Kinetics of Coagulation with Fragmentation: Scaling Behavior and Fluctuations

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(Received 5 May 1986)

The standard coagulation process is generalized to include the effects of fragmentation and a scaling description for the cluster size distribution is developed. The Smoluchowski rate equation is used to calculate the critical exponents describing the steady-state size distribution. Predictions of the scaling and the rate equation are tested by numerical simulations. The mean-field rate-equation results are found to be valid in $d \geq 1$ implying that the *upper critical dimension* d_c is less than 1.

PACS numbers: 64.60.−i, 05.40.+j, 05.70.Ln, 82.70.−y

The phenomenon of coagulation is central to a wide range of physical, chemical, and biological processes and the understanding of it is of considerable importance in many basic and applied problems from colloidal and polymer science[1] to antigen-antibody aggregation[2] and cluster formation in galaxies.[3]

Coagulation processes can be schematically represented by the following reaction mechanism:

$$A_i + A_j \underset{F(i,j)}{\overset{K(i,j)}{\rightleftharpoons}} A_{i+j}, \tag{1}$$

where A_i denotes a cluster containing i elementary units (monomers, particles, etc.), and $K(i,j)$ and $F(i,j)$ are the forward and the reverse rate coefficients representing the coagulation and the fragmentation rates, respectively. Recently, much effort has been devoted to the scaling description of the cluster-size distribution for irreversible aggregation[4] which is described by the Smoluchowski rate equation[5] with $F(i,j)=0$. These studies have led to general scaling descriptions[4] of irreversible aggregation processes which have been verified by experiments.[6] In addition, numerical simulations[7,8] have shown that there exists a critical dimension $d_c=2$ at and above which the mean-field Smoluchowski rate equations provide an accurate description of irreversible aggregation, but below d_c, spatial fluctuations give rise to new kinetic behavior.

There exist a variety of situations in which the reverse reactions are important.[9–14] For example, as clusters grow in size, the possibility of breakup increases. An important characteristic of the reversible process is the formation of a steady-state cluster-size distribution after a long time. This is in contrast to irreversible aggregation where there is a permanent evolution in time as the number of clusters in the system is always decreasing.

In this Letter we generalize the standard coagulation process to include the effects of fragmentation, and we develop a scaling approach for the cluster-size distribution and its moments. We show that under general conditions, the critical exponents describing the steady-state cluster-size distribution and its moments can be determined from a generalized Smoluchowski rate equation[5] for reversible coagulation.[9–14] The predictions of the scaling theory and the Smoluchowski equation are tested by numerical simulations of a simplified model of coagulation. We find that the mean-field rate-equation results are valid in $d \geq 1$, implying that for reversible aggregation $d_c < 1$.

In reversible coagulation two competing processes affect the temporal evolution of the cluster-size distribution and its moments. The coagulation rate $K(i,j)$ decreases the number of clusters, while the breakup rate $F(i,j)$ increases it. There exists a crossover time τ, such that after a sufficiently long time, $t \gg \tau$, a balance is established between the two processes leading to an equilibrium state in which the cluster-size distribution and its moments become independent of time.

The quantity $F(i,j)$, which is the rate at which a cluster of size $i+j$ breaks up into a cluster of size i and a cluster of size j, is assumed to be of the form

$$F(i,j) = k\Phi(i,j), \tag{2}$$

where k is the breakup constant, $\Phi(i,j)$ is a function that describes the dependence of the fragmentation rate on the cluster sizes i and j, and $\phi(1,1)=1$. The

main assumption in the scaling approach to aggregtaion processes[4] is the existence of one characteristic cluster size in the system. Let $S(k,t)$ be the mean cluster size which is defined by

$$S(k,t)=\sum_s s^2 N_s(k,t), \tag{3}$$

where $N_s(k,t)$ is the number of clusters of size s in the system at time t. We generalize the scaling assumption for the cluster-size distribution[4] to reversible aggregation and write

$$N_s(k,t)=s^{-2}f(S(k,t)/s). \tag{4}$$

As in irreversible aggregation,[4] the form of the scaling function $f(x)$ depends on the details of the process.

The scaling behavior of the steady-state cluster-size distribution, $N_s(k,\infty)$, and its moments, therefore, depends on the dependence of the mean cluster size $S(k,\infty)$ on the breakup constant k. Since the average size of the clusters decreases with increasing k, we expect $S(k,\infty)$ to decrease with k as well. Therefore, if $S(k,\infty)$ does scale with k, we assume that in the limit $t \gg \tau$ it will be of the form

$$S(k,\infty)\sim k^{-y}, \tag{5}$$

where, in general, the exponent y depends on the details of the functions $K(i,j)$ and $F(i,j)$. An exponent describing the divergence of τ as $k\to 0$ can also be defined, but this exponent is related to y and does not introduce a new scaling behavior.[8] Assuming that in the steady state $S(k,\infty)$ has the scaling form (5), we find from (4) the scaling form of the cluster-size distribution in the steady state,

$$N_s(k,\infty)=s^{-2}f(sk^y). \tag{6}$$

This implies the scaling form

$$N(k,\infty)\sim k^y \tag{7}$$

for the total number of clusters $N(k,t)=\sum_s N_s(k,t)$.

We now proceed to calculate the exponent y within a mean-field approximation using the Smoluchowski rate-equation approach.[5] In the presence of a breakup rate the generalized Smoluchowski equation can be written as[9-14]

$$dN_s/dt=\tfrac{1}{2}\sum_{i+j=s}[K(i,j)N_iN_j-F(i,j)N_{i+j}]-\sum_{j=1}^{\infty}[K(s,j)N_sN_j-F(s,j)N_{j+s}], \tag{8}$$

where $N_s=N_s(k,t)$. The above equation describes a mean-field situation because both the geometry and the spatial fluctuations in the density of the clusters are neglected. In the steady-state limit $N_s(k,\infty)$ is independent of time and the left-hand side of (8) vanishes.

In order to determine the exponent y we make two assumptions. First, we assume that $K(i,j)$ and $F(i,j)$ satisfy respectively the scaling forms

$$K(i\lambda,j\lambda)=\lambda^{2\omega}K(i,j),\quad F(i\lambda,j\lambda)=\lambda^{\alpha}F(i,j). \tag{9}$$

These scaling forms are satisfied by most of the physically relevant forms of $K(i,j)$ and $F(i,j)$. Second, we assume that the rate equation (8) is invariant under a scaling transformation $k\to\lambda k$ and $s\to\lambda^y s$. Using the scaling forms (6), (2), and (9) in the steady-state limit of (8) we find

$$y=(\alpha+\omega+2)^{-1}. \tag{10}$$

This expression gives an explicit form for y which can be tested numerically. It is interesting to note that in analogy with the dynamic scaling exponent z,[4,8] the dependence of y on the spatial dimension d enters from the homogeneity index of $K(i,j)$.

To test the scaling prediction and the mean-field result for the exponent y we have studied several coagulation processes with a number of different fragmentation constants k. In order to avoid the complexities arising from the geometrical structure of the clusters we employed the particle coalescence model[7] which is an idealized version of the cluster-cluster aggregation model.[15] In this particle coalescence model,[7] clusters are defined to be single lattice sites. When two clusters of masses i and j meet, they coalesce into a heavier single-site cluster of mass $i+j$ at a rate proportional to the reaction kernel $K(i,j)$. Since there is no cluster geometry, the functional form of the reaction matrix can be specified exactly. In the simulations reported here we have assumed a mass-independent sticking probability of unity, i.e., a constant coagulation rate and $\omega=0$. We have assumed that the breakup probability for any of the $s-1$ bonds, chosen randomly, in a cluster of size s is given by $k(s-1)^{\alpha-1}$. This implies that the breakup probability for a particular bond that breaks the cluster of size $i+j$ into a cluster of size i and a cluster of size j is

$$F(i,j)=k(i+j)^{\alpha}. \tag{11}$$

Therefore, the constants α and k are the adjustable parameters in the model. Implicit in this formulation is the fact that the clusters are treelike; i.e., the breaking of one bond is sufficient to split the cluster. This geometrical picture of the aggregates is in agreement with what is observed in experiments[6] and in simulations.[15,16]

The three-dimensional simulation results for the time dependence of the total number of clusters $N(k,t)$ and the mean cluster size $S(k,t)$ are shown in Fig. 1 for $\alpha=-\frac{1}{2}$. As expected, after a sufficiently

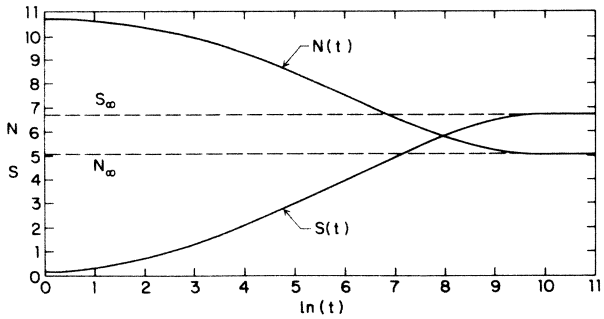

FIG. 1. Approach to the steady-state values for the number of particles (N) and the mean cluster size (S) obtained from a 3D simulation of particle coalescence model with a breakup constant (k) of 2×10^{-5} and an exponent (α) of $-\frac{1}{2}$. Most of our 3D simulations were carried out starting with 50 000 particles on 80^3 lattices and the results from 10–100 such simulations were averaged to obtain these results.

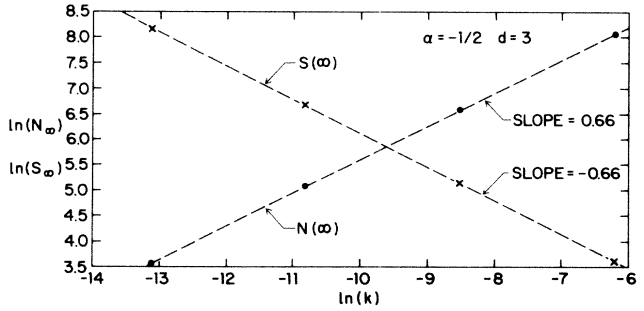

FIG. 2. Dependence of the steady-state values of $N(k,t)$ and $S(k,t)$ on the breakup rate constant (k) obtained from simulations similar to that shown in Fig. 1.

long time, both quantities become time independent and reach their saturation values of $N(k,\infty)$ and $S(k,\infty)$, respectively. To test the scaling relations (5) and (7), we have plotted the logarithms of $N(k,\infty)$ and $S(k,\infty)$ against the logarithm of the breakup constant k in Fig. 2 for our three-dimensional simulations with $\alpha=-\frac{1}{2}$. The straight lines through the data points indicate a power-law dependence of both quantities on k, in agreement with (5) and (7). The slope of the line that describes the decay of $S(k,\infty)$ with k is -0.66 and the slope of the line indicating the divergence of $N(k,\infty)$ with k is 0.66. These results show that $y=0.66$, in agreement with the mean-field prediction of $y=\frac{2}{3}$ from (10).

As a result of the widespread[1-3,9-14] use of the Smoluchowski rate equation,[5] it has been important to determine the range of validity of this equation by the study of the effects of spatial fluctuations on the kinetics of aggregation.[7,8] In irreversible aggregation[7,8] the available data indicate that there exists a critical dimension $d_c=2$ at and above which the effects of spatial fluctuations are unimportant and the rate equation gives an accurate description of the kinetics of irreversible aggregation. In order to assess the range of validity of the Smoluchowski approach for reversible coagulation, we have carried out simulations in $d=1$, 2, and 3. We have found that the values of the exponent y in $d=1$, 2, and 3, for various values of α, are in exact agreement with the mean-field prediction (10). This indicates that in contrast to irreversible aggregation, the spatial fluctuations in the density of the particles are compensated by the fragmentation effect and the mean-field scaling persists down to at least one dimension. Therefore, *the upper critical dimension (d_c) is less than one ($d_c<1$).*

The steady-state cluster-size distribution is expected to scale with the breakup constant k according to (6). Excellent agreement with this scaling prediction is demonstrated in Fig. 3, where the one-dimensional results for $N_s(k,\infty)s^2$ for various values of k scale into a single universal function when plotted against sk^y, for $\alpha=1$. We have found similar agreements with the scaling relation (6) in $d=2$ and 3 and for other values of the parameters α and k.

The actual shape of the scaling function $f(x)$ in (6) depends on α. In particular, for small x, the scaling function $f(x)$ appears to decay as $x^{2-\tau}$ indicating that $N_s(k,\infty)\sim s^{-\tau}$. The value of τ depends on α and decreases from 0.7 for $\alpha=-1$ to zero at $\alpha=0$. For all the values of $\alpha>0$ that we have investigated, τ appears to be zero. In order to investigate the asymptotic form of the cluster-size distribution we have also scaled these distributions by plotting $k^{-2y}N_s(k,\infty)$ against $k^y s$. This scaling is equivalent to (4), because of the scaling relation (5). The results in Fig. 4 show that for $x\gg1$ the scaling function decays as a simple exponential of the form $\exp(-cx)$, where c is a constant. In particular, for $\alpha=0$ it is a pure exponential

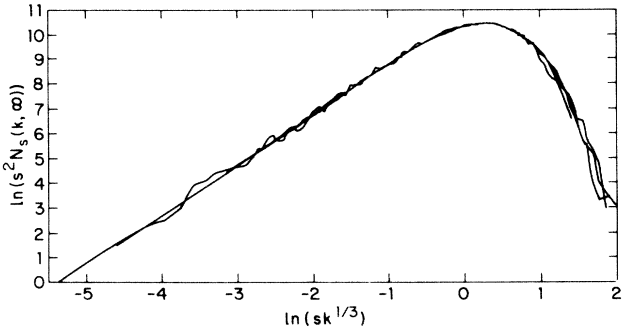

FIG. 3. Scaling of the steady-state cluster-size distribution [$N_s(k,\infty)$] obtained from 1D simulations carried out with use of a breakup exponent (α) of 1 with rate constants (k) of 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7}. These simulations were carried out starting with 50 000 monomers on a lattice of 2^{14} sites with periodic boundary conditions.

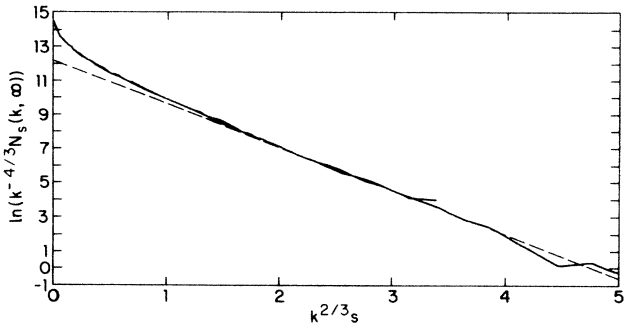

FIG. 4. Scaling of the steady-state cluster-size distribution $[N_s(k,\infty)]$ obtained from 3D simulations carried out with a breakup exponent (α) of $-\frac{1}{2}$ and rate constants (k) of 2×10^{-3}, 2×10^{-4}, and 2×10^{-5}.

for all x, in agreement with the Smoluchowski equation result[9-14] for a constant $K(i,j)$ and $F(i,j)$. Therefore, the simulation results are consistent with a scaling function of the form $f(x)=x^{2-\tau}\exp(-cx)$ for all x.

In conclusion, we studied the generalized version of the standard coagulation process which included the effects of fragmentation. A scaling description for the cluster-size distribution and its moments was developed and the Smoluchowski rate equation was extended to reversible coagulation. Under general assumptions of scaling, the rate equations determine the critical exponent describing the steady-state size distribution and its moments. We have tested the scaling and the rate equation predictions by numerical simulations of a simplified model of reversible coagulation. The simulations show that the spatial fluctuations, which lead to new scaling behavior in irreversible aggregation below the critical dimension,[7,8] are compensated by cluster breakups. Consequently, for reversible aggregation, mean-field rate equation approximation is valid in $d \geq 1$, implying that *the critical dimension* d_c is less than 1.

This research was supported by the National Science Foundation and the U.S. Office of Naval Research.

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