Scaling in Aggregation Process with a Kernel Related to the Reaction Activities *

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We study the kinetics of a reversible aggregation model in which an aggregation reaction occurs between any two clusters and the fragmentation of the larger clusters occurs simultaneously. By investigating the mean-field rate equation of the process with a kernel related to the reaction activities we obtain the asymptotic solution of the cluster-mass distribution. It is found that the kinetic evolution behaviour of the clusters depends crucially on the details of the rate kernel. The cluster-mass distribution in the irreversible aggregation system obeys a conventional scaling law; while for the reversible case, the conventional scaling description of the cluster-mass distribution breaks down and the system falls in a modified scaling region.

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Aggregation is the principal process underlying a variety of natural phenomena such as colloid growth, aerosol formation, droplet growth, and so on.[1−3] In the last few decades, many theoretical developments have been devoted to understanding the kinetic evolution behaviour of the aggregates in the aggregation processes.[4−12] In general, the aggregation process is interesting because it exhibits that the cluster-mass distributions of the aggregates may approach a scaling form in the long-time limit.[4−6] There are also many situations in which the reverse aggregation is of significance.[13−17] For example, the population evolution of a residential district can be regarded as an aggregation-fragmentation biological system with constituent monomers. The immigration of foreign settlers will form a larger population centre, while the emigration of the inhabitants causes a decrease in the population of the centre. Moreover, as the district grows in the population, the possibility of emigration increases. However, most of these works were focused on the coalescence models with a reaction kernel only related to the details of the reactants (the size, the geometry, and so on), and the aggregation processes with a product-dependent reaction kernel remain unexplored.

The reversible aggregation processes can be represented by the reaction scheme

$$A_i + A_j \underset{J(i,j)}{\overset{K(i;j)}{\rightleftharpoons}} A_{i+j},$$

where A_i denotes a cluster consisting of i-mers of A species. The rate of the aggregation reaction between A_i and A_j clusters is equal to $K(i,j)$, and $J(i,j)$ denotes the reverse reaction rate of the cluster A_{i+j} fragmenting into two smaller clusters A_i and A_j. The theoretical approach to the reversible aggregation process can be based on the mean-field assumption, which neglects the spatial fluctuation of the reactant densities and therefore applies to the case that the spatial dimension d of the system is greater than or equal to a critical dimension d_c. When $d < d_c$, the fluctuations in the densities of the reactants may lead to dimension-dependent kinetic behaviour in the long-time limit. For the reversible aggregation processes, it is found that $d_c < 1$.[17]

In this Letter, we assume that for our system the spatial dimension d is greater than unity, and thus the mean-field rate equation can provide an accurate description of our model. The mean-field assumption assumes that the reaction proceeds with a rate proportional to the concentrations of the reactants. Here, the concentration of A clusters with k monomers is denoted as a_k. We propose a model with a kernel related to both the concentrations of the reactants and of the products, i.e., $K(i,j) = I(a_i a_j/a_{i+j})^{\nu}$ and $J(i,j) = J(a_{i+j}/a_i a_j)^{\varpi}$, where $a_i a_j/a_{i+j}$ and $a_{i+j}/a_i a_j$ are defined as the "reaction activities", and ν and ϖ are two positive constants depending on the reaction events. According to the mean-field rate equation given by Family *et al.*,[17] the rate equation for our aggregation-fragmentation model can be written as

$$\frac{\mathrm{d}a_k}{\mathrm{d}t} = \frac{I}{2}\Big[\sum_{i+j=k}\Big(\frac{a_i a_j}{a_{i+j}}\Big)^{\nu} a_i a_j - 2a_k \sum_{j=1}^{\infty}\Big(\frac{a_k a_j}{a_{k+j}}\Big)^{\nu} a_j\Big] - \frac{J}{2}\Big[\sum_{i+j=k}\Big(\frac{a_{i+j}}{a_i a_j}\Big)^{\varpi} a_{i+j} - 2\sum_{j=1}^{\infty}\Big(\frac{a_{k+j}}{a_k a_j}\Big)^{\varpi} a_{k+j}\Big]. \quad (1)$$

We consider the simplest but important case in which there only exist the monomers of A species at

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$t = 0$ and their concentration is equal to A_0. The monodisperse initial condition then reads

$$a_k(0) = A_0\delta_{k1}. \tag{2}$$

Eq. (1) can be solved with the help of ansatz[18]

$$a_k = A(t)[a(t)]^{k-1}. \tag{3}$$

Substituting Eq. (3) into Eq. (1), we transform the governing rate Eq. (1) into two differential equations as follows:

$$\begin{aligned}\frac{\mathrm{d}a}{\mathrm{d}t} &= \frac{IA}{2}\Big(\frac{A}{a}\Big)^{\nu} - \frac{Ja}{2}\Big(\frac{a}{A}\Big)^{\varpi},\\ \frac{\mathrm{d}A}{\mathrm{d}t} &= -\frac{IA^2}{1-a}\Big(\frac{A}{a}\Big)^{\nu} + J\frac{aA}{1-a}\Big(\frac{a}{A}\Big)^{\varpi},\end{aligned} \tag{4}$$

with the corresponding initial conditions

$$a = 0, \quad A = A_0 \quad \text{at } t = 0. \tag{5}$$

From Eqs. (4) one can easily obtain

$$A = A_0(1-a)^2. \tag{6}$$

Eq. (4) can then be rewritten as

$$\begin{aligned}\frac{\mathrm{d}a}{\mathrm{d}t} =& \frac{IA_0}{2}(1-a)^2\Big[\frac{A_0(1-a)^2}{a}\Big]^{\nu}\\ &- \frac{J}{2}a\Big[\frac{A_0(1-a)^2}{a}\Big]^{-\varpi}.\end{aligned} \tag{7}$$

We first discuss the irreversible aggregation process with $J = 0$. Equation (7) then reduces to

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{IA_0^{1+\nu}}{2}(1-a)^{2+2\nu}a^{-\nu}. \tag{8}$$

Introducing a new variable $\alpha = (1-a)^{-1}$, we recast Eq. (8) to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{IA_0^{1+\nu}}{2}(\alpha^2-\alpha)^{-\nu}. \tag{9}$$

We then determine the asymptotic solution of $\alpha(t)$ at large times,

$$\alpha(t) \simeq C_1 t^{1/(2\nu+1)}, \tag{10}$$

where $C_1 = [IA_0^{1+\nu}(2\nu+1)/2]^{1/(2\nu+1)}$. Thus we obtain the asymptotic solution of $a_k(t)$ in the long-time limit,

$$a_k(t) \simeq A_0C_1^{-2}t^{-2/(2\nu+1)}[1 - C_1^{-1}t^{-1/(2\nu+1)}]^k. \tag{11}$$

Eq. (11) can be rewritten as

$$a_k(t) \simeq A_0C_1^{-2}t^{-2/(2\nu+1)}\exp(-x), \tag{12}$$

which is valid in the scaling region

$$k \gg 1, \quad t \gg 1, \quad x = (k/C_1)t^{-1/(2\nu+1)} = \text{finite}. \tag{13}$$

Eq. (12) implies that for the irreversible aggregation system, the evolution of concentration of A clusters falls in a scaling regime at large times. In the scaling region, the average mass of the large clusters increases indefinitely, which may be assumed to play a role analogous to that of the correlation length in the ordinary critical phenomena. Generally, a function $S(t)$ is used to denote the characteristic mass, and the concentration $a_k(t)$ of the aggregates at large times can then be written in the following scaling form:[18]

$$a_k(t) \simeq t^{-w}\Phi[k/S(t)], \quad S(t) \propto t^z. \tag{14}$$

For this case, the scaling function is exponential, $\Phi(x) = \exp(-x)$, and the typical mass is $S(t) \propto t^{1/(2\nu+1)}$. The governing exponents are $w = 2/(2\nu+1)$ and $z = 1/(2\nu+1)$, which depend on the value of the activity index ν. When $\nu = 0$, Eq. (12) reduces to the well-known Smoluchowski solution for the irreversible aggregation model with a constant rate kernel and the universal exponents are $w = 2$ and $z = 1$ (see, e.g., Refs. [1,2]).

It is also instructive determine the total number and the total mass of the clusters. By summing Eq. (11), we find the asymptotic behaviour of the total number in the long-time limit,

$$N(t) = \sum_{k=1}^{\infty} a_k(t) \simeq (A_0/C_1)t^{-1/(2\nu+1)}. \tag{15}$$

The evolution behaviour of total mass is

$$M(t) = \sum_{k=1}^{\infty} ka_k(t) \equiv A_0. \tag{16}$$

These indicate that the total number of the clusters decays as $t^{-1/(2\nu+1)}$ while the total mass obeys the mass conservation law. This is unsurprising for the irreversible aggregation system.

Now we turn to the reversible case. From Eq. (7) we determine the asymptotic solution of $a(t)$ at large times,

$$a(t) \simeq C_2 - C_3\mathrm{e}^{-\gamma t}, \tag{17}$$

where

$$\begin{aligned}C_2 =& [2 + A_0^{-1}(J/I)^{1/(1+\nu+\varpi)}\\ &- \sqrt{A_0^{-2}(J/I)^{2/(1+\nu+\varpi)} + 4A_0^{-1}(J/I)^{1/(1+\nu+\varpi)}}]/2,\\ \gamma =& J(1+C_2)(1+\nu+\varpi)A_0^{-\varpi}C_2^{\varpi}(1-C_2)^{-2\varpi-1}/2,\end{aligned}$$

and C_3 is an integration constant. Thus we obtain the asymptotic solution of $a_k(t)$ for large A_k clusters ($k \gg 1$) at large times,

$$\begin{aligned}a_k(t) \simeq& A_0(1-C_2)^2[1 + 2C_3(1-C_2)^{-1}\\ &\cdot \mathrm{e}^{-\gamma t}]C_2^k\exp(-x), \quad x = (C_3k/C_2)\mathrm{e}^{-\gamma t}.\end{aligned} \tag{18}$$

Eq. (18) indicates that for the reversible aggregation system, the cluster-mass distribution does not

scale according to the conventional scaling definition (14) but it satisfies the modified scaling form,[19] $a_k(t) \simeq b^k[f(t)]^{-w}\Phi[k/S(t)]$, with the typical mass $S(t) \propto [f(t)]^z$. Here, b is a constant and $0 < b < 1$, and $f(t)$ is an unusual time-dependent function such as e^t, $\ln t$, and so on. For this case, the scaling function is exponential, $\Phi(x) = \exp(-x)$, and the function $f(t)$ is also exponential, $f(t) = \mathrm{e}^t$. Thus, we find that the governing exponents are $w = 0$ and $z = \gamma$. The results indicate the evolution behaviour of the system depends crucially on the details of the reaction events (the initial monomer concentration and the rate kernel's indices and coefficients). On the other hand, the modified scaling form implies that two different mass scales are associated with the species. One is a growing scale $S(t) \propto \mathrm{e}^{\gamma t}$, which is forced by the reversible reaction. Another is a time-independent scale $S_A = 1/(1 - C_2)$, which dominates the evolution of the clusters in the long-time limit. When $(J/I)^{1/(1+\nu+\varpi)} \ll A_0$, it is obvious that $C_2 \to 1$ and thus the scale S_A will diverge. It is not difficult to find that the total number $N(t)$ of A clusters decreases with time and $N(t) \to A_0(1 - C_2)$ as $t \to \infty$. Of course, the total mass of the clusters always maintains a constant A_0, which is natural for the aggregation-fragmentation system without annihilation.

Making a comparison between the results of the irreversible aggregation case and those of the reversible one, we find that an important characteristic of the reversible process is the formation of a steady-state cluster-mass distribution after a large time while the total number of the clusters in the irreversible system is always decreasing with time. For the reversible process, the coagulation reaction decreases the number of the clusters while the breakup process increases it. Hence, it is natural to assume that after a sufficiently long time (i.e., $t \gg \tau$ and τ is a crossover time), a balance is established between the two competing processes and the system comes to a steady state. In the steady state, the cluster-mass distribution is independent of time, we find that $a_k(t = \tau) \simeq A_0(1 - C_2)^2 C_2^{k-1}$ for small clusters and $a_k(t = \tau) \simeq A_0(1-C_2)^2 C_2^k \exp[-(C_3 k/C_2)\mathrm{e}^{-\gamma\tau}]$ for large clusters, which are in agreement with the numerical simulation results for $I = 1$, $\nu = \varpi = 0$, and $A_0 \gg J$.[17] The total number of the clusters decreases with time and its steady-state value $N(t = \infty) = A_0(1 - C_2)$ has relations with the details of the reaction events (A_0, I, J, ν, and ϖ). In the case with $IA_0 \gg J$ and $\nu = \varpi = 0$, we obtain $N(t) \propto J$, which is also in accord with the numerical simulation results in Ref. [17].

In summary, we have studied a simple reversible aggregation system of single species on the basis of the mean-field theory. Considering the model with a kernel related to the reaction activities, we analysed the evolution behaviour of the cluster-mass distribution. The cluster-mass distribution in the irreversible aggregation system obeys the conventional scaling law, while the usual scaling description of the mass distribution breaks down in the reversible case and the species scales according to a modified scaling form. The results indicate that the evolution behaviour of the system depends crucially on the details of the reaction rate kernel.

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