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Kinetics of the catalysis-driven aggregation processes

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We study a catalysis-driven aggregation model in which irreversible growth of A aggregates occurs only with the help of the catalyst. The results show that kinetics of the system depends strongly on whether the catalyst coagulates by itself or not. The mass distribution of A clusters obeys a conventional scaling law in the case without self-coagulation of the catalyst, while for the reverse case the evolution of the system falls in a peculiar scaling regime. Our theory applies to diverse phenomena such as the cluster-size distribution in a chemical system.

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The aggregation phenomenon is of widespread interest in many fields of science and technology [1–3]. Typically, let A_i denote a cluster consisting of i monomers, an irreversible aggregation process can be described by the reaction scheme $A_i+A_j\rightarrow A_{i+j}$. That is, the clusters A_i and A_j can bond spontaneously and form a larger cluster A_{i+j}. In the last few decades, many theoretical developments stemmed from the analyses of the evolution behaviors of the aggregates and made kinetics of the aggregation system well understood [4–13]. Theoretical investigations showed that the mass distribution of the aggregates approaches a scaling form in the long-time limit [4–8,10,11]. In general, most of these works focused on the above self-coagulation processes. Kang and Redner [14] introduced a particle coalescence model (PCM). In the PCM, the clusters are defined to be single lattice sites, and the aggregation or annihilation reaction occurs whenever two or more clusters occupy the same lattice site. The PCM can be used to investigate the kinetics of the cluster-cluster aggregation processes in low dimensions [15,16]. On the other hand, the PCM can be viewed as the aggregation or annihilation of the clusters only in the presence of an immobile substance, the "catalytic site." In fact, the catalysis-activated processes play important roles in many technologies as they help in producing required products from the species that are nonreactive in normal physical conditions. Those chemically stable species may enter a reaction in the presence of a third catalytic substance. Recently, Burlatsky *et al.* [17] and Oshanin *et al.* [18] introduced a three molecule reaction model and analyzed the kinetics of the processes by extending the Smoluchowski approach. In the catalysis-activated reaction model (CARM), the 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. However, the irreversible aggregation processes driven by a mobile catalyst remain fully unexplored.

We now define our catalysis-driven aggregation model based on the CARM. In this model, the first elementary reaction step is a reversible reaction, $A_i+B\rightleftharpoons A_iB$, and the second step is an irreversible reaction, $A_iB+A_j\rightarrow A_{i+j}+B^*$, 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. We assume that the reversible reaction reaches its steady state in no time. Thus, the catalytic reaction is controlled by the second step. The catalytic reaction then reads $A_i+A_j+B\overset{K(i;j)}{\rightarrow}A_{i+j}+B^*$, which is similar to the above-mentioned three molecule reaction. Here, $K(i;j)$ is the equivalent catalytic reaction rate.

It is well known that after the catalytic reaction the product of the catalyst may or may not retain its catalytic ability. On the other hand, the catalyst molecules may coagulate by themselves in some cases, and for other cases self-aggregation of the catalyst does not occur. In this paper, we investigate thoroughly the dependence of the kinetics of the aggregation system on the catalyst. We believe that our catalysis-driven aggregation model not only provides a natural description of the evolution of aggregate-mass distribution in the above-mentioned chemical process, but also mimics a wide variety of physical and social phenomena. For example, cooperative business operation of two separate companies proceeds only with the help of an intermediary in some economic activities, which may be regarded as a catalysis-driven aggregation process. On the other hand, the catalysis-driven mechanism exhibits very rich kinetic behavior and is thus of interest in studying the scaling evolution properties of the aggregation system.

We study our model in the mean-field limit. The mean-field approach to the reaction process assumes that the reaction proceeds with a rate proportional to the concentrations of the reactants. The mean-field assumption neglects the spatial fluctuation of the reactant densities and, therefore, applies to the case in which the spatial dimension d of the system is equal to or greater than a critical dimension d_c. As for the case of $d<d_c$, the fluctuations in the reactant densities may lead to a diffusion-controlled kinetics in the long-time limit. It is found that for an irreversible aggregation system $d_c=2$ [6,14]. In our model, the dominant reaction is also an irreversible binary aggregationlike reaction. Hence, it is reasonable that for our system the critical dimension d_c is also equal to 2. The spatial dimension d of our system is assumed to be greater than 2 and the mean-field approach is thus valid.

We first investigate the catalysis-driven aggregation processes without any consumption of the catalyst. Generally,

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*Electronic address: kejianhong@yahoo.com.cn we assume that self-coagulation of the catalyst B, $B_i+B_j \xrightarrow{J(i;j)} B_{i+j}$, coexists with the catalytic reaction, and the aggregation rate is equal to $J(i;j)$. The concentrations of A and B clusters of k-mers are denoted as a_k and b_k, respectively. We consider a simple model with constant reaction rates. All the catalytic aggregation rates $K(i;j)$ equal a constant I_1 and the self-coagulation rates $J(i;j)$ of B clusters equal I_2. Then the mean-field rate equations for the catalysis-driven aggregation process read

$$\frac{da_k}{dt}=\frac{I_1}{2}\sum_{i+j=k}\sum_{l=1}^{\infty} a_i a_j b_l - I_1 a_k \sum_{j=1}^{\infty}\sum_{l=1}^{\infty} a_j b_l,$$

$$\frac{db_k}{dt}=\frac{I_2}{2}\sum_{i+j=k} b_i b_j - I_2 b_k \sum_{j=1}^{\infty} b_j. \tag{1}$$

We consider the simplest but important case of monodisperse initial conditions,

$$a_k(0)=A_0\delta_{k1}, \quad b_k(0)=B_0\delta_{k1}. \tag{2}$$

The rate equations (1) can then be solved with the help of ansatz [10]

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

Substituting Eqs. (3) into Eqs. (1), we can transform the rate equations (1) into the following differential equations:

$$\frac{da}{dt}=\frac{I_1AB}{2(1-b)}, \quad \frac{dA}{dt}=-\frac{I_1A^2B}{(1-a)(1-b)}, \tag{4}$$

$$\frac{db}{dt}=\frac{I_2B}{2}, \quad \frac{dB}{dt}=-\frac{I_2B^2}{1-b}, \tag{5}$$

with the corresponding initial conditions

$$a=0, \quad b=0, \quad A=A_0, \quad B=B_0 \quad \text{at } t=0. \tag{6}$$

From Eqs. (4) and (5), one can easily determine

$$\begin{aligned} a(t)&=\frac{I_1A_0\ln\left(\frac{I_2B_0}{2}t+1\right)}{I_1A_0\ln\left(\frac{I_2B_0}{2}t+1\right)+I_2}, \quad A(t)\\ &=I_2^2A_0\left[I_1A_0\ln\left(\frac{I_2B_0}{2}t+1\right)+I_2\right]^{-2},\\ b(t)&=\frac{I_2B_0t}{I_2B_0t+2}, \quad B(t)=\frac{4B_0}{(I_2B_0t+2)^2}. \end{aligned} \tag{7}$$

Thus we obtain the asymptotic scaling solutions,

$$a_k(t)\simeq\left(\frac{I_2}{I_1}\right)^2 A_0^{-1}(\ln t)^{-2}\exp(-x),$$

$$b_k(t)\simeq 4I_2^{-2}B_0^{-1}t^{-2}\exp(-y), \tag{8}$$

which are valid in the regions $k\gg1$, $t\gg1$, $x=(I_2/I_1A_0)k(\ln t)^{-1}=\text{finite}$, $y=(2/I_2B_0)kt^{-1}=\text{finite}$. In the long-time limit, the cluster-mass distribution of B catalyst approaches a conventional scaling law as follows [10]:

$$c_k(t)\simeq t^{-w}\Phi[k/S(t)], \quad S(t)\propto t^z, \tag{9}$$

where $S(t)$ is the characteristic mass which plays a role analogous to that of correlation length in ordinary critical phenomena. However, A species scales according to the logarithm-correction form $c_k(t)\simeq(\ln t)^{-w}\Phi\{k/S(\ln(t))\}$. In this case, the governing exponents for both species are the same, $w=2$ and $z=1$. The typical mass of A species grows as $\ln t$ while that of B catalyst grows as t. Moreover, both species satisfy the mass conversation law, $M_A(t)=\Sigma_k k a_k=A/(1-a)^2\equiv A_0$ and $M_B(t)=\Sigma_k k b_k=B/(1-b)^2\equiv B_0$, which is natural for the aggregation processes without any consumption of the reactants. On the other hand, it is well known that for a general irreversible aggregation system with a constant rate kernel the cluster-mass distribution approaches the conventional scaling form of Eq. (9) [1,2]. Thus we conclude that this catalysis-driven aggregation mechanism gives a somewhat different kinetic behavior from the conventional aggregation.

For $I_2=0$ case in which B catalyst does not aggregate by itself, the governing equations (1) reduce to

$$\frac{da_k}{dt}=\frac{I_1}{2}\sum_{i+j=k}(a_i a_j b_1)-I_1 a_k\sum_{j=1}^{\infty}(a_j b_1), \quad \frac{db_1}{dt}=0. \tag{10}$$

Under the initial conditions (2), from Eqs. (10) we obtain the well-known Smoluchowski solution for the cluster-mass distribution of A species,

$$a_k(t)\simeq 4A_0(I_1A_0B_0t)^{-2}\exp(-x), \quad x=2k(I_1A_0B_0t)^{-1}, \tag{11}$$

with the scaling exponents $w=2$ and $z=1$. The results imply that for this case A species scales as in an irreversible single-species aggregation system [1,2].

By making a comparison between Eqs. (8) and (11) we find that self-coagulation of the catalyst makes the conventional scaling description of the mass distribution break down and the evolution behavior of the system obeys a logarithm-correction scaling form. The results also imply that the coagulation of the catalyst delays the evolution course of the system.

Second, we turn to investigate the catalysis-driven aggregation processes with the catalyst consumption. After the catalytic reaction, the product B^* of the catalyst loses its catalytic ability and then withdraws from the process. We first consider the case without self-coagulation of the catalyst. The governing mean-field rate equations (10) for the catalysis-driven aggregation processes are then rewritten as

$$\frac{da_k}{dt}=\frac{I_1}{2}\sum_{i+j=k}(a_i a_j b_1)-I_1 a_k\sum_{j=1}^{\infty}(a_j b_1),$$

$$\frac{db_1}{dt}=-\frac{I_1}{2}b_1\sum_{i,j=1}^{\infty}a_i a_j\,. \tag{12}$$

Under the monodisperse initial conditions (2), with the help of the ansatz (3) we transform Eqs. (12) into the following equations:

$$\frac{da}{dt}=\frac{I_1 AB}{2},\quad \frac{dA}{dt}=-\frac{I_1 A^2 B}{1-a},\quad \frac{dB}{dt}=-\frac{I_1 A^2 B}{2(1-a)^2}. \tag{13}$$

From Eqs. (13) we obtain

$$B=B_0-A_0 a, \tag{14}$$

$$\frac{da}{dt}=\frac{I_1 A_0}{2}(1-a)^2(B_0-A_0 a). \tag{15}$$

For simplicity, we omit here the suffix 1 of the aggregation rate l_1 in the following discussions. When $B_0>A_0$, we integrate Eq. (15) and then obtain the asymptotic solution of $a(t)$ in the long-time limit,

$$a(t)\simeq 1-\frac{2}{IA_0(B_0-A_0)}t^{-1}. \tag{16}$$

The asymptotic solutions of $A(t)$ and $B(t)$ are then determined as follows:

$$A(t)\simeq\frac{4}{I^2A_0(B_0-A_0)^2}t^{-2},\quad B(t)\simeq B_0-A_0+\frac{2}{IA_0(B_0-A_0)}t^{-1}. \tag{17}$$

Thus we obtain the scaling solution

$$a_k(t)\simeq\frac{4}{I^2A_0(B_0-A_0)^2}t^{-2}\exp(-x),\qquad x=\frac{2}{IA_0(B_0-A_0)}kt^{-1}. \tag{18}$$

In this case, the typical mass of A species grows as t, and A clusters coalesce each other completely by the action of B catalyst in the end. On the other hand, the total mass of A species obeys the mass conservation law throughout the process, while B catalyst is steadily consumed and only the mass B_0-A_0 remains at last.

When $B_0<A_0$, one can derive the asymptotic solution of $B(t)$ at large times,

$$B(t)\simeq B_0\exp(-\delta t), \tag{19}$$

where $\delta=I(A_0-B_0)^2/2$. The scaling solution of $a_k(t)$ is then given as follows:

$$a_k(t)\simeq A_0\left(1-\frac{B_0}{A_0}\right)^2\left(\frac{B_0}{A_0}\right)^k\exp(-x),\quad x=k\exp(-\delta t). \tag{20}$$

These indicate that the conventional scaling description (9) of the mass distribution breaks down for A clusters in this case and the evolution of the system falls in a peculiar scaling regime. We can modify the conventional scaling form (9) as follow [13]:

$$c_k(t)\simeq h^k[f(t)]^{-w}\Phi\{k/S(f(t))\},\quad S(t)\propto t^z, \tag{21}$$

where h is a constant $(0<h<1)$ and $f(t)$ is an unusual function of time, such as e^t, $\ln t$, 2^t, and so on. In this case, the unusual function is $f(t)=e^t$. The exponents are $w=0$ and $z=I(A_0-B_0)^2/2$. It is found that the exponent z is dependent on the initial concentrations as well as the aggregation rate. Moreover, the modified scaling form (21) indicates that two different mass scales are associated with A species. One is a growing scale $S(t)\sim\exp(\delta t)$, which is forced by the catalysis of B species. Another is a time-independent scale $S=1/(1-h)=A_0/(A_0-B_0)$, which will dominate the evolution behavior of A species in the long-time limit. On the other hand, since A clusters cannot coalesce without the catalyst, the aggregation reaction of A species will cease as soon as the catalyst exhausts. In this case, the catalyst is steadily consumed by the reaction and will be exhausted finally. Thus, only a part of small A clusters can bond each other to form a large cluster with the help of the catalyst, and thus small A clusters dominate over the larger ones in the long-time limit. Moreover, the total number of A clusters, $N_A(t)\simeq A_0-B_0$ at $t\gg 1$, indicates that the aggregation of A clusters cannot be fulfilled in the case of $B_0<A_0$.

In the borderline case of $B_0=A_0$, from Eqs. (14) and (15) we get

$$a(t)=1-(1+IA_0^2t)^{-1/2},\quad A(t)=\frac{A_0}{1+IA_0^2t},\qquad B(t)=A_0(1+IA_0^2t)^{-1/2}. \tag{22}$$

In the long-time limit, we obtain the asymptotic scaling solution,

$$a_k(t)=\frac{A_0}{1+IA_0^2t}[1-(1+IA_0^2t)^{-1/2}]^{k-1}\simeq\frac{1}{IA_0}t^{-1}\exp(-x),\qquad x=\frac{1}{\sqrt{I}A_0}kt^{-1/2}, \tag{23}$$

with the exponents $w=1$ and $z=1/2$. These indicate that all the small A clusters aggregate into a larger cluster by the action of B catalyst and the catalyst is consumed completely in the end. Hence, the large A clusters dominate over the small ones in the long-time limit, which is similar to the first case of $B_0>A_0$. However, the exponents for this case are half as large as those for the case $B_0>A_0$.

Finally, we investigate the case in which self-aggregation of B catalyst coexists with the catalytic reaction. Here, the catalyst is steadily consumed by the catalytic reaction. Then the governing rate equation for A species is the same as Eqs. (1) and that for B catalyst is rewritten as

$$\frac{db_k}{dt}=\frac{I_2}{2}\sum_{i+j=k} b_i b_j - I_2 b_k \sum_{j=1}^{\infty} b_j - \frac{I_1}{2} b_k \sum_{i,j=1}^{\infty} a_i a_j . \tag{24}$$

Under the monodisperse initial conditions (2), by employing the above technique we obtain the asymptotic scaling solutions in the long-time limit,

$$a_k(t) \simeq A_0(1-a_\infty)^2 a_\infty^k \exp(-x), \quad x=C_1 a_\infty^{-1} k \exp(-\gamma t),$$
$$b_k(t) \simeq C_2 b_\infty^k \exp(-\gamma t)\exp(-y),$$
$$y=\frac{1-b_\infty}{2b_\infty} k \exp(-\gamma t), \tag{25}$$

where $C_1 = I_1 A_0 (1-a_\infty)^2/2I_2$, $C_2 = I_1 A_0^2 (1-a_\infty)^2 (1-b_\infty)/2I_2$, $a_\infty = I_1 A_0 \ln\beta_\infty/(I_1 A_0 \ln\beta_\infty + I_2)$, $b_\infty = 1-\beta_\infty^{-1}$, $\gamma = I_1 A_0^2 (1-a_\infty)^2/2$, and β_∞ is a finite constant satisfying the expression $\int_1^{\beta_\infty} dx[I_2/(I_2+I_1 A_0 \ln x)]^2 = I_2 B_0/I_1 A_0^2$. These show that the conventional scaling descriptions of the cluster-mass distributions break down for both A species and B catalyst, but they obey the modified scaling form of Eq. (21). It is obvious that both a_∞ and b_∞ are less than unity. By setting $f(t)=e^t$ we then find that the exponents for A species are $w=0$ and $z=\gamma$ while those for B catalyst are $w=z=\gamma$. This implies that the exponents are dependent on the initial concentrations as well as on the reaction rates. A and B species have the same growing scale $S(t) \propto \exp(-\gamma t)$, and the time-independent scale for A species is $S_A = 1/(1-a_\infty)$, while that for B catalyst is $S_B = 1/(1-b_\infty)$. It is obvious that the catalyst cannot make all the A clusters coagulate together. Hence, no matter how large the initial concentration of the catalyst is, one can find that small A clusters are always conserved in the system. The increase of the catalyst can only improve the output of the larger A aggregates.

In summary, we investigated the catalysis-driven aggregation system with A species and B catalyst to analyze the dependence of kinetics of the aggregation system on the catalyst. The results show that whether the catalyst aggregates by itself or not plays an important role in the kinetic behavior of the system. For the processes without any consumption of the catalyst, the cluster-mass distribution of the system approaches a conventional scaling form in the case without B catalyst's self-coagulation while the evolution behavior of the system obeys a logarithm-correction scaling law in the reverse case. For the cases in which the catalyst is consumed during the catalytic reaction, the evolution of the system with the catalyst's coagulating always obeys a modified law, while the kinetics of the system without self-coagulation of the catalyst depends strongly on the details of the initial concentrations of the reactants.

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