SCALING LAWS OF REVERSIBLE AGGREGATION
IN COMPACT CLUSTER SYSTEMS

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The reversible cluster–cluster aggregation processes in compact cluster systems are studied via a scaling argument and Monte Carlo simulations. To describe the detail effects of fragmentations from tree-like fractal to compact clusters a relative breakup probability \( Q(s_1, s_2) \sim s_1^{-\beta} + s_2^{-\beta} \) with an exponent \( \beta \) is introduced. The mean-field rate equation and numerical simulation results indicate that the critical exponent \( \gamma \), which is defined as \( \langle s(k, \infty) \rangle \sim k^{-\gamma} \), has a value of \((\alpha + \xi - \beta + 2)^{-1} \). It is shown that the scaling properties of the cluster size distributions are determined by the selections of the exponents \( \alpha \), \( \beta \) and \( \xi \).

The phenomenon of coalescence of clusters of particles through diffusion has received considerable attention because it is a basic process in various scientific areas such as the physics of thin film growth and the cluster-assembled materials.\(^1\)\(^2\) Recently, material scientists have been able to observe clusters of atoms or vacancies diffusing on thin film surfaces.\(^3\)\(^-\)\(^6\) The diffusion and coagulation of these clusters affects the morphology of the thin film.

In most of the studies, the growth of clusters is considered as irreversible. However, reversible cluster–cluster aggregation takes place if the bonds connecting the particles can be broken.\(^7\) Such processes are relevant to a number of situations.\(^8\)\(^-\)\(^9\) The kinetics of such process was studied by Family, Meakin and Deutch (FMD).\(^10\) With the effect of fragmentation being considered, the reversible coagulation processes can be represented by the following reaction mechanism\(^14\)

\[
A_{s_1} + A_{s_2} \xrightarrow{K(s_1, s_2)} A_{s_1+s_2},
\]

where \( A_i \) denotes a cluster containing \( i \) elementary units (monomers, particles, etc.), \( K(s_1, s_2) \) is the probability of two clusters of size \( s_1 \) and \( s_2 \) merging into a cluster of size \( s_1 + s_2 \), and \( F(s_1, s_2) \) is the probability of a cluster of size \( s \) breaking into two clusters of size \( s_1 \) and \( s_2 \). In a long time limit the dynamic process and the
scaling properties of a system are determined by the competing of aggregations and fragmentations. The aggregation kernel for mobile islands with a diffusion constant $D(s)$ is given by the Smoluchowski formula $K(s_1, s_2) \sim D(s_1) + D(s_2)$.\(^\text{11}\) The diffusion constant $D(s)$ is dependent on the cluster size and is assumed to follow an inverse power law

$$D(s) = D_0 s^{-\xi}. \quad (2)$$

Different values of exponent $\xi$ correspond to various microscopic mechanisms responsible for island diffusion. In FMD model the fragmentation kernel $F(s_1, s_2)$ of an island of size $s = s_1 + s_2$ is assumed as $F(s_1, s_2) \sim (s_1 + s_2)^\alpha$ which only depends on the island size. It means that for various different binary breakups in a certain cluster they have the same breakup probability. For example, a cluster of size 100 breaking into two clusters of size 1 and 99 has the same probability of breaking into two clusters of size 45 and 55. This is reasonable for tree-like fractal clusters because breaking any one of the bonds is sufficient to split the dendritic cluster.\(^\text{10}\) But this assumption is not suitable for compact or spherical clusters. The breakup of the clusters can be caused by the internal thermodynamics and kinetics. For example, escape of a few of atoms from an island is much easier comparing the detachment of a considerable number of particles from the island. In reversible aggregation processes for compact clusters system, the breakup probability depends not only on the cluster size but also on the detail form of the fragmentation. Considering the fragmentation of a cluster is associated with the morphology of the cluster, the present work is to study the scaling laws of reversible cluster–cluster aggregations from fractal to compact cluster systems. A scaling argument and numerical simulations show that the scaling properties of reversible aggregations depend on the morphology of the clusters.

On the basis of FMD model, we choose the fragmentation kernel as the form of

$$F(s_1, s_2) = k(s_1 + s_2)^\alpha Q(s_1, s_2), \quad (3)$$

where $Q(s_1, s_2)$ is called the relative breakup probability which describes the detail effects of detachments and $k$ is the breakup constant. Based on the following two facts the relative breakup rate is assumed as

$$Q(s_1, s_2) = s_1^{-\beta} + s_2^{-\beta}. \quad (4)$$

First, $Q(s_1, s_2)$ should be symmetrical about $s_1$ and $s_2$. It is invariable in the case of exchanging $s_1$ and $s_2$. Second, the detachments in a compact cluster are caused by the internal diffusion process of the atoms in the cluster. The probability of a fragment escaping from the cluster is determined by the energy barriers of this fragment diffusing in the cluster. Similar to the diffusion constant expression in Eq. (2), we assume the relative breakup rate following an inverse power law form $s_1^{-\beta} + s_2^{-\beta}$. The exponent $\beta$ is associated with the clusters morphology which is determined by various microscopic mechanisms about atoms diffusion in clusters such as temperature, edge barriers, diffusion constant and other factors. Figure 1
Scaling Laws of Reversible Aggregation

Fig. 1. Illustration of the relative breakup rate $Q(s_1, s_2) = s_1^{-\beta} + s_2^{-\beta}$ for a cluster of size 100 ($s_1 + s_2 = 100$) with $\beta = 0, 0.5, 1$ and 2.

gives the sketch map of the relative breakup rate of the cluster with a size of 100. It is shown that for a certain $\beta$ the probability of detachment depends on how the sizes of the two fragments distribute. For example, the relative breakup rate $Q(1, 99)$ with the two pieces of sizes 1 and 99 is much more than the relative breakup rate $Q(45, 55)$ with sizes of 45 and 55. When $\beta = 0$, the relative breakup rate $Q(s_1, s_2)$ becomes constant, it corresponds to FMD model for tree-like cluster. As $\beta$ increases from zero, the morphology of the clusters becomes more and more compact, the difference of $Q(1, 99)$ and $Q(45, 55)$ is increased gradually and the opportunity of detachment becomes less and less as can be seen in Fig. 1.

To analyze the scaling behavior of such a reversible aggregation process we adopt a mean field approximation due to Smoluchowski. In this approach, the density of clusters of size $s$, $n_s(t)$, is assumed to obey the following rate equation

$$\frac{dn_s(t)}{dt} = \sum_{s' = 1}^{s-1} D(s')n_{s'}(t)n_{s-s'}(t) - \sum_{s' = 1}^{\infty} [D(s) + D(s')]n_s(t)n_{s'}(t)$$

$$\quad + \sum_{s' = 1}^{\infty} F(s, s')n_{s+s'}(t) - \sum_{s' = 1}^{s-1} F(s', s - s')n_s(t).$$

(5)

The right-hand side of this equation consists of two gain terms due to the increasing of the clusters of size $s$ and two loss terms due to decreasing the clusters of size $s$.

In reversible coagulation the competition of two processes of aggregation and fragmentation determines the evolution of the cluster size distribution. The aggregation decreases the number of clusters, whereas breakups increase $n_s(t)$, and after a sufficiently long time, $t \to \infty$, a balance is established between the two processes leading to an equilibrium state in which the average cluster size $\langle s(k, \infty) \rangle$ becomes independent of time. The average cluster size decreases with increasing the breaking
constant \( k \), yielding the following scaling relation,\(^{10} \)
\[
\langle s(k, \infty) \rangle \sim k^{-y}.
\]
(6)

In the equilibrium state the left-hand side of Eq. (5) vanishes, and the cluster size distributions \( n_s \) can be scaled with a scaling function \( f(u) \) defined as\(^{12-14} \)
\[
n_s = \langle s \rangle^{-2} f \left( \frac{s}{\langle s \rangle} \right).
\]
(7)

We substitute this form of \( n_s \) into Eq. (5) and change variable from \( s \) to \( u = \frac{s}{\langle s \rangle} \). Using Eqs. (3), (5) and (7) and replacing summation into integration in Eq. (3), one has the following equation
\[
\eta \left[ \int_{0}^{u} \frac{1}{u^\xi} f(u')f(u-u')du' - \int_{0}^{\infty} \left( \frac{1}{u^\xi} + \frac{1}{u'^\xi} \right) f(u)f(u')du' \right]
\]
\[
= \int_{0}^{\infty} (u+u')^{\alpha}(u^{-\beta} + u'^{-\beta})f(u+u')du' - \int_{0}^{u} u^\alpha[u'^{-\beta} + (u-u')^{-\beta}]f(u)du'
\]
(8)

since the integrations in Eq. (8) are all independent of \( k \), the constant \( \eta = k\langle s \rangle^{\alpha+\xi-\beta+2}/D_0 \) does not depend on \( k \), is a constant that implying that \( \langle s \rangle \sim k^{-(\alpha+\xi-\beta+2)^{-1}} \). Comparing with Eq. (6) we get
\[
y = \frac{1}{\alpha + \xi - \beta + 2}.
\]
(9)

When \( \beta = 0 \), this expression reduces to FMD’s result for the case of tree-like clusters.\(^{10} \)

In order to test the scaling relation we have studied a number of reversible processes with several different breakup constants \( k \) and different exponents \( \beta \) using a Monte Carlo simulation method. For ordinary cluster–cluster aggregation computer simulations will consume enormous amounts of computer time since the amount of computer time required for every time step is proportional to the square of the number of possible values of cluster size.\(^{12} \) To circumvent this difficulty the more efficient simulation method which is similar to Kandel’s is developed. Each simulation starts with a set of \( 10^5 \) clusters of various sizes picked according to a chosen initial cluster size distribution. At each time step a pair of clusters is picked at random. Let us denote their sizes by \( s_1 \) and \( s_2 \). Since the mobility of a cluster decreases as its size increases it is assumed that the two clusters are merged into a single cluster of size \( s_1 + s_2 \) with probability \( K(s_1, s_2) \) proportional to \( s_1^{-\xi} + s_2^{-\xi} \).

At the same time another cluster of size \( s' \), \( s' = s'_1 + s'_2 \), is picked at random which is dissociated into two clusters of size \( s'_1 \) and \( s'_2 \) with probability of \( F(s'_1, s'_2) \) which is assumed as \( k(s'_1 + s'_2)^{\alpha}(s'_1^{-\beta} + s'_2^{-\beta}) \). In our simulation the exponents \( \alpha \) and \( \xi \) are chosen as \( \alpha = -3/2, \xi = 3/2 \) (results for other values of \( \alpha \) and \( \xi \) will be presented elsewhere) and the scaling relation Eq. (9) becomes
\[ y = \frac{1}{2 - \beta}. \]  

The exponents \( \beta \) and \( k \) are the adjustable parameters in this case.

The simulation results for the time dependence of the mean cluster size \( \langle s(t) \rangle \) are shown in Fig. 2 for \( k = 7 \times 10^{-2} \). As expected, there exists a crossover time \( \tau \), such that after a sufficient long time, \( t \gg \tau \), a steady balance is established and the saturated value of the average cluster size \( \langle s(k, \infty) \rangle \), which now depends on \( k \) and \( \beta \), is independent of time. It is interesting that as \( \beta \) increases from zero the crossover time \( \tau \) is increased more rapidly. We see from the figure that in steady state the average cluster size \( \langle s \rangle \) is different for different selections of the exponent \( \beta \). The dependence of the average cluster size \( \langle s \rangle \) and the total number of clusters \( N \) on the relative breakup rate exponent \( \beta \) is shown in the inset of Fig. 2. When \( \beta \) increases the average cluster size \( \langle s \rangle \) increases, whereas the total number of clusters decreases first slowly and then rapidly. When \( \beta \) approaches to 2, we find \( \langle s \rangle \to \infty \) and \( N \to 1 \), and there is no balance established in a long time limit. This is reasonable since we can see from the relative breakup rate shown in Fig. 1 that the breakup becomes more and more difficult as \( \beta \) increases. This result is also predictable from Eq. (10), when \( \beta \to 2 \), \( y \to \infty \), the average cluster size becomes infinite and the scaling law of Eq. (6) is invalid. In this case the cluster–cluster aggregation process becomes irreversible. To test the scaling relation in Eq. (9), we plot the logarithm of \( \langle s \rangle \) against the logarithm of the breakup constant \( k \) in Fig. 3 with \( \alpha = -3/2 \), \( \xi = 3/2 \), \( \beta = 0, 0.5 \) and 1. The straight lines through the data points indicate a power-law dependence of \( \langle s \rangle \) on \( k \) with \( \langle s \rangle \sim k^{-y} \). From the slopes of lines the exponents \( y \) are obtained as follows: \( \beta = 0, y = 0.5; \beta = 0.5, y = 0.67; \beta = 1, y = 1 \). These results agree excellently with the mean-field prediction of \( y = (\alpha + \xi - \beta + 2)^{-1} \).

Fig. 2. Approach to the steady state of the mean cluster size for \( k = 7 \times 10^{-2} \), \( \alpha = -3/2 \) and \( \xi = 3/2 \). \( \langle s(t) \rangle \) is the mean cluster size at time \( t \), and when \( t \to \infty \) it reaches \( \langle s \rangle \). The inset graph shows the dependence of \( \langle s \rangle \) and the total number of clusters \( N \) on the exponent \( \beta \).
The steady state distribution of cluster size after a sufficient long time is also obtained from our simulations. The scaling function $f(u)$ is defined in Eq. (7). Figure 4 shows the cluster size distribution for different breakup constants $k$ in the case of $\alpha = -3/2$, $\xi = 3/2$ and $\beta = 0.5$. Our simulations are carried out starting from a set of $10^5$ clusters, all of size 1, and the results are obtained from the average of 50–100 simulations. The dependence of the number of clusters on their size is shown in Fig. 4(a). We find that the cluster size distribution depends on the breakup constant $k$. As $k$ increases the number of small clusters grows and the number of large clusters reduces gradually. When we use the scaling relation of Eq. (7) to scale the cluster size distribution $n_s$, the scaling function $f(u)$ versus the scaled cluster size $u = s/(\langle s \rangle)$ is obtained shown in Fig. 4(b). Clearly, there is excellent data collapse and all the distributions fall on a single curve. This implies that the scaling function $f(u)$ is independent of the breakup constant $k$. We can predicate from Eq. (8) that the scaling function depends on the choices of parameters $\alpha$, $\beta$ and $\xi$. The simulation results of cluster size distributions for three different values of $\beta$ are shown in Fig. 5. It is obtained from an average of one hundred simulation results in the case of $k = 7 \times 10^{-2}$, $\alpha = -3/2$, $\xi = 3/2$ and $\beta = 0$, 0.5, 1, respectively. We see from Fig. 5(a) that as $\beta$ grows from zero the number of large clusters increases and the number of small clusters decreases. Therefore the average cluster size of the system in the steady state increases with $\beta$. This is reasonable since the exponent $\beta$ describes the difficulty of breaking a cluster. The scaled cluster size distributions for three different $\beta$ are shown in Fig. 5(b). It is obviously that the scaling function depends on $\beta$, so there are different scaling laws for different $\beta$. This result implies that as the cluster morphology changes from fractal to compact the scaled cluster size distribution varies. This is compatible with some experiment results.
Fig. 4. (a) A log-log plot of cluster size distributions resulting from the simulations with \( \alpha = -3/2, \xi = 3/2 \) and \( \beta = 0.5 \) for various breakup constants \( k \). (b) The scaled cluster size distributions of (a) form a single curve.

In Ratsch’s model\textsuperscript{13} the passage from a fractal island to a compact island arises naturally as the energy barrier decreases. The change in the scaling function agrees nearly quantitatively with a corresponding scaling function observed by Stroscio for Fe/Fe(001).\textsuperscript{14}

In summary, we have studied the reversible aggregation process by introducing a relative breakup probability \( Q(s_1, s_2) \sim s_1^{-\beta} + s_2^{-\beta} \) with an exponent \( \beta \), which describes the detail effects of fragmentation from dendritic, fractal to compact clusters. In actual thin film systems the morphology of a cluster is determined by the attachment and fragmentation of atoms at the circumference of the islands. Clearly, both kinds of processes relate to the temperature, edge barriers, diffusion constant and other factors. Thus, the breakup rate in the reversible aggregation will effect the forming of the complex morphology of the cluster. Our model describes a more general reversible aggregation process comparing with FMD model. The exponent \( \beta \) is associated with the microscopic mechanisms about atoms diffusion in clusters. The mean-field approach and numerical simulation results indicate that the exponent \( y \), defined as \( \langle s \rangle \sim k^{-y} \), has a value of \( (\alpha + \xi - \beta + 2)^{-1} \). The simulation results
Fig. 5. The simulation results in the case of $\alpha = -3/2$, $\xi = 3/2$ and $k = 7 \times 10^{-2}$ for three different $\beta$. (a) A log-log plot of the cluster size distributions. (b) The scaled cluster size distributions of (a).

of steady state cluster size distribution show that the cluster size distribution $n_s$ depends on the breakup constant $k$ and the parameters $\alpha$, $\beta$, and $\xi$, but the scaling function from the scaled cluster size distribution $f(u)$ only depends on the selections of $\alpha$, $\beta$, and $\xi$. This implies that the scaling function is associated with the morphology of clusters, which is agree with some experiment results. Our simulation results show that the universality of the reversible cluster–cluster aggregation is determined by the selections of the exponents $\alpha$, $\beta$, and $\xi$.

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