j;l) = Fl$ is proportional to the catalyst aggregate total mass.

From Eqs. (12) and (13), we can obtain $M_1^B(t) = B_0$ and $M_1^C(t) = C_0$, and equation (23) can be rewritten as

$$\frac{\mathrm{d}a}{\mathrm{d}t} = KA_0B_0(1-a)^2 - FC_0a. \tag{24}$$

This Riccati equation can be solved under the initial condition (16), yielding

$$a(t) = \frac{KA_0B_0(1-\mathrm{e}^{-C_5t})}{\left(KA_0B_0 + \frac{1}{2}FC_0 + C_5\right) - \left(KA_0B_0 + \frac{1}{2}FC_0 - C_5\right)\mathrm{e}^{-C_5t}}, \tag{25}$$

where $C_5 = \sqrt{KFA_0B_0C_0 + (1/4)C_0^2F^2}$.

Using the expression $A = A_0(1-a)^2$, the aggregate size distribution of species A can then be solved exactly

to be

$$a_k(t) = A_0 \left[\frac{\left(\frac{1}{2}FC_0 + C_5\right) + \left(C_5 - \frac{1}{2}FC_0\right) \mathrm{e}^{-C_5 t}}{\left(KA_0B_0 + \frac{1}{2}FC_0 + C_5\right) - \left(KA_0B_0 + \frac{1}{2}FC_0 - C_5\right) \mathrm{e}^{-C_5 t}} \right]^2 \times \left[\frac{KA_0B_0(1 - \mathrm{e}^{-C_5 t})}{\left(KA_0B_0 + \frac{1}{2}FC_0 + C_5\right) - \left(KA_0B_0 + \frac{1}{2}FC_0 - C_5\right) \mathrm{e}^{-C_5 t}} \right]^{k-1}. \tag{26}$$

In the scaling region of $k \gg 1$ and $t \gg 1$, it becomes

$$a_k(t) \simeq A_0(1 - C_6)^2 C_6^k \exp[-kC_7 \mathrm{e}^{-C_5 t}], \tag{27}$$

where $C_6 = KA_0B_0/(KA_0B_0 + (1/2)FC_0 + C_5)$ and $C_7 = 2C_5(KA_0B_0 + (1/2)FC_0 + C_5)^{-1}$.

This solution indicates that the aggregate size distribution of species A does not satisfy the conventional scaling form as Eq. (11), but it approaches the following modified scaling form:[25]

$$a_k(t) \simeq b^k \Phi[-k/S_A(t)], \quad S_A(t) \propto [f(t)]^z, \tag{28}$$

where b is a constant and $0 < b < 1$, and $f(t) = \exp(t)$. This result also implies that there are two different scales associated with the aggregate size distribution. One is a growing scale $S_A(t) \propto \mathrm{e}^t$, which is due to the aggregation process of the aggregates; the other is a time-independent scale $S_A = 1/(1 - C_6)$, which will dominate the evolution behaviour of the aggregates in the long-time limit.

The total aggregate number $M_0^A(t)$ can then be determined to be

$$M_0^A = A_0(1 - a) = A_0 \frac{\left(\frac{1}{2}FC_0 + C_5\right) + \left(C_5 - \frac{1}{2}FC_0\right) \mathrm{e}^{-C_5 t}}{\left(KA_0B_0 + \frac{1}{2}FC_0 + C_5\right) - \left(KA_0B_0 + \frac{1}{2}FC_0 - C_5\right) \mathrm{e}^{-C_5 t}}. \tag{29}$$

This implies that the total aggregate number of species A decreases with time at the beginning of the processes and will approach a stable value $1 - C_6$ after a long time, which reveals that in this case the catalysis-coagulation (which appears in the form of KA_0B_0) and the catalysis-fragmentation (which appears in the form of FC_0) play the same important roles in the evolution of species A and a balance between the roles of catalysis-coagulation and catalysis-fragmentation will be established in the long-time limit.

3.2. Case of general ν and μ

Now we turn to the general cases. First, we can derive the asymptotic solution of $T(t)$ as follows:

$$T(t) = \frac{K}{2} \int_0^t M_\nu^B(t') \mathrm{d}t' \simeq \begin{cases} C_8 t^\nu & \text{for } \nu > 0, \\ \ln(1 + t) & \text{for } \nu = 0, \\ C_9 - C_8 t^\nu & \text{for } -1 < \nu < 0, \\ C_{10} - 4I^{-2}B_0^{-1} \ln(IB_0 t) t^{-1} & \text{for } \nu = -1, \\ C_9 - C_{11} t^{-1} & \text{for } \nu < -1, \end{cases} \tag{30}$$

where

$$C_8 = KC_1 \Gamma(1 + \nu)/\nu, \; C_9 = \Gamma(1 + \nu) K B_0^\nu \int_0^\infty (2 + IB_0 t')^{-2} \sum_{j=1}^\infty j^\nu \left(\frac{IB_0 t'}{1 + IB_0 t'}\right)^{j-1} \mathrm{d}t',$$

$$C_{10} = K \int_0^\infty \frac{4 \ln(1 + IB_0 t'/2)}{It'(2 + IB_0 t')} \mathrm{d}t' \quad \text{and} \quad C_{11} = KC_1 \sum_{j=1}^\infty j^\nu.$$

Then, we investigate the solution of Eq. (23) in several cases as follows.

3.2.1. Case $\nu > \mu$ and $\nu \geq -1$

In the case of $\nu \geq 0$, from Eqs. (12) and (13), we can easily find that

$$\frac{FM_\mu^C}{KA_0M_\nu^B} \simeq \begin{cases} C_{12}t^{\mu-\nu} & \text{for } \mu > -1, \\ C_{13}\ln(JC_0t)t^{-\nu-1} & \text{for } \mu = -1, \\ C_{14}t^{-\nu-1} & \text{for } \mu < -1, \end{cases} \quad (31)$$

where

$$C_{12} = F(KA_0)^{-1}C_3C_1^{-1},$$
$$C_{13} = 4F(KJ^2A_0C_0C_1)^{-1}$$

and

$$C_{14} = F(KA_0)^{-1}C_4C_1^{-1}.$$

We introduce a new function $\gamma = T^2(t)M_\mu^C/M_\nu^B$. In this case, it is found that $\lim_{t\to\infty} T \to \infty$ and $\lim_{t\to\infty}\gamma \to \infty$, and from Eq. (23) one can determine the following asymptotic solution of $a(t)$ in the long-time limit:[35]

$$a(t) \simeq 1 - \left[\frac{FM_\mu^C(t)}{KA_0M_\nu^B(t)}\right]^{1/2}. \quad (32)$$

When $\mu > -1$, we substitute $FM_\mu^C/KA_0M_\nu^B \simeq C_{12}t^{\mu-\nu}$ into Eq. (32) and derive the following asymptotic solution:

$$a(t) \simeq 1 - C_{12}^{1/2}t^{(\mu-\nu)/2}. \quad (33)$$

The aggregate size distribution of species A is then obtained as follows:

$$a_k(t) \simeq A_0C_{12}t^{-(\nu-\mu)}\exp[-k/S_A(t)] \quad (34)$$

with

$$S_A(t) \simeq C_{12}^{-1/2}t^{(\nu-\mu)/2}.$$

It satisfies the conventional scaling form as Eq. (11) with the scaling parameters $w = \nu - \mu$ and $z = (1/2)(\nu - \mu)$. This indicates that in this case the exponents are non-universal and dependent on the value of $\nu - \mu$, which reflects the competition between the catalysis-coagulation and the catalysis-fragmentation.

When $\mu = -1$, in the same way we obtain the aggregate size distribution to be

$$a_k(t) \simeq A_0C_{13}\ln(JC_0t)t^{-\nu-1}\exp[-k/S_A(t)],$$
$$S_A(t) \simeq C_{13}^{-1/2}\left(\frac{t^{\nu+1}}{\ln JC_0t}\right)^{1/2}, \quad (35)$$

which obeys the generalized scaling law[36]

$$a_k(t) \simeq [f(t)]^{-w_1}[g(t)]^{-w_2}\Phi[k/S_A(t)],$$
$$S_A(t) \propto [f(t)]^{z_1}[g(t)]^{z_2} \quad (36)$$

with $f(t) = [\ln(JC_0t)]^{-1}$, $g(t) = t$ and the exponents $w_1 = 1$, $w_2 = \nu + 1$, $z_1 = 1/2$ and $z = (1/2)(\nu + 1)$.

When $\mu < -1$, in the same way we obtain the aggregate size distribution to be

$$a_k(t) \simeq A_0C_{14}t^{-\nu-1}\exp[-k/S_A(t)],$$
$$S_A(t) \simeq C_{14}^{-1/2}t^{(\nu+1)/2}. \quad (37)$$

It also approaches the conventional scaling form with the scaling exponents $w = \nu + 1$ and $z = (1/2)(\nu + 1)$, which indicates that for this case the exponents are non-universal and dependent on the value of $\nu + 1$. This shows that in this case the effect of the catalysis-fragmentation is week because of $\mu < -1$ and the evolution is dominated by the catalysis-coagulation.

In summary, in these subcases above with $\nu > \mu$ and $\nu \geq 0$, the characteristic aggregate size of species A is

$$S_A(t) \propto \begin{cases} t^{(\nu-\mu)/2} & \text{for } \mu > -1, \\ t^{(\nu+1)/2}[\ln(JC_0t)]^{-1/2} & \text{for } \mu = -1, \\ t^{(\nu+1)/2} & \text{for } \mu < -1. \end{cases} \quad (38)$$

This indicates that $S_A(t)$ grows much faster in the case of $\mu < -1$ than in the cases of $\mu > -1$ and $\mu = -1$. And in the cases of $\mu < -1$ and $\mu = -1$, the catalysis-coagulation process dominates the evolution behaviour. In the case of $\mu = -\infty$ where the catalysis-fragmentation process is restrained, $S_A(t)$ grows as $S_A(t) \propto t^{(\nu+1)/2}$, which is not the same as that in the previous studied model in which there existed only the catalysis-driven irreversible aggregation.[26] This indicates that although the role of catalysis-fragmentation is comparatively very weak, we may not ignore this role.

In the case of $-1 < \nu < 0$, it is found that $\lim_{t\to\infty} T \to C_9$, from Eq. (23) one can determine the following asymptotic solution of $a(t)$ at a long time:

$$a(t) \simeq C_{15} - (1 - C_{15})^2O_1(t), \quad (39)$$

where $O_1(t) = K\int_t^\infty (1/2)M_\nu^B(t')\mathrm{d}t' \simeq -C_8t^\nu$, and C_{15} is a finite positive constant. The two constants C_9 and C_{15} have the implicit relation $C_9 = \int_0^{C_{15}}[A_0(1-a)^2 - KM_\nu^Ba/FM_\mu^C]\mathrm{d}a$, and asymptotically we obtain $C_{15} \simeq C_9/(1 + C_9)$. Thus we obtain the asymptotic solution of the aggregate size distribution to be

$$a_k(t) \simeq A_0(1-C_{15})^2[C_{15} - (1-C_{15})^2O_1(t)]^{k-1}. \quad (40)$$

In the scaling region of $t \gg 1$ and $k \gg 1$, equation (40) can be further rewritten as

$$a_k(t) \simeq A_0(1-C_{15})^2 C_{15}^k \exp[-k/S_A(t)],$$
$$S_A(t) = -\frac{C_{15}}{C_8(1-C_{15})^2} t^{-\nu}. \quad (41)$$

Equation (41) indicates that in this case the aggregate size distribution $a_k(t)$ follows the same modified scaling form as Eq. (28). This result also implies that there are two different scales associated with the aggregate size distribution. The growing scaling law is $S_A(t) \propto t^{-\nu}$ and time-independent scaling law $S_A = 1/(1-C_{15})$. On the other hand, it is not difficult to find that the total density of the aggregates decreases with time at the beginning of the processes and will retain the quantity $1-C_{15}$ after a sufficiently long time. An important characteristic of this system with $T(t=\infty) \to C_9$ is the formation of a steady-state aggregate size distribution after a large time, which is different from the above discussed subcase of $T(t=\infty) \to \infty$.

In the case of $\nu = -1$, it is found that $\lim_{t\to\infty} T \to C_{10}$, similar to the above subcase, we could directly give the long-time scaling law as follows:

$$a_k(t) \simeq A_0(1-C_{16})^2[C_{16}-(1-C_{16})^2 O_2(t)]^{k-1}, \quad (42)$$

where

$$\begin{aligned} O_2(t) &= \frac{K}{2}\int_t^\infty M_{-1}^B(t')\,\mathrm{d}t' \\ &\simeq \int_t^\infty \frac{K\ln(1+IB_0t'/2)}{2It'(1+IB_0t')}\,\mathrm{d}t' \\ &\simeq K\ln(IB_0t)/I^2B_0t \end{aligned}$$

and

$$C_{16} \simeq C_{10}/(1+C_{10}).$$

In the scaling region of $t \gg 1$ and $k \gg 1$, equation (42) can be further rewritten as

$$a_k(t) \simeq A_0(1-C_{16})^2 C_{16}^k \exp[-k/S_A(t)],$$
$$S_A(t) \simeq \frac{C_{16}}{(1-C_{16})^2}\frac{I^2B_0t}{K\ln(IB_0t)}. \quad (43)$$

It approaches the same modified scaling form as Eq. (28), the growing scaling law is $S_A(t) \propto t/\ln(IB_0t)$ and the time-independent scaling law is $S_A = 1/(1-C_{16})$.

In these cases, the growing scaling law indicates that under the monodisperse initial conditions, the catalysis-coagulation process dominates over the catalysis-fragmentation process at the beginning of the processes; while the time-independent scale implies that after a sufficiently long time a balance will be established between the two processes. Hence, the system reaches a steady state finally, in which the aggregate size distribution of species A is independent of time. It implies that both the roles of the catalysis-coagulation and the catalysis-fragmentation are weak.

3.2.2. Case $\nu = \mu$

In the case of $\nu > -1$, it is found that $\lim_{t\to\infty} FM_\mu^C/KA_0M_\nu^B \to C_{12}$, from Eq. (23) one can determine the asymptotic solution to be

$$a(t) \simeq \frac{4-4\exp[-C_{18}T(t)]}{(C_{17}+\sqrt{C_{12}})^2-(C_{17}-\sqrt{C_{12}})^2\exp[-C_{18}T(t)]}, \quad (44)$$

where $C_{17} = \sqrt{4+C_{12}}$ and $C_{18} = \sqrt{C_{12}^2+4C_{12}}$. And $T(t)$ is expressed in Eq. (30).

When $\nu \geq 0$, from Eq. (30) we can know that $\lim_{t\to\infty} T(t) \to \infty$. Inserting it into Eq. (44) one can obtain the asymptotic solution of the aggregate size distribution at a large time,

$$\begin{aligned} a_k(t) &\simeq A_0\frac{4C_{12}}{(C_{17}+\sqrt{C_{12}})^2}\left[\frac{4}{(C_{17}+\sqrt{C_{12}})^2}\right]^k \\ &\quad\times \exp[-k/S_A(t)], \\ S_A(t) &= \frac{(C_{17}+\sqrt{C_{12}})^2}{4C_{18}}\,\mathrm{e}^{C_{18}T(t)}, \end{aligned} \quad (45)$$

which approaches the above-mentioned modified scaling form of Eq. (28). The two scaling laws associated with the aggregates are the growing scaling law $S_A(t) \propto \exp[C_{18}T(t)]$ and the time-independent scaling law $S_A = (C_{12}+C_{18}+2)/(C_{12}+C_{18})$. Moreover, the total density of the aggregates may retain the quantity $(C_{12}+C_{18}+2)/(C_{12}+C_{18})$ in the long-time limit. Therefore, each $a_k(t)$ will have a certain non-zero value finally.

When $-1 < \nu < 0$, from Eq. (30) we know that $\lim_{t\to\infty} T(t) \to C_9$. Equation (44) reduces to the following asymptotic equation:

$$a(t) \simeq \frac{4-4\,\mathrm{e}^{-C_{18}C_9}-4\,\mathrm{e}^{-C_{18}C_9}C_{18}O_1(t)}{(C_{17}+\sqrt{C_{12}})^2-(C_{17}-\sqrt{C_{12}})^2\exp[-C_{18}C_9]}, \quad (46)$$

where $O_1(t) \simeq -C_8t^\nu$. Thus, we obtain the aggregate size distribution $a_k(t)$, which approaches the modified

scaling form in the scaling region of $t \gg 1$ and $k \gg 1$,

$$a_k(t) \simeq A_0 \frac{4C_{12}}{(C_{17}+\sqrt{C_{12}})^2} C_{19}^k \exp[-k/S_A(t)] \quad (47)$$

with

$$S_A(t) = C_{20}^{-1} t^{-\nu},$$

where

$$C_{19} = \frac{4 - 4\exp(-C_{18}C_9)}{(C_{17}+\sqrt{C_{12}})^2 - (C_{17}-\sqrt{C_{12}})^2 \exp[-C_{18}C_9]}$$

and

$$C_{20} = -\frac{C_{18}C_8 \exp(-C_{18}C_9)}{2 - 2\exp(-C_{18}C_9)}.$$

Here the growing scaling law is $S_A(t) \propto t^{-\nu}$ and the time-independent scaling law is $S_A = 1/(1 - C_{19})$.

When $\nu \leq -1$, similar to the above subcase, we can directly give the long-time modified scaling form of $a_k(t)$ as

$$\begin{aligned} a_k(t) &\simeq A_0 \frac{4C_{21}}{(C_{22}+\sqrt{C_{21}})^2} C_{24}^k \exp[-k/S_A(t)], \\ S_A(t) &= C_{25} h(t), \end{aligned} \quad (48)$$

where

$$C_{21} \simeq FI^2 B_0 (KJ^2 A_0 C_0)^{-1}$$

for $\nu = -1$ and

$$C_{21} = FC_4 (KA_0 C_2)^{-1}$$

for $\nu < -1$. And

$$C_{22} = \sqrt{4 + C_{21}},$$

$$C_{23} = \sqrt{C_{21}^2 + 4C_{21}},$$

$$C_{24} = \frac{4 - 4\exp(-C_{23}T_\infty)}{(C_{22}+\sqrt{C_{21}})^2 - (C_{22}-\sqrt{C_{21}})^2 \exp[-C_{23}T_\infty]}$$

and

$$C_{25} = \frac{C_{22}C_8 \exp(-C_{22}T_\infty)}{2 - 2\exp(-C_{22}T_\infty)}.$$

From Eq. (30), we can also know that T_∞ equals C_{10} for $\mu = -1$ and C_9 for $\mu < -1$.

Here $h(t)$ is obtained in different cases:

$$\begin{aligned} h(t) &= \left[\frac{K}{2}\int_t^\infty M_\nu^B(t')\,\mathrm{d}t'\right]^{-1} \\ &\simeq \begin{cases} \dfrac{I^2 B_0 t}{K \ln(IB_0 t)} & \text{for } \nu = -1, \\ C_{11}^{-1} t & \text{for } \nu < -1. \end{cases} \end{aligned} \quad (49)$$

The aggregate size distribution follows the same modified scaling form of Eq. (28), and there are also two scaling laws associated with the aggregates: the growing scaling law $S_A(t) \propto h(t)$ and the time-independent scaling law $S_A = 1/(1 - C_{24})$.

As in the above case with $\nu = \mu = 1$, we can obtain the evolution behaviour of the total aggregate number $M_0^A(t)$ using the relation $M_0^A = A_0(1-a)$ and find that in these cases $M_0^A(t)$ will approach some stable values after a long time. It reveals that after a long time a balance is established between the two competing processes, the catalysis-coagulation and the catalysis-fragmentation, and the system comes to a steady state. In the steady state, the aggregate size distribution will be independent of time and small aggregates can survive together with the larger ones.

3.2.3. Case $\nu < \mu$ and $\mu \geq -1$

In this case, from Eq. (23) one can deduce that $a(t)$ grows with time at the beginning of the processes, then reaches a maximum value satisfying the equation $KM_\nu^B(1-a)^2 = FA_0 M_\mu^C a$, and finally decreases to a certain value. The analytic solution of $a(t)$ is dependent strongly on the value of $\int_0^t M_\mu^C(t')\,\mathrm{d}t'$ at $t \to \infty$.

In the first subcase of $\nu \geq 0$, it is found that $\lim_{t\to\infty} \int_0^t M_\mu^C(t')\,\mathrm{d}t' \to \infty$ and $\lim_{t\to\infty} T(t) \to \infty$. From Eq. (23) we obtain the asymptotic solution in the long-time limit to be

$$a(t) \simeq \frac{KA_0 M_\nu^B(t)}{FM_\mu^C(t)} \simeq C_{12}^{-1}(1+t)^{-(\mu-\nu)}. \quad (50)$$

Thus we find that the aggregate size distribution approaches the scale-free form, i.e.,

$$a_k(t) \simeq A_0 [C_{12}^{-1}(1+t)^{-(\mu-\nu)}]^{k-1}. \quad (51)$$

In the second subcase of $\nu < 0$, when $\mu \geq 0$ it is found that $\lim_{t\to\infty} \int_0^t M_\mu^C(t')\,\mathrm{d}t' \to \infty$ and $\lim_{t\to\infty} T(t) \to T_\infty$, where T_∞ is a positive constant. From Eq. (23) we obtain the following asymptotic solution in the long-time limit:

$$a(t) \simeq \exp\left[-\frac{F}{2}\int_0^t M_\mu^C(t')\,\mathrm{d}t'\right]. \quad (52)$$

Using the solution of $M_\mu^C(t)$ in Eq. (13), we derive $a(t)$ from Eq. (52) as

$$a(t) \simeq \begin{cases} \exp[-C_8'(1+t)^\mu] & \text{for } \mu > 0, \\ (1+t)^{-1} & \text{for } \mu = 0, \end{cases} \quad (53)$$

where $C_8' = FC_3\Gamma(1+\mu)/\mu$. Thus we find that the aggregate size distribution approaches the scale-free

form

$$a_k(t) \simeq \begin{cases} A_0 \exp[-(k-1)C_8'(1+t)^{\mu}] & \text{for } \mu > 0, \\ A_0(1+t)^{1-k} & \text{for } \mu = 0. \end{cases} \tag{54}$$

In these two subcases, only the monomer aggregates can survive finally, which is not surprising because the catalysis-fragmentation process may dominate over the catalysis-coagulation process at a large time.

When $-1 \le \mu < 0$, it is found that

$$\lim_{t\to\infty} \int_0^t M_{\mu}^C(t')\,\mathrm{d}t' \to C_{26},$$

where C_{26} equals

$$C_9' = \Gamma(1+\mu)FC_0^{\mu} \int_0^{\infty} (2+JC_0t')^{-2} \times \sum_{j=1}^{\infty} j^{\mu} \left(\frac{JC_0t'}{1+JC_0t'}\right)^{j-1} \mathrm{d}t'$$

for $\mu > -1$ and

$$C_{10}' = F \int_0^{\infty} \frac{4\ln(1+JC_0t'/2)}{Jt'(2+JC_0t')}\,\mathrm{d}t'$$

for $\mu = -1$, respectively. From Eq. (23) we obtain the asymptotic solution in the long-time limit,

$$a(t) \simeq C_{27} + P(t), \tag{55}$$

where

$$C_{27} = \exp(-C_{26}/2)$$

and

$$P(t) = \int_t^{\infty} [C_{27}M_{\mu}^C(t')/2]\,\mathrm{d}t'.$$

Using the solution of $M_{\mu}^C(t)$, we can write out the explicit form of $P(t)$ as

$$P(t) \simeq \begin{cases} -C_8'C_{24}(1+t)^{\mu} & \text{for } -1 < \mu < 0, \\ C_{10}'\dfrac{F\ln(JC_0t/2)}{J^2C_0t} & \text{for } \mu = -1. \end{cases} \tag{56}$$

Then we obtain the scaling law for the aggregate size distribution,

$$a_k(t) \simeq (1-C_{27})^2 C_{27}^k \exp[-k/S_A(t)] \tag{57}$$

with

$$S_A(t) = [P(t)]^{-1}.$$

It satisfies the same modified scaling form Eq. (28) with the growing scaling law $S_A(t) \propto 1/P(t)$ and the time-independent scaling law $S = 1/(1-C_{27})$. Moreover, this situation is consistent with our earlier discussed cases where $a_k(t)$ retains a certain value in the steady state.

3.2.4. Case $\nu < -1$ and $\mu < -1$

If $\nu < -1$ and $\mu < -1$, from Eqs. (12) and (13) we can obtain the asymptotic solutions of M_{ν}^B and M_{μ}^C at a large time, i.e., $M_{\nu}^B(t) = I^{-2}B_0^{-1}t^{-2}\sum_{l=1}^{\infty} l^{\nu}$ and $M_{\mu}^C(t) = J^{-2}C_0^{-1}t^{-2}\sum_{l=1}^{\infty} l^{\mu}$. Substituting these solutions into Eq. (23), it can be reduced into

$$\frac{\mathrm{d}a}{\mathrm{d}T} = (1-a)^2 - C_{28}a, \tag{58}$$

where $C_{28} = KJ^2C_0\sum_{l=1}^{\infty} l^{\nu}(FA_0I^2B_0\sum_{l=1}^{\infty} l^{\mu})^{-1}$.

This Riccati equation can be solved under the initial condition (16) yielding

$$a(T) = \frac{4 - 4\,\mathrm{e}^{-C_{29}T}}{(C_{30}+\sqrt{C_{28}})^2 - (C_{30}-\sqrt{C_{28}})^2\,\mathrm{e}^{-C_{29}T}}, \tag{59}$$

where $C_{29} = \sqrt{C_{28}^2 + 4C_{28}}$ and $C_{30} = \sqrt{4+C_{28}}$.

Substituting $T(t) \simeq C_9 - C_{11}t^{-1}$ into Eq. (59), we can further obtain the explicit solution of $a(t)$:

$$a(t) \simeq \frac{4 - 4\,\mathrm{e}^{-C_{29}C_9} - 4\,\mathrm{e}^{C_{29}C_{11}t^{-1}}}{(C_{30}+\sqrt{C_{28}})^2 - (C_{30}-\sqrt{C_{28}})^2\,\mathrm{e}^{-C_{29}C_9}}. \tag{60}$$

With the relation of $A = A_0(1-a)^2$, the aggregate size distribution of species A can then be obtained to be

$$a_k(t) \simeq A_0\Big[\frac{(C_{28}+C_{29}) - (C_{28}-C_{29})\,\mathrm{e}^{-C_{29}C_9}}{(C_{30}+\sqrt{C_{28}})^2 - (C_{30}-\sqrt{C_{28}})^2\,\mathrm{e}^{-C_{29}C_9}}\Big]^2 \times \Big[\frac{4 - 4\,\mathrm{e}^{-C_{29}C_9} - 4\,\mathrm{e}^{C_{29}C_{11}t^{-1}}}{(C_{30}+\sqrt{C_{28}})^2 - (C_{30}-\sqrt{C_{28}})^2\,\mathrm{e}^{-C_{29}C_9}}\Big]^{k-1}. \tag{61}$$

It approaches the following scaling form in the scaling region of $k \gg 1$ and $t \gg 1$:

$$a_k(t) \simeq \frac{4A_0C_{28}}{(C_{30}+\sqrt{C_{28}})^2} C_{31}^k \exp[-k/S_A(t)] \tag{62}$$

with

$$S_A(t) = C_{32}^{-1}\,\mathrm{e}^{-1/t},$$

where

$$C_{31} = \frac{4 - 4\,\mathrm{e}^{-C_{29}C_9}}{(C_{30}+\sqrt{C_{28}})^2 - (C_{30}-\sqrt{C_{28}})^2\,\mathrm{e}^{-C_{29}C_9}}$$

and

$$C_{32} = \frac{4\,\mathrm{e}^{C_{29}C_{11}}}{4 - 4\,\mathrm{e}^{-C_{29}C_9}}.$$

It approaches the same modified scaling form as Eq. (28).

The solution shows that in this case the balance still holds between the two competing processes and the system comes to a steady state, where the parameters of μ and ν are not necessarily equal. This implies that both the roles of the catalysis-coagulation and the catalysis-fragmentation are weak.

To make a clear picture of the kinetic behaviours of the system in our model, we summarize the above results in different cases in Table 1.

Table 1. Summary of the kinetic evolution behaviours of species A through the catalysis-coagulation and catalysis-fragmentation processes.

case	kinetic evolution behaviours of species A
$\nu = \mu$	$a_k(t)$ obeys the modified scaling form, and the evolution is dominated by the catalysis-coagulation and catalysis-fragmentation processes equally and a balance is established between the two competing processes after a long time.
$\nu > \mu$ and $\nu \geq -1$	
(i) $\nu \geq 0$	i) If $\mu > -1$, $a_k(t)$ obeys the conventional scaling form and the evolution is dominated by the catalysis-coagulation and catalysis-fragmentation processes equally;
	ii) If $\mu = -1$, $a_k(t)$ obeys the generalized scaling form and the evolution is dominated by the catalysis-coagulation process;
	iii) If $\mu < -1$, $a_k(t)$ obeys the conventional scaling form and the evolution is dominated by the catalysis-coagulation process;
(ii) $-1 \leq \nu < 0$	$a_k(t)$ obeys the modified scaling form and the evolution is dominated by the catalysis-coagulation process and a balance is established between the two competing processes after a long time.
$\nu < \mu$ and $\mu \geq -1$	
(I) $\nu \geq 0$	$a_k(t)$ approaches the scale-free form and the evolution is dominated by the catalysis-fragmentation process;
(II) $\nu < 0$	1) If $\mu \geq 0$, $a_k(t)$ approaches the scale-free form and the evolution is dominated by the catalysis-fragmentation process;
	2) If $-1 \leq \mu < 0$, $a_k(t)$ obeys the modified scaling form and a balance is established between the two competing processes after a long time.
$\nu < -1$ and $\mu < -1$	$a_k(t)$ obeys the modified scaling form, and the two competing processes are both weak and a balance is established after a long time.

4. Summary

We have proposed an aggregation model where species A aggregates evolve by the catalysis-coagulation and catalysis-fragmentation, while two species catalyst aggregates perform self-coagulation processes. Based on the mean-field theory, we investigated the roles of these two competing catalysis-driven processes in the kinetic evolution behaviours of species A aggregates by the generalized Smoluchowski rate equation.

It is natural that the kinetic evolution behaviour of the aggregates depends crucially on the details of the rate kernels. In this paper the catalysis-coagulation and the catalysis-fragmentation rate kernels are chosen to be $K(i,j;l) \propto l^{\nu}$ and $F(i,j;l) \propto l^{\mu}$, respectively, where l is the size of the catalyst aggregate, and ν and μ are two parameters reflecting the dependence of the catalysis reaction on the size of the catalyst aggregate, or the catalysis ability of the catalyst aggregate. The relation between the values of parameters ν and μ reflects the competition between the two catalysis processes: the catalysis-coagulation and catalysis-fragmentation.

The investigation reveals that the kinetic behaviours of species A fall into three categories in different cases with different relations between ν and μ. (i) When $\nu > \mu$ and $\nu \geq 0$, the aggregate size distribution $a_k(t)$ of the species A obeys the conventional or generalized scaling law, which implies that the kinetic behaviour of species A is dominated by the catalysis-coagulation. (ii) When $\nu = \mu$, $\nu < \mu$

but $-1 \leq \mu < 0$ or $\nu < 0$ and $\mu < 0$, the aggregate size distribution obeys a modified scaling law, and after a sufficiently long time, a balance is established between the two competing processes and the system comes to a steady state. (iii) When $\nu < \mu$ and $\nu \geq 0$ or $\nu < 0$ but $\mu \geq 0$, the aggregate size distribution approaches the scale-free form, which shows that the catalysis-fragmentation process may dominate the evolution process and at a large time only the monomer aggregates can survive.

In short, the competing role of the catalysis-coagulation and catalysis-fragmentation in the kinetic aggregation behaviours is not simply determined by the relation between the two parameters ν and μ, but also dependent on the values of these two parameters.

References

[1] Drake R L 1972 *Topics of Current Aerosol Research* ed. by Hidy G M and Brook J R (New York: Pergamon)

[2] Friedlander S K 1977 *Smoke, Dust and Haze: Fundamental of Aerosol Behaviour* (New York: Wiley)

[3] Pimpinelli A and Villain J 1998 *Physics of Crystal Growth* (Cambridge: Cambridge University Press)

[4] Meakin P 1992 *Rep. Prog. Phys.* **55** 157

[5] Smoluchowski M V 1916 *Phys. Z.* **17** 557

[6] Vicsek T and Family F 1984 *Phys. Rev. Lett.* **52** 1669

[7] Kang K and Redner S 1984 *Phys. Rev.* A **30** 2833

[8] Xue Y and Chen G Z 2002 *Chin. Phys.* **11** 684

[9] Ke J H, Lin Z Q and Wang X H 2003 *Chin. Phys.* **12** 443

[10] Ke J H, Lin Z Q and Wang X H 2003 *Chin. Phys. Lett.* **20** 151

[11] Wang X H, Ke J H and Lin Z Q 2004 *Chin. Phys.* **13** 755

[12] Krapivsky P L 1993 *Physica* A **198** 135

[13] Ben-Naim E and Krapivsky P L 1995 *Phys. Rev.* E **52** 6066

[14] Family F, Meakin P and Deutch J M 1986 *Phys. Rev. Lett.* **57** 727

[15] McGrady E D and Ziff R M 1987 *Phys. Rev. Lett.* **58** 892

[16] Tomas S and Raul T 1992 *Phys. Rev.* A **46** 2039

[17] Chen Y, Han A J, Ke J H and Lin Z Q 2006 *Chin. Phys.* **15** 1896

[18] Li J W, Lin B L and Huang Y C 2007 *Chin. Phys.* **16** 753

[19] Li J W, Lin B L and Huang Y C 2008 *Chin. Phys.* B **17** 473

[20] Ke J H, Chen X S and Lin Z Q 2010 *Chin. Phys.* B **19** 026802

[21] Shen W W, Li P P and Ke J H 2010 *Acta Phys. Sin.* **59** 6681 (in Chinese)

[22] Burlatsky S F and Ovchinnikov A 1980 *Russ. J. Phys. Chem.* **54** 1741

[23] Burlatsky S F and Moreau M 1995 *Phys. Rev.* E **51** 2363

[24] Oshanin G, Stemmer A, Luding S and Blumen A 1995 *Phys. Rev.* E **52** 5800

[25] Ke J H and Lin Z Q 2002 *Phys. Rev.* E **66** 062101

[26] Ke J H and Lin Z Q 2004 *J. Phys.* A: *Math. Gen.* **37** 3967

[27] Ke J H, Wang X H, Lin Z Q and Zhuang Y Y 2004 *Physica* A **338** 356

[28] Allcock H R, Lampe F W and Mark J E 2003 *Contemporary Polymer Chemistry* (Pearson Education, Upper Saddle River, NJ)

[29] Spouge J L 1988 *Phys. Rev. Lett.* **60** 871

[30] Family F, Meakin P and Deutch J M 1986 *Phys. Rev. Lett.* **57** 727

[31] Ernst M H, Hendriks E M and Ziff R M 1982 *J. Phys.* A: *Math. Gen.* **15** 743

[32] Leyvraz F and Redner S 2002 *Phys. Rev. Lett.* **88** 068301

[33] Lin Z Q, Ke J H and Ye G X 2006 *Phys. Rev.* E **74** 046113

[34] Wang H F, Lin Z Q and Gao Y 2008 *Chin. Phys.* B **17** 1490

[35] Ke J H, Cai X O and Lin Z Q 2004 *Phys. Lett.* A **331** 281

[36] Lin Z Q and Ke J H 2003 *Phys. Rev.* E **67** 031103