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Solvable single-species aggregation–annihilation model for chain-shaped cluster growth

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Abstract

We propose a single-species aggregation–annihilation model, in which an aggregation reaction between two clusters produces an active cluster and an annihilation reaction produces an inert one. By means of the mean-field rate equation, we respectively investigate the kinetic scaling behaviours of three distinct systems. The results exhibit that: (i) for the general aggregation–annihilation system, the size distribution of active clusters consistently approaches the conventional scaling form; (ii) for the system with the self-degeneration of the cluster's activities, it takes the modified scaling form; and (iii) for the system with the self-closing of active clusters, it does not scale. Moreover, the size distribution of inert clusters with small size takes a power-law form, while that of large inert clusters obeys the scaling law. The results also show that all active clusters will eventually transform into inert ones and the inert clusters of any size can be produced by such an aggregation–annihilation process. This model can be used to mimic the chain-shaped cluster growth and can provide some useful predictions for the kinetic behaviour of the system.

1. Introduction

In the last few decades, considerable researches have been devoted to the nonequilibrium cluster growth phenomenon [1–17], which is of fundamental interest to the understanding of diverse natural processes, such as aerosol formation, crystal growth, star formation, droplet growth, and so on. Most of these works have been focused on the kinetic behaviour of cluster growth through the binary coalescence mechanism, $A_i + A_j \rightarrow A_{i+j}$, where A_i denotes a cluster consisting of i monomers [5–13]. This is, the clusters A_i and A_j can bond spontaneously to form a larger cluster A_{i+j}. Most intriguingly, such processes have exhibited that the size

distribution of clusters may approach a scaling form in the long-time limit [8–10]. Additionally, much effort has also been paid to investigating the kinetics of the basic bimolecular annihilation reactions, $A+A \rightarrow 0$ [18–21] and $A+B \rightarrow 0$ [22–28], which are of great significance in many basic and applied problems such as the recombination of an electron–hole and annihilation of localized triplet electronic states of aromatic molecules in rigid solution [29].

Krapivsky was the first to generalize the above-mentioned bimolecular annihilation scheme to a pairwise annihilation scheme of clusters, $A_{i+j} + B_j \rightarrow A_i$ or $A_i + B_{i+j} \rightarrow B_j$, and to investigate the competition between the aggregation and annihilation processes of a two-species system [30]. Ben-Naim and Krapivsky proposed another complete annihilation scheme, $A_i + B_j \rightarrow 0$, and then studied the kinetic behaviour of the aggregation processes with complete annihilation [31]. Recently, the evolution kinetics of aggregation–annihilation processes has been extensively investigated by the rate equation approach as well as Monte Carlo simulation [32–35]. In these works, aggregation reactions occur between any two clusters of the same species and annihilation reactions simultaneously occur between any two clusters of different species. It is found that such aggregation–annihilation processes give rise to rich cluster growth kinetics. In most practical situations, it may be sound to establish the above-mentioned schemes for aggregation and annihilation reactions. However, there also exist some situations in which both aggregation and annihilation reactions could occur between two clusters of the same species [36, 37]. For example, in a single-component chemical system with chain-shaped polymers, two polymers can bond together to form an active open polymer chain, and meanwhile, the emerging of two clusters can also produce an inert closed chain (i.e., a ring). Moreover, the open chains can continue to participate in subsequent reactions, while the closed chains will withdraw from the reaction system because they lose reactive edges. The polymerization that produces an open polymer chain can be regarded as an aggregation process, while that which yields a closed chain is considered as an annihilation process. To the best of our knowledge, the competition between the aggregation and annihilation processes of such a single-species system remains unexplored.

In this work, we propose a single-species aggregation–annihilation model, in which two clusters of type A bond to form a larger active cluster according to the aggregation reaction, $A_i + A_j \xrightarrow{I_1(i;j)} A_{i+j}$, and they emerge to produce a larger inert cluster according to the complete annihilation reaction, $A_i + A_j \xrightarrow{I_2(i;j)} 0$. Here, $I_1(i;j)$ represents the aggregation rate kernel and $I_2(i;j)$ the annihilation rate kernel. We believe that this single-species aggregation–annihilation model may mimic a wide variety of physical and chemical phenomena such as the above-mentioned example (see, e.g., [16]). It is also believed that our model is of interest in studying the scaling properties of its own evolution behaviours. Here, we devote ourselves to investigating the kinetic behaviour of the chain-shaped cluster growth based on the single-species aggregation–annihilation model. It is found that the size distribution of active clusters takes a conventional scaling form with nonuniversal scaling exponents, while the evolution behaviour of inert clusters falls in two distinct kinetic regimes.

This model is studied in the mean-field limit. The mean-field assumption neglects the spatial fluctuations of the reactant concentrations and, therefore, typically applies to the case in which the spatial dimension d of the system is equal to or greater than an upper critical dimension d_c. For $d < d_c$, the fluctuations in the spatial distribution of the reactants may give rise to dimension-dependent kinetics. There are some simulation models for cluster growth through diffusion-controlled aggregation of clusters, such as the particle coalescence (PC) and cluster–cluster aggregation (CCA) model [6–8, 11, 12], which can be used to find out the upper critical dimension. The simulation results have shown that for pure aggregation processes, $d_c = 2$ [11, 12]. For the pure n-component annihilation processes, the upper critical dimension

is $d_c = 4(n-1)/(2n-3)$ [38], which reduces to $d_c = 2$ in the limit $n \to \infty$. Since our model interpolates between pure aggregation and pure infinite-component annihilation, it is natural to expect that for our system the upper critical dimension is the same, $d_c = 2$. This assumption may be confirmed to a certain extent by the fact that for two-species aggregation–annihilation processes, the upper critical dimension is also $d_c = 2$ [31, 32]. In this work, we assume that the spatial dimension d of our system is greater than 2 and, therefore, the mean-field approach can be used to analytically investigate the kinetic behaviour of our model.

The rest of the paper is organized as follows. In section 2, we propose a general single-species aggregation–annihilation model and then determine the analytical solution of the cluster size distribution by solving the mean-field rate equation. In section 3, we investigate the kinetics of the aggregation–annihilation processes with the self-degeneration of the activities of active clusters. In section 4, we further study the kinetic behaviour of the same reaction processes but with the self-closing of active clusters. Finally, a brief summary is given in section 5.

2. General single-species aggregation–annihilation processes

At time t, the concentration of the active clusters (or equivalently, open chains) consisting of k monomers is denoted as $a_k(t)$. As we aim to obtain the analytical solution of the time-dependent concentration $a_k(t)$ and then discuss the kinetic evolution of the cluster growth, we propose here a simple model with constant rate kernels, i.e., $I_1(i; j) = I_1$ and $I_2(i; j) = I_2$ (here I_1 and I_2 are two nonzero constants). In the mean-field limit, an element reaction is assumed to proceed at a rate proportional to the concentrations of the reactants. Thus, the evolution of the concentration $a_k(t)$ can be investigated by the rate equation approach. The generalized Smoluchowski rate equation for this single-species general aggregation–annihilation model can be written as

$$\frac{\mathrm{d}a_k}{\mathrm{d}t} = \frac{I_1}{2}\sum_{i+j=k} a_i a_j - I_1 a_k \sum_{j=1}^{\infty} a_j - I_2 a_k \sum_{j=1}^{\infty} a_j. \tag{1}$$

In equation (1), the first term on the right-hand side accounts for the gain in $a_k(t)$ due to the aggregation reactions between the active clusters A_i and A_{k-i} ($i = 1, 2, \ldots, k-1$), and the second and third terms account for the loss in $a_k(t)$ due to the aggregation and annihilation reactions between the active cluster A_k and any other active clusters.

Introducing the generating function, $G(y, t) = \sum_{j=1}^{\infty} y^j a_j(t)$, we recast equation (1) to

$$\frac{\partial G}{\partial t} = \frac{I_1}{2}G^2 - (I_1 + I_2)M_0 G, \tag{2}$$

with the shorthand notation $M_0(t) = \sum_{j=1}^{\infty} a_j(t)$. Equation (2) can be solved straightforwardly to yield

$$G(y, t) = \frac{G_0(y)E(t)}{1 - G_0(y)\int_0^t \frac{I_1}{2}E(t')\,\mathrm{d}t'}, \tag{3}$$

where $G_0(y) = \sum_{j=1}^{\infty} y^j a_j(0)$ and $E(t) = \exp[-(I_1 + I_2)\int_0^t M_0(t')\,\mathrm{d}t']$. Obviously, we have $G(1, t) = M_0(t)$. When $y = 1$, equation (2) reduces to

$$\frac{\mathrm{d}M_0}{\mathrm{d}t} = -\frac{1}{2}(I_1 + 2I_2)M_0^2. \tag{4}$$

From equation (4) one readily deduces the exact solution of $M_0(t)$ as follows:

$$M_0(t) = M_0(0)\left[1 + \frac{I_1 + 2I_2}{2}M_0(0)t\right]^{-1}, \tag{5}$$

where the constant $M_0(0)$ is the initial total number of active clusters. It is found that the total number $M_0(t)$ decays as t^{-1} at large times. We substitute equation (5) into (3) and then obtain the general solution of $G(y,t)$ under arbitrary initial conditions,

$$G(y,t) = \frac{G_0(y)(1+C_1t)^{-2(I_1+I_2)/(I_1+2I_2)}}{1-G_0(y)M_0^{-1}(0)\left[1-(1+C_1t)^{-I_1/(I_1+2I_2)}\right]}, \tag{6}$$

where $C_1 = (I_1+2I_2)M_0(0)/2$.

By expanding equation (6) in powers of y one can then deduce the general solution of $a_k(t)$ for the system with arbitrary initial data. Here, we consider the simplest but important case in which there only exist monomer clusters at $t = 0$ and their concentration is equal to A_0, i.e., $a_k(0) = A_0\delta_{k1}$. Obviously, $G_0(y) = A_0y$ and $M_0(0) = A_0$. Under the monodisperse initial condition, we expand the resulting generating function (6) in series and then obtain the exact solution of the size distribution of active clusters as follows:

$$a_k(t) = A_0(1+C_1t)^{-2(I_1+I_2)/(I_1+2I_2)}\left[1-(1+C_1t)^{-I_1/(I_1+2I_2)}\right]^{k-1}. \tag{7}$$

Equation (7) shows that each $a_k(t)$ consistently decays with time and finally decreases to zero. Hence, for our system no active clusters can survive finally. In the region of $k \gg 1$ and $t \gg 1$, equation (7) can be approximately rewritten as

$$a_k(t) \simeq A_0(C_1t)^{-2(I_1+I_2)/(I_1+2I_2)}\exp(-x), \qquad x = k(C_1t)^{-I_1/(I_1+2I_2)}, \tag{8}$$

which approaches the conventional scaling form (see, e.g., [8, 30, 31, 34, 35]),

$$a_k(t) \sim t^{-w}\Phi[k/S(t)], \qquad S(t) \propto t^z. \tag{9}$$

Here, $S(t)$ is the typical cluster size which plays a role analogous to that of the correlation length in ordinary critical phenomena, and the exponents (w and z) represent the scaling properties of the cluster size distribution. In this case, the scaling function is an exponential form, $\Phi(x) = \exp(-x)$, and the governing exponents are nonuniversal constants, $w = 2(I_1+I_2)/(I_1+2I_2)$ and $z = I_1/(I_1+2I_2)$, which are dependent on the values of the rate constants.

We then determine the total size of active clusters, $M_1(t) = \sum_{j=0}^{\infty} ja_j(t) = A_0(1+C_1t)^{-2I_2/(I_1+2I_2)}$. This indicates that the total size of active clusters decays with time and all the clusters finally turn out to be inert ones.

It is also instructive to investigate the size distribution of inert clusters (or equivalently, closed polymer chains) under the above-mentioned monodisperse initial condition. At time t, the concentration of inert clusters consisting of k monomers is denoted as $b_k(t)$. It is obvious that $b_1(t) \equiv 0$. Then $b_k(t)$ ($k > 1$) evolves according to the following differential equation:

$$\frac{\mathrm{d}b_k}{\mathrm{d}t} = \frac{I_2}{2}\sum_{i+j=k} a_ia_j. \tag{10}$$

We insert equation (7) into (10) and then obtain

$$b_k(t) = \frac{I_2}{2}A_0^2\int_0^t \mathrm{d}t'(k-1)(1+C_1t')^{-4(I_1+I_2)/(I_1+2I_2)}\left[1-(1+C_1t')^{-I_1/(I_1+2I_2)}\right]^{k-2}. \tag{11}$$

Equation (11) is directly integrated to yield

$$\begin{aligned} b_k(t) = {} & C_2(1+C_1t)^{-2(I_1+I_2)/(I_1+2I_2)}\left[1-(1+C_1t)^{-I_1/(I_1+2I_2)}\right]^{k-1} \\ & + C_3k^{-1}(1+C_1t)^{-1}\left[1-(1+C_1t)^{-I_1/(I_1+2I_2)}\right]^{k} \\ & + C_4k^{-2(I_1+I_2)/I_1}\int_{k(1+C_1t)^{-I_1/(I_1+2I_2)}}^{k} \mathrm{d}y\left(1-\frac{y}{k}\right)^k y^{2I_2/I_1}, \end{aligned} \tag{12}$$

where $C_2 = I_2A_0/I_1$, $C_3 = 2I_2(I_1 + I_2)A_0/I_1^2$, and $C_4 = 2I_2(I_1 + I_2)(I_1 + 2I_2)A_0/I_1^3$. In the region of $k \gg 1$ and $t \gg 1$, equation (12) can be asymptotically rewritten as

$$b_k(t) \simeq k^{-2(I_1+I_2)/I_1}\left[(C_2x + C_3)x^{(I_1+2I_2)/I_1}\exp(-x) + C_4\int_x^k \mathrm{d}y\left(1 - \frac{y}{k}\right)^k y^{2I_2/I_1}\right], \quad (13)$$

with the scaling variable $x = k(C_1t)^{-I_1/(I_1+2I_2)}$. For $1 \ll k \ll (C_1t)^{I_1/(I_1+2I_2)}$, the size distribution $b_k(t)$ of inert clusters takes the power-law form,

$$b_k(t) \sim k^{-2(I_1+I_2)/I_1}, \quad (14)$$

which is asymptotically independent of time. For $k \gg (C_1t)^{I_1/(I_1+2I_2)}$, $b_k(t)$ approaches the conventional scaling form (9) as follows:

$$b_k(t) \sim (C_1t)^{-2(I_1+I_2)/(I_1+2I_2)}\exp(-x), \qquad x = k(C_1t)^{-I_1/(I_1+2I_2)}, \quad (15)$$

with the scaling exponents $w = 2(I_1 + I_2)/(I_1 + 2I_2)$ and $z = I_1/(I_1 + 2I_2)$. The results indicate that there exists a typical size $S(t) = (C_1t)^{I_1/(I_1+2I_2)}$ which divides the above two distinct evolution regimes of the size distribution of inert clusters. The most interesting result is that the concentration $b_k(t)$ of inert clusters with size $k \ll S(t)$ almost retains a constant value in the long-time limit. This growth property of inert clusters may be of significance in some practical chemical processes such as polymerization.

We also analyse the evolution behaviours of the total number and the total size of inert clusters. Summing up equation (10), one can obtain

$$\frac{\mathrm{d}M_0^\flat}{\mathrm{d}t} = \frac{I_2}{2}M_0^2, \qquad \frac{\mathrm{d}M_1^\flat}{\mathrm{d}t} = I_2M_0M_1, \quad (16)$$

where $M_0^\flat(t) = \sum_{j=2}^\infty b_j(t)$ and $M_1^\flat(t) = \sum_{j=2}^\infty jb_j(t)$. Equation (16) is readily integrated to yield

$$M_0^\flat(t) = \frac{I_2A_0^2}{2C_1}[1 - (1 + C_1t)^{-1}], \qquad M_1^\flat(t) = A_0[1 - (1 + C_1t)^{-2I_2/(I_1+2I_2)}], \quad (17)$$

which shows that both the total number and the total size of inert clusters slowly increase with time. And in the long-time limit, $M_0^\flat(t) \simeq I_2A_0/(I_1 + 2I_2)$ and $M_1^\flat(t) \simeq A_0$.

3. The processes with the self-degeneration of the cluster's activities

Next, we investigate another cluster growth system, in which, besides the aggregation and annihilation schemes of active clusters similar to those for the above model, the monomers at the ends of an active cluster may spontaneously lose their reactive activities due to some factors and withdraw from the reaction processes, namely, $A_k \to$ inert. The self-degeneration rate of the activities of active clusters is set to be a constant J. Then the governing rate equation for active clusters reads

$$\frac{\mathrm{d}a_k}{\mathrm{d}t} = \frac{I_1}{2}\sum_{i+j=k} a_ia_j - I_1a_k\sum_{j=1}^\infty a_j - I_2a_k\sum_{j=1}^\infty a_j - Ja_k. \quad (18)$$

In equation (18), the last term on the right-hand side accounts for the loss in $a_k(t)$ due to the activity degeneration of the clusters A_k. Moreover, for a realistic chemical system with dilution, the loss term $-Ja_k$ in equation (18) can also represent the dilution of the whole system at a constant rate.

Summing up equation (18), one can obtain

$$\frac{\mathrm{d}M_0}{\mathrm{d}t} = -\frac{1}{2}(I_1 + 2I_2)M_0^2 - JM_0, \quad (19)$$

which is exactly solved to give

$$M_0(t) = \frac{M_0(0)\mathrm{e}^{-Jt}}{C_6 - C_5\mathrm{e}^{-Jt}}, \tag{20}$$

where $C_5 = (I_1 + 2I_2)M_0(0)/2J$ and $C_6 = C_5 + 1$. Moreover, multiplying equation (18) with k and summing over all k, we obtain

$$\frac{\mathrm{d}M_1}{\mathrm{d}t} = -M_1(I_2M_0 + J). \tag{21}$$

From equation (21) we deduce

$$M_1(t) = M_1(0)\mathrm{e}^{-Jt}(C_6 - C_5\mathrm{e}^{-Jt})^{-2I_2/(I_1+2I_2)}. \tag{22}$$

In this system, both the total number and the total size of active clusters decays exponentially at $t \gg 1$, and thus all the active clusters cannot finally survive.

We then determine the size distribution of active clusters. Equation (18) can also be solved by the method of the generating function. Introducing the generating function, $H(y,t) = \sum_{j=1}^{\infty} y^k a_k(t)$, one can transform equation (18) into

$$\frac{\partial H}{\partial t} = \frac{I_1}{2}H^2 - [(I_1 + I_2)M_0 + J]H. \tag{23}$$

From equation (23) one then deduces the general solution of $H(y,t)$ under arbitrary initial conditions,

$$H(y,t) = \frac{H_0(y)\mathrm{e}^{-Jt}(C_6 - C_5\mathrm{e}^{-Jt})^{-2(I_1+I_2)/(I_1+2I_2)}}{1 - H_0(y)M_0^{-1}(0)\left[1 - (C_6 - C_5\mathrm{e}^{-Jt})^{-I_1/(I_1+2I_2)}\right]}, \tag{24}$$

with the shorthand notation $H_0(y) = \sum_{j=1}^{\infty} y^j a_j(0)$. Here we also consider the case under the simple monodisperse initial condition, $a_k(0) = A_0\delta_{k1}$. Expanding the resulting generating function (24) in powers of y, we obtain the exact solution of the size distribution of active clusters as follows:

$$a_k(t) = A_0\mathrm{e}^{-Jt}(C_6 - C_5\mathrm{e}^{-Jt})^{-2(I_1+I_2)/(I_1+2I_2)}\left[1 - (C_6 - C_5\mathrm{e}^{-Jt})^{-I_1/(I_1+2I_2)}\right]^{k-1}. \tag{25}$$

In the region of $k \gg 1$ and $t \gg 1$, equation (25) can be approximately rewritten as

$$a_k(t) \simeq A_0C_6^{-2(I_1+I_2)/(I_1+2I_2)}\left[1 - C_6^{-I_1/(I_1+2I_2)}\right]^k \mathrm{e}^{-Jt}\exp(-x), \qquad x = C_7k\mathrm{e}^{-Jt}, \tag{26}$$

where $C_7 = I_1C_5C_6^{-2(I_1+I_2)/(I_1+2I_2)}[1-C_6^{-I_1/(I_1+2I_2)}]^{-1}/(I_1+2I_2)$. Equation (26) indicates that for this system the conventional scaling description (9) of the cluster size distribution breaks down and $a_k(t)$ approaches the modified scaling form (see, e.g., [30, 34]),

$$a_k(t) \sim \lambda^k[f(t)]^{-w}\Phi[k/S(t)], \qquad S(t) \propto [f(t)]^z, \tag{27}$$

where $f(t)$ is an increasing time function and λ is a constant satisfying $0 < \lambda < 1$. In this case, $f(t) = \mathrm{e}^t$. The governing exponents are nonuniversal, $w = z = J$, and the scaling function is $\Phi(x) = \exp(-x)$. Moreover, the modified scaling form (27) also implies that there are two different scales, the growing scale $S(t) \propto [f(t)]^z$ and the time-independent scale $S = \lim_{t\to\infty} M_2(t)/M_1(t) = (1-\lambda)^{-1}$, that are associated with active clusters. The growing scale $S(t)$ is driven crucially by the self-degeneration of the cluster's activities in the beginning of the reaction processes, but the time-independent scale S will dominate the evolution behaviour of the system in the long-time limit. For this case, $S(t) \propto \mathrm{e}^t$ and $S = C_6^{I_1/(I_1+2I_2)}$. Moreover, $a_k(t)$ also decays with time and finally vanishes.

We then turn to investigate the size distribution $b_k(t)$ of inert clusters under the monodisperse initial condition. Obviously, the rate equation for inert clusters in this system is the same as that in the above section. Inserting equation (25) into (10), we obtain

$$\dot{b}_k(t) = \frac{I_2}{2} A_0^2 (k-1) \mathrm{e}^{-2Jt} (C_6 - C_5 \mathrm{e}^{-Jt})^{-4(I_1+I_2)/(I_1+2I_2)} \left[1 - (C_6 - C_5 \mathrm{e}^{-Jt})^{-I_1/(I_1+2I_2)}\right]^{k-2}. \tag{28}$$

In the region of $k \gg 1$ and $t \gg 1$, equation (28) can be integrated to yield the following asymptotic solution:

$$b_k(t) \simeq k^{-1} \left[1 - C_6^{-I_1/(I_1+2I_2)}\right]^k \left[\frac{I_2 A_0}{I_1 C_7} x + \frac{2 I_2 J}{I_1^2}\right] \exp(-x), \tag{29}$$

with the shorthand notation $x = C_7 k \mathrm{e}^{-Jt}$. Equation (29) indicates that the size distribution of inert clusters satisfies the unusual scaling form, $a_k(t) \sim h^k k^{-\tau} \Phi[k/S(t)]$, with the exponentially growing scaling variable $S(t) \propto \mathrm{e}^{Jt}$. For $1 \ll k \ll \mathrm{e}^{Jt}$, the size distribution of inert clusters asymptotically takes the form

$$b_k(t) \sim k^{-1} [1 - C_6^{-I_1/(I_1+2I_2)}]^k. \tag{30}$$

For $k \gg \mathrm{e}^{Jt}$, $b_k(t)$ approaches the modified scaling form (27) as follows:

$$b_k(t) \sim [1 - C_6^{-I_1/(I_1+2I_2)}]^k \mathrm{e}^{-Jt} \exp[-k/S(t)], \tag{31}$$

with the growing scale $S(t) = C_7^{-1} \mathrm{e}^{Jt}$ and the time-independent scale $S = C_6^{I_1/(I_1+2I_2)}$. In contrast with the above general aggregation–annihilation processes, the typical size that divides two distinct evolution regimes of inert clusters is an exponentially increasing function, $S(t) = \mathrm{e}^{Jt}$. It is also of interest to determine the total number and the total size of inert clusters. Using equations (20) and (22), we deduce the following exact solutions:

$$M_0^{\flat}(t) = C_8 - C_5^{-1} C_8 \ln F(t) - C_8 \mathrm{e}^{-Jt} [F(t)]^{-1}, \tag{32}$$

$$M_1^{\flat}(t) = A_0 + 2 I_1^{-1} J - 2 I_1^{-1} J [F(t)]^{I_1/(I_1+2I_2)} - A_0 \mathrm{e}^{-Jt} [F(t)]^{-2I_2/(I_1+2I_2)}, \tag{33}$$

where $C_8 = I_2 A_0^2/(2JC_5)$ and $F(t) = C_6 - C_5 \mathrm{e}^{-Jt}$. At large times, equations (32) and (33) can be approximately rewritten as $M_0^{\flat}(t) \simeq C_8 - C_5^{-1} C_8 \ln C_6$ and $M_1^{\flat}(t) = A_0 + 2J/I_1 - 2 I_1^{-1} J C_6^{I_1/(I_1+2I_2)}$. These results indicate that the inert clusters of any size can be conserved by the dynamics of the aggregation–annihilation processes even with cluster consumption.

4. The processes with the self-closing of active clusters

Finally, we propose a somehow actual system, in which two active clusters bond together to form an active cluster at a constant rate I_1 and an inert one at a constant rate I_2; meanwhile, an active cluster whose size is larger than unity spontaneously becomes a ring (i.e., an inert cluster) with the constant probability J. The corresponding rate equations for this system are

$$\frac{\mathrm{d}a_1}{\mathrm{d}t} = -I_1 a_1 \sum_{j=1}^{\infty} a_j - I_2 a_1 \sum_{j=1}^{\infty} a_j, \tag{34}$$

and

$$\frac{\mathrm{d}a_k}{\mathrm{d}t} = I_1 \left(\frac{1}{2} \sum_{i+j=k} a_i a_j - a_k \sum_{j=1}^{\infty} a_j\right) - I_2 a_k \sum_{j=1}^{\infty} a_j - J a_k \qquad \text{for } k > 1. \tag{35}$$

In equation (35), the last term on the right-hand side accounts for the loss in $a_k(t)$ owing to the self-closing of the active clusters A_k ($k > 1$). One can easily find out, by comparing

equations (34) and (35) with equation (18), that this model differs from the previous model in section 3 only in the behaviour of monomers.

Summing up equations (34) and (35), we obtain

$$\frac{\mathrm{d}a_1}{\mathrm{d}t} = -(I_1 + I_2)a_1 M_0, \qquad \frac{\mathrm{d}M_0}{\mathrm{d}t} = -\left(\frac{I_1}{2} + I_2\right) M_0^2 - J M_0 + J a_1. \tag{36}$$

From equation (36) one readily obtains the first-order approximation solutions of $a_1(t)$ and $M_0(t)$ at large times,

$$a_1(t) \simeq \frac{a_1(0)}{1 + a_1(0)(I_1 + I_2)t}, \qquad M_0(t) \simeq \frac{M_0(0)}{1 + M_0(0)(I_1 + I_2)t}. \tag{37}$$

Substituting equation (37) into the differential equation (35) of $a_2(t)$, one can then determine the long-time asymptotical solution

$$a_2(t) \simeq \frac{J}{2I_1}\left[\frac{I_1 a_1(0)}{J + J(I_1 + I_2)a_1(0)t}\right]^2. \tag{38}$$

Further, substituting equations (37) and (38) into equation (35) yields the asymptotical solution of $a_3(t)$ at large times,

$$a_3(t) \simeq \frac{J}{2I_1}\left[\frac{I_1 a_1(0)}{J + J(I_1 + I_2)a_1(0)t}\right]^3. \tag{39}$$

The rest may be deduced by analogy. In the long-time limit, the asymptotical solution of $a_k(t)$ can be expressed as

$$a_k(t) \simeq c_k \frac{J}{I_1}\left[\frac{I_1 a_1(0)}{J + J(I_1 + I_2)a_1(0)t}\right]^k, \tag{40}$$

where c_k is a series of constants satisfying $c_k = (1/2)\sum_{i+j=k} c_i c_j$ and $c_1 = 1$. Equation (40) implies that for this case the conventional scaling description of the cluster size distribution breaks down and $a_k(t)$ takes a power-law form. Obviously, $a_k(t)$ decreases with time and vanishes in the limit $t \to \infty$. We then determine the total size of active clusters. Multiplying equations (34) and (35) with k and summing them up, we obtain

$$\frac{\mathrm{d}M_1}{\mathrm{d}t} = -I_2 M_0 M_1 - J M_1 + J a_1. \tag{41}$$

From equation (41) one can derive the first-order approximation solution of $M_1(t)$ in the long-time limit,

$$M_1(t) \simeq (I_1 + I_2)^{-1} t^{-1}. \tag{42}$$

The results show that the total number and the total size of active clusters both decay consistently with time. Hence, the active clusters will finally be consumed completely.

We then investigate the evolution behaviour of inert clusters. The governing rate equation for $b_k(t)$ ($k \geqslant 2$) reads

$$\frac{\mathrm{d}b_k}{\mathrm{d}t} = \frac{I_2}{2}\sum_{i+j=k} a_i a_j + J a_k. \tag{43}$$

Substituting equation (40) into (43) and integrating it, one can determine the large-time asymptotical solution of $b_k(t)$ as follows:

$$b_k(t) \simeq d_k(k-1)^{-1}[I_1 J^{-1} a_1(0)]^{k-1} - d_k(k-1)^{-1}[I_1^{-1} J(I_1 + I_2)t]^{-k+1}, \tag{44}$$

where $d_k = Jc_k/I_1$. Further, equation (44) can be rewritten as $b_k(t) \simeq d_k(k-1)^{-1}[I_1 J^{-1} a_1(0)]^{k-1}$. So, the inert clusters also do not scale according to the scaling law. Moreover, summing up equation (43), we obtain

$$\frac{\mathrm{d}M_0^{\flat}}{\mathrm{d}t} = \frac{I_2}{2}M_0^2 + JM_0 - Ja_1, \qquad \frac{\mathrm{d}M_1^{\flat}}{\mathrm{d}t} = I_2 M_0 M_1 + JM_1 - Ja_1. \tag{45}$$

Substituting equations (37) and (42) into equation (45), one can readily deduce that $M_0^{\flat}(t)$ and $M_1^{\flat}(t)$ both increase with time and finally reach nonzero constant values. So, the inert clusters of any size can finally be conserved. The results indicate that the evolution behaviour of the system is crucially controlled by the self-closing of active clusters.

5. Summary

We have proposed a simple single-species aggregation–annihilation model for chain-shaped cluster growth, in which the emerging of two clusters can produce either an active cluster or an inert one. In the mean-field limit, we have investigated the kinetic behaviours of several different systems with constant rate kernels by employing the rate equation approach. It is found that the scaling behaviour of the cluster size distribution depends strongly on the details of the reaction events such as the rate kernels.

For the general aggregation–annihilation system, the size distribution $a_k(t)$ of active clusters approaches the conventional scaling form (9), while the evolution behaviour of the size distribution $b_k(t)$ of inert clusters falls in two distinct kinetic regimes divided by a typical size $S(t) = (C_1 t)^{I_1/(I_1+2I_2)}$. For $1 \ll k \ll S(t)$, $b_k(t)$ takes a power-law form, while for $k \gg S(t)$, $b_k(t)$ also scales according to the conventional form (9). Moreover, all active clusters will eventually transform into inert clusters, and inert clusters of any size can finally be conserved.

For an aggregation–annihilation system with the self-degeneration of the activities of active clusters, the cluster size distribution $a_k(t)$ obeys the modified scaling law (27). The cluster size distribution $b_k(t)$ takes a power-law form for $1 \ll k \ll \mathrm{e}^{Jt}$, while for $k \gg \mathrm{e}^{Jt}$, it approaches the modified scaling form (27). In this system, active clusters will also finally be consumed completely. In contrast with the above system, only a part of active clusters can transform into inert clusters. Finally, the system consists of all kinds of inert clusters and 'active' clusters that lose reactive activities.

We have also proposed an actual system in which, besides the aggregation and annihilation reactions, an active cluster may close itself to become an inert ring. It is found that the scaling description of the size distribution breaks down for both active and inert clusters. The size distribution of active clusters takes the power-law form, $a_k(t) \sim t^{-k}$, and that of inert clusters approaches another power-law form, $b_k(t) \sim d_k(k-1)^{-1}[I_1 J^{-1} a_1(0)]^{k-1}$. However, all active clusters also completely transform finally into inert clusters.

This single-species aggregation–annihilation model may be expected to provide useful theoretical predictions of the kinetic evolution for some chemical processes, especially for the polymerization of chain-shaped polymers.

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