Scaling in Aggregation with Breakup Simulations and Mean-Field Theory

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An extended scaling description of the cluster size distribution $N_s(t,k)$ in time-dependent coagulation-fragmentation processes (k is a small breakup rate constant) is presented as $N_s(t,k) \sim s^{-2}h(sk^y, tk^x)$ and its validity is confirmed by computer simulations. This scaling form includes the scaling description of irreversible and steady-state processes as limiting cases for both short and long times compared to a crossover time $\tau(k) \sim k^{-x}$. A mean-field theory is analyzed and its limits of validity are explored.

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In the kinetics of irreversible aggregation the statistical description of the clustering processes simplifies as time progresses and cluster sizes grow. The characteristic cluster size increases algebraically, $S(t) \sim t^z$, and the size distribution obeys a scaling form. The existence of scaling has been established in experimental,[1,2] computer,[3] and theoretical[4] studies.

Fragmentation processes become increasingly important as clusters grow and the competition between fragmentation and coagulation may lead to a steady state.[5-9] The size distribution again obeys a scaling form[7] when clusters are measured relative to their mean size $S(\infty,k)$. The value of this quantity is determined by the breakup constant k, measuring the relative strength of the rate constants for fragmentation and coagulation reactions. For small k the characteristic size decreases according to a power law, $S(\infty,k) \sim k^{-y}$.[7] The constant k determines a typical crossover time $\tau(k) \sim k^{-x}$, specified by a new exponent x that will be determined below. For times $t \ll \tau(k)$ clustering is essentially described by irreversible aggregation, and for $t \gg \tau(k)$ by steady-state aggregation.

Our main goal is to extend these scaling laws to time-dependent aggregation-fragmentation processes and to test the scaling description using computer simulations. We also study the mean-field equations and their range of validity. We hope that our results will stimulate experimentalists to obtain the detailed information on real aggregation-fragmentation systems needed to explore the kinetic scaling behavior.

The essential characteristics of the clustering reactions $A_i + A_j \rightleftarrows A_{i+j}$ of clusters of size i and j are controlled by the dependence of the forward and backward rate constants, respectively $K(i,j)$ and $kF(i,j)$, on the sizes of the reactants or reaction products. More specifically, $K(bi,bj) = b^\lambda K(i,j)$ and $F(bi,bj) = b^\alpha F(i,j)$. Here we restrict ourselves to nongelling coagulation reactions ($\lambda \leqq 1$) (Ref. 4) and to nonshattering fragmentation reactions ($\alpha \geqq -1$).[10]

Before formulating the extended scaling laws, we need to summarize some scaling relations. In irreversible aggregation the size distribution approaches $N_s(t) \sim s^{-2}f_0(u)$ where the scaling variable is $u = s/S(t) \sim st^{-z}$. In reversible aggregation the size distribution $N_s(t,k)$ also depends on the breakup parameter k and so does the mean cluster size $S(t,k)$. The steady-state quantities show scaling behavior if the mean cluster size is sufficiently large or k is sufficiently small,[7] namely $S(\infty,k) \sim k^{-y}$ as $k \rightarrow 0$, and $N_s(\infty,k) \sim s^{-2}f(u)$ with $u = s/S(\infty,k) \sim sk^y$. Mean-field predictions for these exponents are $z = 1/(1-\lambda)$ and $y = 1/(2+\alpha-\lambda)$ where λ and α are the degrees of homogeneity of the reaction kernels.

Next, we define the "scaling limit" as $t,s \rightarrow \infty$ and $k \rightarrow 0$ with $T = tk^y$ fixed. In general, the size distribution $N_s(t,k)$ depends on three arguments; in the scaling limit it approaches a scaling form depending only on two arguments. We assume that there exists one characteristic time $\tau(k)$, which increases as $\tau(k) \sim k^{-x}$ for $k \rightarrow 0$, and one characteristic cluster size $S(t,k)$, in terms of which time and size variables should be measured. For t much larger than the crossover time $\tau(k)$ the clustering process has reached a steady state; for t much smaller than $\tau(k)$ one has essentially irreversible aggregation. This implies the following scaling form for the mean cluster size:

$$S(t,k) \sim k^{-y}\psi(T); \quad T = t/\tau(k) = tk^x. \tag{1}$$

To match the behavior of irreversible aggregation as $k \rightarrow 0$, the function ψ must increase algebraically, $\psi(T) \sim T^z$, and must be independent of k, implying $y = zx$. To match the steady-state scaling behavior,

$\psi(T)$ must approach a constant, $\psi(\infty)=1$. The scaling form for the size distribution can be written as

$$N_s(t,k)=s^{-2}f(u,T)=s^{-2}h(sk^y,tk^x), \qquad (2)$$
$$u=s/S(t,k)=sk^y/\psi(tk^x).$$

To match the irreversible and steady-state scaling forms we impose $f(u,0)=f_0(u)$ and $f(u,\infty)=f(u)$. Here $f_0(u)$ is the "short" time scaling form, valid for $t \ll \tau(k)$ and $f(u)$ is the steady-state scaling form, valid for $t \gg \tau(k)$.[7,9]

The extended scaling relations lead to a variety of predictions that can be verified in experiments and computer simulations. We first mention data collapse for $k^yS(t,k)$, plotted versus tk^x with $y=xz$, where z follows from $S(t,k) \sim t^z$ for $t \ll \tau(k)$. Furthermore, the scaling form (1) depends, in general, on two scaling arguments: $u=s/S(t,k)$ and $T=t/\tau(k)$. The implied data collapse for $s^2N_s(t,k)$ plotted versus $s/S(t,k)$ or sk^y at fixed $T=tk^x$, as well as for $s^2N_s(t,k)$ plotted versus tk^x at fixed $s/S(t,k)$ or at fixed sk^y has been fully confirmed in our computer simulation.

We have simulated several aggregation processes with different breakup constants k using the particle coalescence model,[7] where an s-cluster occupies only a single lattice site. If the diffusion coefficient of an s-cluster is $D_s=s^\gamma$, the kernel for Brownian coagulation is $K(i,j)=(D_i+D_j)=i^\gamma+j^\gamma$ with homogeneity degree $\lambda=\gamma$. The breakup rate of an s-cluster into an i- and a j-cluster $(i+j=s)$ is assumed to have the form $kF(i,j)=k(i+j)^\alpha$. We shall refer to a specific model by the homogeneity indices (γ,α). The breakup was simulated as in Ref. 7, where one fragment is put on the site of the original cluster and the second one on a nearest-neighbor site, chosen at random. We refer to this implementation of fragmentation as correlated fission.

Confirmation of extended scaling for $S(t,k)$ is shown in Fig. 1 through data collapse at four different fission constants k for the 3D simulation of the $(\gamma,\alpha)=(-2,-1)$ model with diffusion coefficient $D_s \sim s^\gamma$ implying a homogeneity index $\lambda=\gamma=-2$ for coagulation, and with a fragmentation rate $F(i,j)=(i,j)^\alpha$ for correlation fission. The s and t variables in Eq. (1) are rescaled in accordance with the mean-field exponents $y=1/(2+\alpha-\lambda)=\frac{1}{3}$ and $x=(1-\lambda)y=1$. At short times $S(t,k)$ approaches the small-T or irreversible scaling form $S \sim t^z$. This form holds for $T=tk<e^{0.5}$ where fragmentation has no effect. The measured dynamic exponent, $z_{\text{sim}} \approx 0.34$, is in very good agreement with the mean-field prediction $z=1/(1-\gamma)=\frac{1}{3}$. For $e^{0.5}<T<e^2$ (intermediate scaling) $S(t,k)$ crosses over to its large-T or steady-state scaling form, where coagulation and fragmentation are in balance. Furthermore, 3D simulations for the models $(\gamma,\alpha)=(0,-1)$, $(0,0)$, $(0,1)$, $(-1,0)$, and $(-2,-1)$ all show behavior for the mean cluster size in very good agreement with Eq. (2). Of course, for larger k values the time of approach to the irreversible

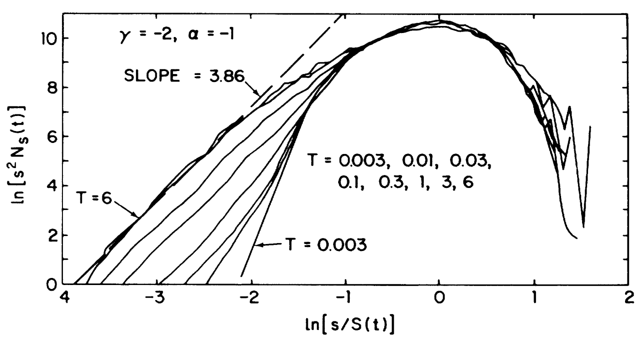

FIG. 1. Scaling of the time dependence of the mean particle size $S(t)$ obtained from several three-dimensional simulations carried out with the particle coalescence model with correlated fission at four different fission rate constants k. Each simulation was carried out starting with 50000 particles of unit mass on an 80^3 lattice.

scaling form, say t_0, may be equal to or even larger than the crossover time, $\tau(k)=k^{-x}$, to the steady-state form. If so, the $k^xS(t,k)$ curves do not exhibit small-T scaling. This happens, for instance, in the model $(\gamma,\alpha)=(-1,0)$ at $k \approx 0.01$ where $t_0 \approx 20$ and $\tau(k)=k^{-2/3} \approx 21$.

Numerical simulations[3] and theoretical considerations[11] have shown that above a critical dimension $d_c=2$, the mean-field equations provide an accurate description of irreversible aggregation, but below d_c spatial fluctuations give rise to new kinetic behavior. Recent simulations of reversible aggregation in the steady state[7] indicate that the mean-field prediction for the exponent y, $y=1/(2+\alpha-\lambda)$, is valid at dimensionality $d=1$, suggesting that $d_c<1$ for reversible aggregation. However, our simulations of time-dependent aggregation with correlated fission confirm the validity of extended scaling in one dimension but show that the dynamic exponent is no longer given by the mean-field exponent $z=1/(1-\lambda)$. In all our one-dimensional simulations the results are consistent with the idea that $z=1/(2-\lambda)$, $y=1/(2+\alpha-\lambda)$, and $x=y/z$.

Furthermore, in our 2D simulations, plots of $k^yS(t,k)$ versus $T=tk^x$ with mean-field exponents show very good data collapse for $T \sim \infty$. However, for small and intermediate values of T the slope is changing with k. Here, data collapse is very much improved by a logarithmic correction, i.e., by our plotting k^yS versus $k^xt/\ln t$.

The scaling predictions (2) for the full size distribution have also been compared with the 3D simulation data for the coalescence models $(\gamma,\alpha)=(0,0)$, $(0,1)$, $(-1,2)$, $(-2,-1)$, and $(-1,0)$ with correlated fission for different k and t values and were fully confirmed by data collapse at fixed $T=tk^x$ for different k and s, or at fixed $u=sk^y$ for different k and t.

We further note that the scaling prediction (2) for the full size distribution is in conflict with the alternative scaling *Ansatz* $N_s(t,k) \sim s^2f(s/S(t,k))$ proposed in Ref. 8, where $f(u)$ depends only on a single scaling argument, as opposed to $f(u,T)$ in (2). Their *Ansatz* is exact for $K=F=\text{const}$, i.e., in the scaling limit the exact solution of Blatz and Tobolski[5] shows that $S(t,k) = k^{-1/2}\psi(tk^{1/2})$ with $\psi(x)=2(1-e^{-x})/(1+e^{-x})$ and that the size distribution reduces to the above scaling form with $f(x)=4x^2\exp(-2x)$. However, the alternative *Ansatz* is in conflict with the exact result for the steady-state scaling form in detailed-balance models,[9] viz., $f(u)=u^{1/y}e^{-u}/\Gamma(1/y)$, which depends explicitly on the fragmentation exponent a through y. The corresponding scaling form $f_0(u)$ for irreversible aggregation cannot depend on a. Furthermore, a scaling form $f(u,T)$ with a strong T dependence at small u is, in general, found in computer simulations of 3D particle coalescence, if the fragmentation kernel $F(i,j)$ and diffusion coefficient $D_s=s^2$ depend on cluster sizes (see Fig. 2).

The combined process of coagulation and fragmentation can be described by Smoluchowski's coagulation-fragmentation equation for the size distribution $N_s(t,k)$ of s-clusters, as given by Eq. (8) of Ref. 7. Fragmentation rates are proportional to a (small) breakup constant k. Our setting $k=0$ yields the ordinary Smoluchowski equation for $N_s(t,0)$ in irreversible aggregation; our setting $dN_s/dt=0$ yields an equation for the steady-state size distribution $N_s(\infty,k)$ in reversible aggregation. In the present analysis the breakup kernel is restricted to the form $F(i,j)=(i+j)^a$. The coagulation kernel is specified through $K(bi,bj)=b^\lambda K(i,j)$ with $\lambda \leqq 1$ and $K(i,j)\sim i^\mu j^\nu$ as $j \gg 1$. For large sizes, long times, and small breakup constant k (extended scaling limit), the size variable may be treated as continuous and the size distribution is expected to approach the solution $N(s,t,k)$ of the continuous version of the coagulation equation. This equation has the exact scaling property $N(s,t,k)=k^{2y}N(sk^y,tk^x)$, valid for arbitrary values of the breakup constant k, provided the exponents x and y are chosen as $y=1/(2+a-\lambda)$ and $x=(1-\lambda)y$. The restrictions $a \geqq -1$ and $\lambda \leqq 1$ guarantee that the exponent $y>0$.[8]

Analysis of the mean-field equation also provides detailed information[12] about the scaling form of the size distribution. The results are very different from irreversible aggregation.[4] Here we quote only some results for steady-state scaling that are relevant for our further discussion; namely, at small scaling argument $u=s/S(\infty,k)$ the size distribution is described by the power law $s^2N_s(\infty,k)\sim u^{2-\tau}$. The results for τ are

$$\tau = \begin{cases} \lambda - a \quad [\text{case (i)}], \\ (1+\lambda)/2 \quad [\text{case (ii)}], \\ \mu \quad [\text{case (iii)}], \end{cases} \tag{3}$$

where case (i) is ($\mu > 1+a$; $\lambda > 1+2a$), case (ii) is ($\mu > 1+\nu$; $\lambda < 1+2a$), and case (iii) is ($\mu < 1+a$, $\mu < 1+\nu$). The three cases refer to regions in the $\{\mu,\nu,a\}$-parameter space that characterize the coagulation ($\mu,\nu,\lambda=\mu+\nu$) and breakup (a) processes. The physical region in the (μ,ν) diagram is further limited by the constraints $\lambda \leqq 1$, $\nu \leqq 1$, and $a \geqq -1$. On the borderline between (i) and (ii), where $\tau=1+a$, and between (ii) and (iii), where $\tau=1+\nu$, the exponent τ changes continuously and the small-u form of $f(u)$ contains extra powers of logarithms. However, the exponent τ changes discontinuously across the borderline between (i) and (iii). If the borderline is approached from above [case (i)] or below [case (iii)], its limiting value is, respectively, $\tau_+=1+\nu$ or $\tau_-=1+a$. The τ value on the borderline is unknown.

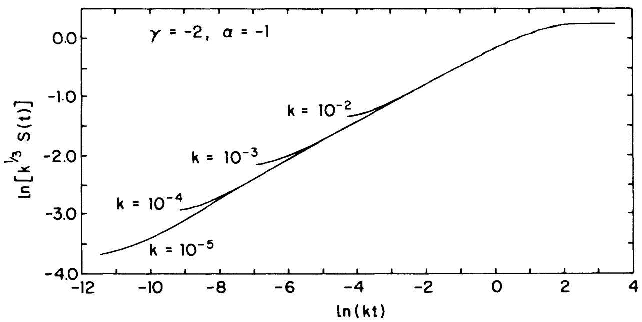

FIG. 2. Some results from a three-dimensional simulation with use of the particle coalescence model with uncorrelated fission. In this case, eight simulations were used. This figure shows how the scaling function $f(u)$ changes as $T=tk^x$ changes from small to large values.

In the last part of this Letter the simulation results for the size distribution are compared with the corresponding mean-field results for Brownian coagulation with a rate $K(i,j)=i^\gamma+j^\gamma$ with $\lambda=\gamma\leqq 0$ and $\nu=0$, combined with fission with a rate $kF(i,j)=k(i+j)^a$. For constant coagulation kernels ($\gamma=0$), the results of 3D simulations for correlated fission are in excellent agreement with the mean-field results, as has been tested for $a=1$ and 0. Next we decrease the mobility $D_s\sim s^\gamma$ of the large clusters ($\gamma<0$) and perform 3D simulations of the coalescence models $(\gamma,a)=(-1,0)$, $(-1,1)$, and $(-2,-1)$ with correlated fission. In mean-field theory these models belong to case (iii) of Eq. (3), where the exponent τ equals $\mu=\gamma$. Qualitatively, the size distribution has the same shape as in Fig. 2. The small-T-scaling curve in our simulations corresponds at small u approximately to $f_0(u)\sim u\exp(-b/u)$ of irreversible aggregation.[1,4] The large-T-scaling curve is very different at small u, viz. $f(u)\sim u^{2-\tau}$. The exponents $2-\tau$ for the (γ,a) models are measured from the slopes to be 1.9, 2.0, and 3.2, respectively. On the other hand, the corresponding mean-field exponents are given as 3, 3, and 4, respectively.

To understand these deviations from mean-field theory we have also performed 3D simulations of the same models with *uncorrelated* fission, where the positions of the two fragments are uncorrelated in the spirit of the mean-field theory. This was achieved by our leaving one fragment at the site of the original cluster and putting

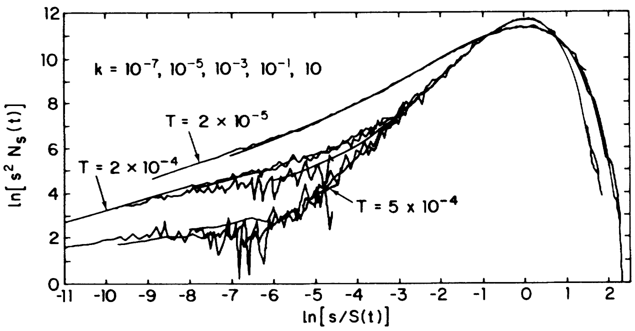

FIG. 3. Scaling collapse of the size distributions obtained from Monte Carlo simulations of the coagulation-fragmentation equation of Smoluchowski with a coagulation exponent $\lambda=\frac{1}{2}$ and fragmentation exponent $\alpha=1$. Each simulation was started out with 2×10^5 unit masses and the results from several hundred simulations were averaged for each fission rate constant (k). Here results obtained from simulations with five different fission rate constants are shown.

the second one at random anywhere on the lattice. The resulting exponent $2-\tau$ was then found to be 2.9, 2.9, and 3.9, respectively, in good agreement with the mean-field results. Thus, if the mobility of large clusters is small, spatial correlations created by correlated fission have long-time effects on the cluster size distribution, causing a breakdown of the mean-field predictions in its detailed description of the cluster size distribution.

The asymptotic results in Eq. (3) yield no estimates for the range of T and u values where these exponents are relevant. As the available analytical information from Smoluchowski's coagulation-fragmentation equation is rather limited, Monte Carlo simulations of this equation have been carried out with the method of Ref. 7. Within the general class of mean-field models $K(i,j)=(ij)^{\lambda/2}$ and $F(i,j)=(i+j)^\alpha$, we performed Monte Carlo simulations for the parameter values $(\gamma,\alpha)=(-\frac{1}{2},-1)$, $(-\frac{1}{2},0)$, $(\frac{1}{2},-1)$, $(\frac{1}{2},0)$, and $(\frac{1}{2},1)$. The last three pairs correspond to a coagulation kernel $K=(ij)^{1/4}$ which belongs to class I ($\mu=\frac{1}{4}$) of irreversible aggregation. In Fig. 3 we have plotted Monte Carlo simulation results for the size distribution in the mean-field models $(\gamma,\alpha)=(\frac{1}{2},1)$. Here the irreversible scaling form $f_0(u)\sim u^{2-\tau_0}$ has an algebraic tail for $u\ll1$ with an exponent $\tau_0=1+\lambda=\frac{3}{2}$.[4] At the shortest time available, $T\approx2\times10^{-5}$, the scaling form $f(u,T)$ corresponds approximately to $f(u,0)=f_0(u)$ and the agreement between the simulated and analytical values of the exponent $2-\tau_0$, respectively 0.6 and 0.5, is reasonable. At the longest available time, $T\approx5\times10^{-4}$, the scaling function has reached its asymptotic form $f(u,\infty)=f(u)$ for $u>e^{-5}$ with a slope of 1.7, in good agreement with the analytic result $2-\tau=\frac{7}{4}$ [$\tau=\frac{1}{4}$, case (iii)]. For still smaller clusters ($u<e^{-5}$) the tail is crossing over to its large-T form.

The mean-field model with $(\gamma,\alpha)=(\frac{1}{2},-1)$ is the only model in our simulations that belongs to case (i) of steady-state scaling, where $\tau=\lambda-\alpha=\frac{3}{2}$. The simulated value of the exponent $\tau_{\rm sim}\approx1.4$ is in fair agreement with the analytic result. It is also the only case in our Monte Carlo simulations where the exponent τ is larger than unity. As long as $\tau<1$ the total numbers of clusters $N(\infty,k)=\sum N_s(\infty,k)\sim k^y$ is inversely proportional to $S(\infty,k)\sim k^{-y}$. However, if $\tau>1$ we find $N(\infty,k)\sim[S(\infty,k)]^{\tau-2}$. For the model $(\lambda,\alpha)=(\frac{1}{2},-1)$ under consideration, this yields $N(\infty,k)\sim k$ and $S(\infty,k)\sim k^{-2}$ as $k\to\infty$. Sorensen, Zhang, and Taylor conclude incorrectly that N is, in general, inversely proportional to S.

Our main conclusions are the following: (i) The extended scaling laws, involving cluster size, time, and breakup constant, are confirmed in 1D, 2D, and 3D simulations of the particle coalescence model with fission and supply strong evidence for an upper critical dimensionality $d_c=2$. (ii) The detailed predictions on the size distribution (e.g., exponent τ) obtained by analytic and Monte Carlo solutions of Somulchowski's mean-field equation disagree with the simulation results for correlated fission, but agree for uncorrelated fission. (iii) For times on the order of or larger than the crossover time $\tau(k)$, the scaling *Ansatz* of Ref. 8 is, in general, in conflict both with the results from computer simulations and with analytic and Monte Carlo results obtained from Smoluchowski's equations.

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[1]S. K. Friedlander, *Smoke, Dust and Haze* (Wiley, New York, 1977).

[2]D. A. Weitz and M. Oliveria, Phys. Rev. Lett. **52**, 1433 (1984).

[3]D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983); K. Kang and S. Redner, Phys. Rev. A **30**, 2833 (1984); P. Meakin and H. E. Stanley, J. Phys. A **17**, L173 (1984); K. Kang and S. Redner, Phys. Rev. Lett. **52**, 955 (1984).

[4]P. G. J. van Dongen and M. H. Ernst, Phys. Rev. Lett. **54**, 1396 (1985).

[5]P. L. Blatz and R. V. Tobolski, J. Chem. Phys. **49**, 77 (1945).

[6]P. G. J. van Dongen and M. H. Ernst, J. Stat. Phys. **37**, 301 (1984).

[7]F. Family, P. Meakin, and J. M. Deutch, Phys. Rev. Lett. **57**, 727 (1987).

[8]C. M. Sorenson, H. X. Zhang, and T. W. Taylor, Phys. Rev. Lett. **59**, 363 (1987).

[9]M. H. Ernst and P. G. J. van Dongen, Phys. Rev. A **36**, 435 (1987).

[10]E. D. McGrady and R. M. Ziff, Phys. Rev. Lett. **58**, 892 (1987).

[11]D. Elderfield, J. Phys. A **20**, L135 (1987).

[12]M. H. Ernst and P. Meakin, to be published.