Kinetics of catalytically activated aggregation–fragmentation process*

Gao Yan(高 艳)[a)], Wang Hai-Feng(王海锋)[a)†],
Lin Zhen-Quan(林振权)[b)], and Xue Xin-Ying(薛新英)[a)]

[a)] *Key Laboratory of Ecophysics and Department of Physics, College of Science, Shihezi University, Shihezi* 832003, *China*
[b)] *Department of Physics, Wenzhou University, Wenzhou* 325027, *China*

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We propose a catalytically activated aggregation–fragmentation model of three species, in which two clusters of species A can coagulate into a larger one under the catalysis of B clusters; otherwise, one cluster of species A will fragment into two smaller clusters under the catalysis of C clusters. By means of mean-field rate equations, we derive the asymptotic solutions of the cluster-mass distributions $a_k(t)$ of species A, which is found to depend strongly on the competition between the catalyzed aggregation process and the catalyzed fragmentation process. When the catalyzed aggregation process dominates the system, the cluster-mass distribution $a_k(t)$ satisfies the conventional scaling form. When the catalyzed fragmentation process dominates the system, the scaling description of $a_k(t)$ breaks down completely and the monodisperse initial condition of species A would not be changed in the long-time limit. In the marginal case when the effects of catalyzed aggregation and catalyzed fragmentation counteract each other, $a_k(t)$ takes the modified scaling form and the system can eventually evolve to a steady state.

Keywords: aggregation, fragmentation, catalytically activated reaction, rate equation

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1. Introduction

The aggregation phenomenon is of considerable importance in a variety of fields, such as astronomy, where planetary systems form via collisions of planetesimals,[1] chemical physics, where polymeric chains chemically bond and form polymeric networks or gels,[2,3] and social science.[4−11] In some practical situations, the reverse process of coagulation (namely, fragmentation of clusters) also plays an important role in the dynamic evolution of cluster growth. Examples include breakup of liquid droplets[12] and atomic nuclei,[13] polymer degradation,[14] shattering of solid objects,[15,16] meteor impacts and mineral grinding. Coagulation and fragmentation processes are ubiquitous in nature and are thus of great importance. Examples include reversible colloidal aggregation, polymer degradation and addition, floc disintegration and coagulation, and aggregation-breakage processes in Taylor–Couette flow. In recent decades, a great deal of effort has been devoted to understanding the kinetics of coagulation–fragmentation processes.[17−25] Most intriguingly, much research has shown that the size distribution of clusters in coagulation and coagulation–fragmentation systems can approach a scaling form in the long-time limit.[18,23−25] Moreover, an irreversible coagulation system always evolves permanently with time, while a reversible process can evolve to a steady state after a sufficiently long time.[23,24]

As far as we know, most of this work focused on the processes in which the aggregation reaction and fragmentation reaction spontaneously occur between the clusters of the same species, and a few studies paid attention to the aggregation and fragmentation processes, which occur only in the presence of another substance—a catalyst. In fact, catalytically activated reactions are widespread in nature and are used in a variety of technological and industrial applications,[26] even in sociology and economics. And recently, considerable interest has been aroused in a variety of aggregation phenomena involving catalytically activated reactions.[27−30] Lin *et al.*[31] introduced the mutually catalyzed birth of population

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†Corresponding author. E-mail: whfeng08@yahoo.cn

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and assets in exchange-driven aggregation growth to study the interaction between the population and the asset aggregates. In our recent work,[32] we studied the competition between catalyzed birth and catalyzed death in exchange-driven aggregation growth. The results show that this competition between the two mechanisms gives rise to much more abundant kinetic behaviours. In this paper, we propose a catalytically activated aggregation–fragmentation model to study the competition between the catalysis-driven aggregation process and the catalysis-driven fragmentation process. In this model, there are three distinct species of clusters in the system: A, B, and C. Two type-B (or type-C) clusters can bond to form a larger cluster when they meet, which can be described as the reaction $B_i + B_j \xrightarrow{K_1(i,j)} B_{i+j}$ (or $C_i + C_j \xrightarrow{K_2(i,j)} C_{i+j}$). Here, B_i denotes a cluster consisting of i monomers and $K_1(i,j)$ denotes the reaction rate kernel at which two clusters coagulate together. But the coagulation of A clusters occurs only with the help of B clusters, which can be described as $A_i + A_j + B_l \xrightarrow{I(i,j;l)} A_{i+j} + B_l$, where $I(i,j;l)$ is the catalysis-driven aggregation rate kernel and similarly, the fragmentation of A clusters occurs only with the help of C clusters, $A_{i+j}+C_l \xrightarrow{J(l;i,j)} A_i+A_j+C_l$, where $J(l;i,j)$ is the catalysis-driven fragmentation rate kernel. By discussing the evolution behaviours of the systems, we found that the cluster-mass distributions $a_k(t)$ of species A depended strongly on the competition between the catalysis-driven aggregation process and the catalysis-driven fragmentation process.

The paper is organized as follows. In Section 2, we introduce the catalytically activated aggregation–fragmentation model and describe the outline of the generalized Smoluchowski's rate equation approach to study the kinetic evolution behaviours of the aggregate size distributions. A brief summary is given in Section 3.

2. Analytical solution of catalytically activated aggregation–fragmentation model

In our model, we assume that the self-coagulation rate kernels of species B and C are both independent of the size of reactants, namely, $K_1(i,j) = K_1$, $K_2(i,j) = K_2$ (here K_1 and K_2 are two constants). It is sound for some chemical and biological systems, especially for the polymerization of chain-shaped polymers that have only two energetic reactive edges. Similarly, we consider here that the catalysis-driven aggregation and fragmentation rate kernels of species A are both independent of the sizes of A aggregates. On the other hand, the catalyzed aggregation and fragmentation rates may have a relation with the impacting efficiency of the impacting clusters. In this model, a cluster is characterized only by its size and the impacting efficiency may be dependent on the size of the impacting cluster. In a spirit similar to Ref. [33], we also consider that the overall impacting efficiency of an l-mer can vary as l^u (here u is the homogeneity index characterizing the catalytic surface of an l-mer, e.g., for compact clusters $u = 2/3$,[34,35] and it is found that for many chemical and biological systems, $0 \leq u < 1$). Thus, the catalyzed aggregation and catalyzed fragmentation rate kernels in this model are assumed to be $I(i,j;l) = Il^{\upsilon}$, $J(l;i,j) = Jl^{\omega}$, respectively, and in this paper, we only discuss the case of $0 \leq \upsilon < 1$ and $0 \leq \omega < 1$.

Since our system is assumed to be of spatial homogeneity in the mean-field limit, the theoretical approach to the model can be based on the Smoluchowski rate equation given by Family *et al.*,[18] which assumes that the reaction proceeds at a rate proportional to the reactant concentrations. The governing rate equation for this model then reads

$$\frac{\mathrm{d}a_k}{\mathrm{d}t} = \frac{I}{2}\sum_{i+j=k}\sum_{l=1}^{\infty} l^{\upsilon} a_i a_j b_l - I a_k \sum_{j=1}^{\infty}\sum_{l=1}^{\infty} l^{\upsilon} a_j b_l + J\sum_{j,l=1}^{\infty} l^{\omega} a_{k+j} c_l - \frac{J}{2}\sum_{i+j=k}\sum_{l=1}^{\infty} l^{\omega} a_{i+j} c_l, \quad (1)$$

$$\frac{\mathrm{d}b_k}{\mathrm{d}t} = \frac{K_1}{2}\sum_{i+j=k} b_i b_j - K_1 b_k \sum_{j=1}^{\infty} b_j, \quad (2)$$

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = \frac{K_2}{2}\sum_{i+j=k} c_i c_j - K_2 c_k \sum_{j=1}^{\infty} c_j. \quad (3)$$

In Eq. (1), the first term on the right-hand side accounts for the gain in $a_k(t)$ due to the coagulation processes between $a_i(t)$ and $a_{k-i}(t)$ aggregates ($i = 1, 2, \ldots, k-1$) driven by catalyst B, $A_i + A_{k-i} + B_l \xrightarrow{Il^{\upsilon}} A_k + B_l$; while the second term accounts for the loss in $a_k(t)$ due to merging processes that the $a_k(t)$ aggregates bond with any other aggregates driven by catalyst B, $A_k + A_i + B_l \xrightarrow{Il^{\upsilon}} A_{k+i} + B_l$. The last two terms account for the gain and loss in $a_k(t)$ due to the catalyzed breakage processes driven by catalyst C: $A_{k+j} + C_l \xrightarrow{Jl^{\omega}} A_k + A_j + C_l$, and

$A_k + C_l \xrightarrow{Jl^{\omega}} A_i + A_j + C_l$. In Eq. (2) [similarly in Eq. (3)], the first term on the right-hand side accounts for the gain in $b_k(t)$ due to the coagulation processes between $b_i(t)$ and $b_{k-i}(t)$ aggregates $(i = 1, 2, \ldots, k-1)$, $B_i + B_{k-i} \xrightarrow{K_1} B_k$; while the second term accounts for the loss in $b_k(t)$ due to merging processes where the $b_k(t)$ aggregates bond with any other aggregates, $B_k + B_i \xrightarrow{K_1} B_{k+i}$.

The υ-th moment of the aggregate size distribution $a_k(t)$ of A-species can be expressed as

$$M_{\upsilon}^{A}(t) = \sum_{j=1}^{\infty} j^{\upsilon} a_j(t).$$

In particular,

$$M_0^A(t) = \sum_{j=1}^{\infty} a_j(t)$$

and

$$M_1^A(t) = \sum_{j=1}^{\infty} j a_j(t)$$

are the total number and the total mass of A-species aggregates, respectively. That is the same for B and C-species.

Using the expression of the moments of the aggregate size distributions, equations (1)–(3) can be respectively rewritten as

$$\frac{\mathrm{d}a_k}{\mathrm{d}t} = \left(\frac{I}{2}\sum_{i+j=k} a_i a_j - I a_k \sum_{j=1}^{\infty} a_j\right) M_{\upsilon}^{B} + \left(J\sum_{j=1}^{\infty} a_{k+j} - \frac{J}{2}\sum_{i+j=k} a_{i+j}\right) M_{\omega}^{C}, \quad (4)$$

$$\frac{\mathrm{d}b_k}{\mathrm{d}t} = \frac{K_1}{2}\sum_{i+j=k} b_i b_j - K_1 b_k M_0^B, \quad (5)$$

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = \frac{K_2}{2}\sum_{i+j=k} c_i c_j - K_2 c_k M_0^C. \quad (6)$$

The B and C clusters perform only the same coagulation processes, so their evolution kinetic behaviours are the same and relatively simple. The kinetics of simple coagulation process have been studied in the former work under the monodisperse initial condition $b_k(0) = B_0\delta_{k1}$ and $c_k(0) = C_0\delta_{k1}$ (B_0 and C_0 are the initial aggregate concentrations of B and C-species, respectively).[36] The accurate solution to the aggregate size distribution of B-species (similarly for C-species) is

$$b_k(t) = 4B_0(K_1B_0t + 2)^{-2}\left(1 - \frac{2}{K_1B_0t + 2}\right)^{k-1}. \quad (7)$$

In the scaling regime of $k \gg 1$ and $t \gg 1$, it can be asymptotically rewritten as

$$b_k(t) \simeq 4K_1^{-2}B_0^{-1}t^{-2}\exp(-x), \quad x = 2K_1^{-1}B_0^{-1}kt^{-1}, \quad (8)$$

which satisfies the conventional scaling law,[37,38]

$$f_k(t) \simeq t^{-\alpha}\Phi[k/S(t)], \quad S(t) \propto t^{\beta}, \quad (9)$$

with the scaling function $\Phi(x) = \exp(-x)$. The $S(t) = \frac{1}{2}K_1B_0t$ is the characteristic size of B aggregates, which plays a role analogous to the correlation length in critical phenomena. And $\alpha = 2$ and $\beta = 1$ are the scaling exponents.

From Eq. (7), we further derive the total number and total mass of B aggregates

$$M_0^B(t) = 2B_0(2 + K_1^{-1}B_0t)^{-1} \simeq 2K_1^{-1}t^{-1}, \quad M_1^B(t) = B_0, \quad (10)$$

i.e., the total number decays linearly with time as t^{-1}, and the total mass is conserved.

Now we focus on the kinetics of A clusters. Under the monodisperse initial conditions, $a_k(0) = A_0$, equation (4) can be solved with the help of an ansatz (the application of this ansatz has been thoroughly discussed in our previous work[31,32]),

$$a_k(t) = A(t)[a(t)]^{k-1}. \quad (11)$$

Substituting Eq. (11) into Eq. (4), we can transform the rate equations (4) to the following equations:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{IA}{2}M_{\upsilon}^{B} - \frac{J}{2}M_{\omega}^{C}a, \quad (12)$$

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -\frac{IA^2}{1-a}M_{\upsilon}^{B} + \frac{JA}{1-a}M_{\omega}^{C}a, \quad (13)$$

with the initial conditions

$$a(0) = 0, \quad A(0) = A_0. \quad (14)$$

From Eqs. (12) and (13) one can readily obtain

$$A = A_0(1-a)^2. \quad (15)$$

This indicates that the total mass of A clusters is naturally conserved by the dynamics of the catalyzed aggregation–fragmentation model,

$$M_A(t) = \sum_{j=1}^{\infty} j a_j(t) = \frac{A}{(1-a)^2} \equiv A_0.$$

This is reasonable because neither species-B-catalyzed aggregation of species A nor species-C-catalyzed fragmentation of species A can change its total mass.

Substituting Eq. (15) into Eq. (12), we recast it to

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{IA_0}{2} M_\upsilon^B (1-a)^2 - \frac{J}{2} M_\omega^C a. \tag{16}$$

Thus, the problem is reduced to deriving the expression for $a(t)$ from Eq. (16). And from Eq. (16), we find that the influence of species-B-catalyzed aggregation of species A is reflected by the υ-th moment of the aggregate size distribution $b_k(t)$ of catalyst B and similarly, the influence of species-C-catalyzed fragmentation of species A is reflected by the ω-th moment of the aggregate size distribution $c_k(t)$ of catalyst C.

First, we give the υ-th moment of the aggregate size distribution $b_k(t)$ of catalyst B from Eq. (7) as

$$\begin{aligned} M_\upsilon^B(t) &= \sum_{j=1}^{\infty} j^\upsilon b_j(t) \\ &\simeq \Gamma(1+\upsilon) B_0 \left(1 + \frac{1}{2} K_1 B_0 t\right)^{\upsilon-1}, \end{aligned} \tag{17}$$

where $\zeta(n) = \sum\limits_{l=1}^{\infty} l^{-n} \quad (n > 1)$ is the Riemann zeta function. Similarly, the ω-th moment of the distribution $c_k(t)$ of catalyst C is

$$\begin{aligned} M_\omega^C(t) &= \sum_{j=1}^{\infty} j^\omega c_j(t) \\ &\simeq \Gamma(1+\omega) C_0 \left(1 + \frac{1}{2} K_2 C_0 t\right)^{\omega-1}. \end{aligned} \tag{18}$$

In the following, we thoroughly investigate the dependence of the kinetics of the catalyzed aggregation–fragmentation system on the competition between species-B-catalyzed aggregation of species A and species-C-catalyzed fragmentation of species A in several different cases.

2.1. The system with $K_1 = K_2 = 0$

We first discuss the most special case where neither catalyst B nor catalyst C can coagulate by itself, that is, $K_1 = K_2 = 0$. In this special case, the governing rate equations of species B and C [Eqs. (2) and (3)] become

$$\frac{\mathrm{d}b_k}{\mathrm{d}t} = 0, \tag{19}$$

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = 0. \tag{20}$$

From these two rate equations and the monodisperse initial conditions of species B and C, we find $b_k(t) = b_k(0) = B_0\delta_{k1}$, and $c_k(t) = c_k(0) = C_0\delta_{k1}$, that is, there are only B monomer catalyst and C monomer catalyst. So, the coagulation of species A catalyzed by B monomer can be described as $A_i + A_j + B_1 \xrightarrow{I} A_{i+j} + B_1$, and the fragmentation of species A catalyzed by C monomer can be described as $A_{i+j} + C_1 \xrightarrow{J} A_i + A_j + C_1$.

In the above section, we have changed the governing rate equation (1) of species A into Eq. (16), and from Eqs. (17) and (18) one can easily judge in this special case that the two moments of catalysts B and C are both constants, $M_\upsilon^B(t) = B_0$, $M_\omega^C(t) = C_0$, so the kinetics of the system are reflected by the following equation,

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{IA_0B_0}{2}(1-a)^2 - \frac{JC_0}{2}a. \tag{21}$$

From Eq. (21), we obtain the exact solution of $a(t)$ as

$$a(t) = \frac{C_1 - C_2\exp(-C_3t)}{1-\exp(-C_3t)}, \tag{22}$$

where

$$C_1 = \frac{2IA_0B_0 + JC_0 - \sqrt{(JC_0)^2 + 4IJA_0B_0C_0}}{2IA_0B_0},$$

$$C_2 = \frac{2IA_0B_0 + JC_0 + \sqrt{(JC_0)^2 + 4IJA_0B_0C_0}}{2IA_0B_0},$$

and

$$C_3 = \frac{1}{2}\sqrt{(JC_0)^2 + 4IJA_0B_0C_0}.$$

We further derive the exact solution of $A(t)$ from Eq. (15),

$$A(t) = A_0\left[\frac{1 - C_1 + (C_2-1)\,\mathrm{e}^{-C_3t}}{1 - \mathrm{e}^{-C_3t}}\right]^2. \tag{23}$$

Thus, the aggregate size distribution of species A is exactly derived as

$$\begin{aligned} a_k(t) &= A_0\left[\frac{1 - C_1 + (C_2-1)\,\mathrm{e}^{-C_3t}}{1 - \mathrm{e}^{-C_3t}}\right]^2 \\ &\quad \times \left(\frac{C_1 - C_2\,\mathrm{e}^{-C_3t}}{1 - \mathrm{e}^{-C_3t}}\right)^{k-1}. \end{aligned} \tag{24}$$

In the region of $t \gg 1$, equation (24) can be asymptotically rewritten as

$$\begin{aligned} &a_k(t) \simeq A_0(1-C_1)^2 C_1^k \exp[-k/S(t)], \\ &S(t) = C_1C_2^{-1}\,\mathrm{e}^{C_3t}. \end{aligned} \tag{25}$$

Equation (25) shows that the usual scaling form (9) breaks down for this case and the aggregate size distribution satisfies the modified scaling form,[39]

$$f_k(t) \simeq \lambda^k [f(t)]^{-\omega} \Phi[k/S(t)], \quad S(t) \propto [f(t)]^z. \tag{26}$$

Here, $f(t)$ is a monotonically increasing function of time. And the governing scaling exponents, w and z, describe the scaling properties of the aggregate size distribution. In this case, $f(t) = \mathrm{e}^t$, $w = 0$, and $z = C_3$. Moreover, it is well known that the usual scaling form has only one scale $S(t)$. Equation (26) shows that the modified scaling form comprises two scales: the growing scale $S(t)$ and the time-independent scale $S = \lim_{t\to\infty} M_2(t)/M_1(t) \simeq (1+\lambda)/(1-\lambda)$. The growing scale denotes the evolution of the aggregates driven by catalyzed aggregation and catalyzed fragmentation, while the time-independent scale dominates the kinetic behaviour of the system in the long-time limit. For this case, the growing scale is $S(t) = C_1 C_2^{-1}\,\mathrm{e}^{C_3 t}$, which indicates that under the monodisperse initial condition, species-B-catalyzed aggregation of species A dominates over species-C-catalyzed fragmentation of species A at the beginning of the process; and the time-independent scale is $S = (1+C_1)/(1-C_1)$, which 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 cluster-mass distribution is independent of time.

Moreover, the total number of species A is obtained as

$$N_A(t) = M_0^A(t) = A_0\left[\frac{1 - C_1 + (C_2 - 1)\,\mathrm{e}^{-C_3 t}}{1 - \mathrm{e}^{-C_3 t}}\right], \quad (27)$$

which means that the total number decreases with time and remains a finial value $A_0(1-C_1)$ in the steady state.

2.2. System with $K_1 = 0$ and $K_2 \neq 0$

We then discuss the case where catalyst B does not coagulate by itself, and only catalyst C coagulates as $C_i + C_j \xrightarrow{K_2} C_{i+j}$. The coagulation of species A catalyzed by B monomer can still be described as $A_i + A_j + B_1 \xrightarrow{I} A_{i+j} + B_1$, but the fragmentation of species A catalyzed by C clusters becomes $A_{i+j} + C_l \xrightarrow{Jl^\omega} A_i + A_j + C_l$.

In this case, the governing rate equation of species B is the same as Eq. (19), and that of species C is the same as Eq. (3). Then we can judge that the moment of catalyst B holds as a constant, $M_\upsilon^B(t) = B_0$, but the moment of catalyst C can vary with time as Eq. (18).

Thus, the governing rate equation of species A in this case becomes

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{IA_0B_0}{2}(1-a)^2 - \frac{J}{2}M_\omega^C a. \quad (28)$$

It is difficult to derive the exact solutions of $a(t)$ from Eq. (28). We then turn to discuss the asymptotic but more interesting behaviours of Eq. (28) in the long time limit. We assume that the system reaches its steady state at $t \to \infty$ and the steady conditions are given as

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{IA_0B_0}{2}(1-a)^2 - \frac{J}{2}M_\omega^C a = 0. \quad (29)$$

Then we determine the asymptotic solution of $a(t)$ in the long-time limit,

$$a(t) \simeq 1 - C_4 t^{-\frac{1}{2}(1-\omega)}, \quad (30)$$

where $C_4 = [2^{1-\omega}\Gamma(1+\omega)J(IA_0B_0)^{-1}C_0^\omega K_2^{\omega-1}]^{1/2}$. The cluster size distribution is obtained to satisfy the conventional scaling form,[37,38]

$$a_k(t) \simeq C_4^2 A_0 t^{-(1-\omega)}\exp(-x), \quad x = k/S(t), \quad (31)$$

where the typical size $S(t) = C_4^{-1}t^{\frac{1}{2}(1-\omega)}$ and the scaling exponents $\alpha = 1-\omega$, $\beta = (1-\omega)/2$. The fact of $a_k(t)$ following the conventional form implies that in this case the influence of species-B-catalyzed aggregation of species A is greater than that of species-C-catalyzed fragmentation of species A, that is, the aggregation of species A driven by catalyst B dominates the system [the aggregate size distribution satisfies the conventional scaling law in simple aggregation growth, which can be seen from Eq. (8)].

Moreover, the total number of species A is derived,

$$N_A(t) \simeq C_4 A_0 t^{-\frac{1}{2}(1-\omega)}, \quad (32)$$

which indicates that in the long-time limit, species A will completely coagulate. This is reasonable because catalyst C will completely coagulate into one giant cluster at large times while the B monomer would not change, so in the long-time limit, the catalyzed aggregation process dominates over the catalyzed fragmentation process and species A completely coagulates under the catalysis of the B monomer. And the comparison of Eqs. (10) and (32) concludes that in this case, $N_A(t)$ decays with time more slowly than in the simple aggregation case, which is just the effect of species-C-catalyzed fragmentation of species A.

2.3. System with $K_1 \neq 0$ and $K_2 = 0$

In this case, catalyst C does not coagulate by itself, and only catalyst B coagulates as $B_i + B_j \xrightarrow{K_1} B_{i+j}$. The coagulation of species A catalyzed by B

clusters becomes $A_i + A_j + B_l \xrightarrow{Il^{\upsilon}} A_{i+j} + B_l$, and the fragmentation of species A catalyzed by C monomer is $A_{i+j} + C_1 \xrightarrow{J} A_i + A_j + C_1$.

In this case, the governing rate equation of species C is the same as Eq. (20), and that of species B is the same as Eq. (2). The moment of catalyst C holds as a constant, $M_{\omega}^{C}(t) = C_0$, but the moment of catalyst B can vary with time as Eq. (17).

The governing rate equation of species A in this case is

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{IA_0}{2} M_{\upsilon}^{B} (1-a)^2 - \frac{JC_0}{2} a. \tag{33}$$

If the system can reach the steady state at $t \to \infty$, we have

$$\frac{IA_0}{2} M_{\upsilon}^{B} (1-a)^2 - \frac{JC_0}{2} a = 0. \tag{34}$$

Equation (34) gives $a(t) \sim t^{1-\upsilon} \to \infty$, but our ansatz Eq. (11) implies that $0 < a(t) < 1$ should be obeyed for all time $t > 0$, so we can conclude that the system cannot reach the steady state in this case. This is not surprising because $M_{\upsilon}^{B}(t) \sim t^{-(1-\upsilon)} \to 0$ at $t \to \infty$, equation (33) can be asymptotically rewritten as

$$\frac{\mathrm{d}a}{\mathrm{d}t} \sim -\frac{JC_0}{2} a. \tag{35}$$

The asymptotical solution is

$$a(t) \sim C_5 \exp\left(-\frac{JC_0}{2} t\right), \tag{36}$$

where C_5 is an integration constant. The cluster size distribution is then derived as

$$a_k(t) \sim C_5^{k-1} A_0 \exp\left(-\frac{(k-1)JC_0}{2} t\right). \tag{37}$$

It is obvious that the scaling form of cluster size distribution $a_k(t)$ breaks down completely in this case. Moreover, we derive the total number of species A,

$$N_A(t) \sim A_0 \left[1 - C_5 \exp\left(-\frac{JC_0}{2} t\right)\right] \to A_0, \tag{38}$$

which indicates that in the long-time limit, the catalyzed fragmentation process dominates over the catalyzed aggregation process, so species A will completely fragment under the catalysis of monomer C and come back to its monodisperse initial condition. In fact, we can judge that at the beginning of the process, species-B-catalyzed aggregation of species A dominates over the monomer-C-catalyzed fragmentation of species A, and $N_A(t)$ decreases with time; but after a sufficiently long time, all the B clusters bond together to form one giant cluster, the dominating process becomes monomer-C-catalyzed fragmentation of species A and reasonably, $N_A(t)$ increases with time, that is, species A will completely break up to its initial conditions under the catalysis of monomer C. So, we conclude that when the catalyzed fragmentation process dominates the system, the monodisperse initial condition of species A would not be changed in the long-time limit.

2.4. System with $K_1 \neq 0$ and $K_2 \neq 0$

In this case, both the B and C catalysts coagulate by themselves as $B_i + B_j \xrightarrow{K_1} B_{i+j}$ and $C_i + C_j \xrightarrow{K_2} C_{i+j}$, so, the coagulation of species A catalyzed by B clusters is $A_i + A_j + B_l \xrightarrow{Il^{\upsilon}} A_{i+j} + B_l$, and the fragmentation of species A catalyzed by C clusters is $A_{i+j} + C_l \xrightarrow{Jl^{\omega}} A_i + A_j + C_l$.

The governing rate equations of the two catalysts are the same as Eqs. (2) and (3), so the two moments can vary with time as Eqs. (17) and (18), then the governing rate equation of species A in this case is

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{IA_0}{2} (1-a)^2 M_{\upsilon}^{B}(t) - \frac{J}{2} a M_{\omega}^{C}(t). \tag{39}$$

From Eq. (39), we can judge that the competition between the catalyzed aggregation process and catalyzed fragmentation process is reflected by the two catalysis rate kernel parameters.

When $\upsilon > \omega$, we assume that the system reaches its steady state at $t \to \infty$ and the steady conditions are given as

$$\frac{IA_0}{2} M_{\upsilon}^{B} (1-a)^2 - \frac{J}{2} M_{\omega}^{C} a = 0. \tag{40}$$

From Eq. (40), one can easily obtain the asymptotical solution of $a(t)$ at large times

$$a(t) \simeq 1 - C_6 t^{-\frac{1}{2}(\upsilon-\omega)}, \tag{41}$$

where

$$C_6 = \left[\frac{2^{\upsilon-\omega} J\Gamma(1+\omega) C_0^{\omega} K_2^{\omega-1}}{IA_0 \Gamma(1+\upsilon) B_0^{\upsilon} K_1^{\upsilon-1}}\right]^{1/2}.$$

Then the cluster size distribution is obtained to satisfy the conventional scaling form,

$$a_k(t) \simeq C_6^2 A_0 t^{-(\upsilon-\omega)} \exp(-x), \quad x = k/S(t), \tag{42}$$

with the typical size $S(t) = C_6^{-1} t^{\frac{1}{2}(\upsilon-\omega)}$. And it is easy to find that the total number $N_A(t)$ decreases with time as $t^{-\frac{1}{2}(\upsilon-\omega)}$, which means that the effect of species B catalyzed species A aggregation is greater

than that of species C catalyzed species A fragmentation, that is, the catalyzed aggregation process dominates the system, so in the long-time limit, species A will completely coagulate.

When $\upsilon = \omega = \mu$, we still assume that the system reaches its steady state at $t \to \infty$, then we have

$$\frac{IA_0}{2} M_\mu^B (1-a)^2 - \frac{J}{2} M_\mu^C a = 0. \tag{43}$$

From Eq. (43) we find

$$\begin{aligned} & a(t) \to a_\infty \\ &= 1 - \sqrt{\left(\frac{JC_0^\mu K_2^{\mu-1}}{2IA_0 B_0^\mu K_1^{\mu-1}}\right)^2 + \frac{JC_0^\mu K_2^{\mu-1}}{IA_0 B_0^\mu K_1^{\mu-1}}} \\ &\quad - \frac{JC_0^\mu K_2^{\mu-1}}{2IA_0 B_0^\mu K_1^{\mu-1}}, \end{aligned}$$

which indicates that the effects of catalyzed aggregation and catalyzed fragmentation counteract each other and a balance can be established between the two processes. Hence, the system reaches a steady state finally.

Now we discuss the asymptotical kinetics of the system near the equilibrium point. In the long-time limit, we introduce a new variable $\tilde{a}(t) = a_\infty - a(t)$ and then recast Eq. (39) into an asymptotical equation as follows,

$$\frac{\mathrm{d}\tilde{a}}{\mathrm{d}t} \simeq -C_7 t^{\mu-1} \tilde{a}^2 - \gamma t^{\mu-1} \tilde{a}, \tag{44}$$

where

$$C_7 = 2^{-\mu} \Gamma(1+\mu) IA_0 B_0^\mu K_1^{\mu-1}$$

and

$$\gamma = 2^{-\mu} \Gamma(\mu)[2IA_0(1-a_\infty) B_0^\mu K_1^{\mu-1} + JC_0^\mu K_2^{\mu-1}].$$

Equation (44) is a Bernoulli equation and can be asymptotically solved in the long-time limit,

$$\tilde{a}(t) \simeq \begin{cases} C_8 t^{-\gamma}, & \mu = 0, \\ C_9 \, \mathrm{e}^{-\gamma t^\mu}, & \mu > 0, \end{cases} \tag{45}$$

where C_8 and C_9 are two integration constants.

Then the cluster size distribution is obtained to satisfy the modified scaling form,

$$a_k(t) \simeq A_0 (1-a_\infty)^2 a_\infty^k \exp[-k/S(t)], \tag{46}$$

where $S(t) = C_8^{-1} a_\infty t^{\gamma_2}$ for $\mu = 0$ and $S(t) = C_9^{-1} a_\infty \, \mathrm{e}^{\gamma_3 t^\mu}$ for $\mu > 0$. The total number of A-species $N_A(t) = M_0^A(t) \to A_0(1-a_\infty)^2$, which indicates that the total number can remain a certain value in the long-time limit. Hence, after a sufficiently long time, a balance will be established between species-B-catalyzed aggregation of species A and species-C-catalyzed fragmentation of species A, that is, the system can eventually evolve to a steady state.

When $\upsilon < \omega$, the effect of species C catalyzed species A framentation is greater than that of species B catalyzed species A aggregation, so one can easily judge that the system cannot evolve to a steady state, and the monodisperse initial condition of species A would not be changed in the long-time limit.

3. Summary

In summary, we have proposed a three-species (A, B, and C) catalytically activated reaction model with competition between the catalyzed aggregation process and the catalyzed fragmentation process. In the system, the clusters of catalysts B and C can coagulate by themselves, and meanwhile, A clusters can coagulate under the catalysis of B clusters and break up under the catalysis of C clusters. The analytical solution of the cluster size distribution $a_k(t)$ was deduced by means of the rate-equation approach. It was found that the kinetics of the system are very different from those of the common aggregation–fragmentation model, and the evolution behaviours of species A are crucially dependent on whether the catalyst aggregates coagulate by themselves or not. When catalyst B does not coagulate by itself and only catalyst C coagulates, the catalyzed aggregation process dominates the system and $a_k(t)$ satisfies the conventional scaling form. When only catalyst B coagulates by itself, the catalyzed fragmentation process dominates the system and the monodisperse initial condition of species A would not be changed in the long-time limit. When neither catalyst B nor catalyst C coagulates by itself, a balance between catalyzed aggregation and fragmentation will be established and $a_k(t)$ takes the modified scaling form. When both B and C catalysts coagulate by themselves, the competition between catalyzed aggregation and catalyzed fragmentation is reflected by the catalyzed aggregation rate kernel parameter υ and catalyzed fragmentation rate kernel parameter ω: in the case of $\upsilon > \omega$, catalyzed aggregation dominates the system and $a_k(t)$ satisfies the conventional scaling form; in the case of $\upsilon < \omega$, catalyzed fragmentation dominates the system and the monodisperse initial condition of species A would not be changed in the long-time limit; and in the case of $\upsilon = \omega$, a balance between catalyzed aggregation and catalyzed

fragmentation can be established and the system can eventually evolve to a steady state.

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