

Numerical Solutions to the Smoluchowski Aggregation-Fragmentation Equation

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We numerically solved the Smoluchowski rate equation for different combinations of fragmentation and aggregation kernels. The average cluster size, number of clusters, and cluster size distribution were calculated as functions of time and found to reach equilibrium values. Scaling and functional form of the cluster size distribution have been obtained. Detailed comparison with previously reported analytical predictions was made and satisfactory agreement was found. © 1991 Academic Press, Inc.

1. INTRODUCTION

The process of irreversible aggregation of small particles to form larger entities is behind many physical phenomena in broadly diverse areas of physics, chemistry, astronomy, and biology. The study of such phenomena has experienced a rebirth in the past decade largely due to the realization that the resulting aggregates of such processes may be described as fractals and that the cluster size distributions display universal scaling behavior (1, 2).

A more general point of view would include the possibility that an aggregate breaks apart or fragments as well as aggregates. Then irreversible aggregation would be a special case when the fragmentation rate is zero. Many real systems would involve both processes occurring simultaneously to lead to an equilibrium with constant size distribution, mean size, etc., and, in fact, this is of considerable importance in polymerization, gelation, and colloid science in general (3-11).

The general, mean field rate equation which describes the evolution of the cluster size distribution is the Smoluchowski equation

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} [K(i, j)n_i n_j - F(i, j)n_{i+j}] - \sum_{j=1}^{\infty} [K(k, j)n_k n_j - F(k, j)n_{k+j}]. \quad [1]$$

This equation describes the rate of change of the concentration, n_k , of clusters with k monomers per cluster (k -mers). $K(i, j)$ is the aggregation kernel describing the aggregation reaction rate of an i -mer plus a j -mer, and $F(i, j)$ is the fragmentation kernel describing the fragmentation of an $(i + j)$ -mer into an i -mer and a j -mer. Perhaps the most important consequence of this equation compared to the pure aggregation case when $F = 0$ is that it can lead to stable equilibrium solutions for the cluster mean size and size distribution.

The first work on aggregation-fragmentation systems was that of Blatz and Tobolsky (3) who desired to model polymerization-depolymerization reactions. They solved Eq. [1] for the special case where both kernels were constant. They found an equilibrium dependent on the relative magnitudes of the constant K and F . Family *et al.* (7) assumed that the scaling ansatz known to hold for pure aggregation also held in the steady state and showed the existence of a critical exponent describing

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the equilibrium cluster-size distribution. Sorensen *et al.* (8) extended the use of the aggregation scaling ansatz to all time and managed to derive expressions for the equilibrium mean size and characteristic time to reach equilibrium in terms of the relative strengths of the kernels and the monomer concentration. They also derived conditions for stability of the equilibrium, an exponent relation between the aggregation, fragmentation, and equilibrium regimes, and showed that for small deviations from equilibrium the relaxation is exponential. Their derivation was criticized, however, by Vigil and Ziff (9) who showed that certain parameters used by Sorensen *et al.* as constants were in fact not constants. More recently, Meakin and Ernst (10) extended the concept of scaling of the cluster-size distribution to show that scaling early in the growth process, when aggregation dominated, was described by well-known "conventional" concepts; but later as the system approached equilibrium, the scaling transformed into another form. Thus the simple scaling assumption used by Sorensen *et al.* does not hold and one must question their results. Finally, Vigil and Ziff (11) have presented a study of certain special cases of the kernels in Eq. [1] and found that a stability criterion equivalent

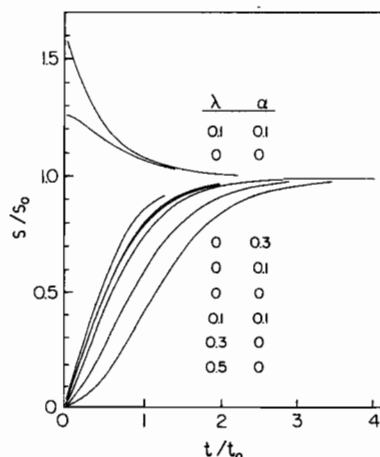


FIG. 1. Reduced size vs. reduced time to demonstrate the evolution of the mean size for a variety of sum kernel combinations, $K(i, j) = (i + j)^\lambda$ and $F(i, j) = (i + j)^\alpha$.

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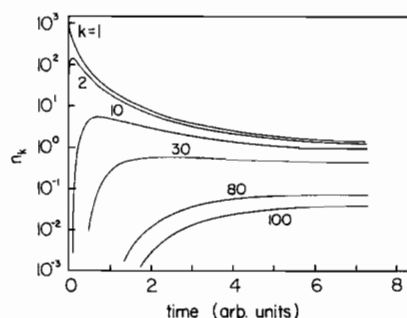


FIG. 2. $n_k(t)$ vs. time for a variety of k values. The initial distribution was $n_k(0) = 1000 \delta_{1,k}$. Kernels used were $K(i, j) = (i + j)^{0.1}$ and $F(i, j) = (i + j)^{0.1}$ which yields $s_0 = 63.3$.

to that developed by Sorensen *et al.* held. We see a number of very interesting phenomena arising from Eq. [1]: equilibrium, stability/instability, critical exponents and relations, and new scaling concepts. A question remains, however, concerning the validity of the results of Sorensen *et al.* derived from their simple scaling assumption. Thus it seems the clear light of experiment would be helpful, and it is the purpose of this paper to report numerical experiments involving Eq. [1] to visualize and test these various predictions. We find that, to a degree, everyone is correct. Our numerical results support the work of Vigil and Ziff (9) and Meakin and Ernst (10) yet show that the approximations inherent in the analysis of Sorensen *et al.* (8) are not severe, hence their theoretical predictions have useful accuracy.

II. THEORETICAL REVIEW

Sorensen *et al.* began with the Smoluchowski equation including both aggregation and fragmentation, Eq. [1], to study the mean cluster size evolution. They assumed the cluster size distribution was described by the scaling ansatz

$$n_k(t) = M_1 s(t)^{-2} \phi(x). \quad [2]$$

In Eq. [2], M_1 is the first moment of the size distribution, where the moments are defined by $M_i = \sum_k k^i n_k$, $s(t)$ is the mean size defined as

$$s(t) = M_2/M_1, \quad [3]$$

and $\phi(x)$ is the scaling function with $x = k/s$. The kernels were assumed to be homogeneous functions of their arguments, i.e., $K(ci, cj) = c^\lambda K(i, j)$ and $F(ci, cj) = c^\alpha F(i, j)$. Furthermore, following Family *et al.*, the strengths of the kernels, k_c and k_f , were defined by $K(i, j) = k_c \Psi(i, j)$ and $F(i, j) = k_f \Phi(i, j)$, where $\Psi(1, 1) = \Phi(1, 1) = 1$.

They then found the rate of change of the second moment, hence that of s as well, using Eq. [1] in integral form. This led to a differential equation for s ,

$$\dot{s} = M_1 a k_c s^\lambda - b k_f s^{\alpha+2}. \quad [4]$$

In Eq. [4] a and b were taken to be constants given by

$$a = \int_0^\infty dx \int_0^\infty dy xy \Psi(x, y) \phi(x) \phi(y) \quad [5]$$

and

$$b = \int_0^\infty dx \int_0^\infty dy xy \Phi(x, y) \phi(x+y). \quad [6]$$

It is these parameters that Vigil and Ziff (9) showed were dependent on the order of the moment used in deriving Eq. [4] and hence could not be rigorously constant. Thus at best a and b are only approximately constant and

it is one of the purposes of this paper to evaluate the consequences of this approximation.

Given this approximation, that a and b are constants, Eq. [4] yields equilibrium solutions. The long-time equilibrium size, s_0 , and the characteristic time to reach equilibrium, t_0 , were found to be

$$s_0 = (M_1 a k_c / b k_f)^{1/y} \quad [7]$$

and

$$t_0 = \frac{s_0^{1-\lambda}}{M_1 a k_c} = (M_1 a k_c)^{-(\alpha+1)y} (b k_f)^{(\lambda-1)y}, \quad [8]$$

where

$$y = (\alpha - \lambda + 2)^{-1}. \quad [9]$$

This last relation is the exponent found by Family *et al.* Furthermore, Eq. [4] allowed stable solutions when $y > 0$ and unstable when $y \leq 0$. The total number of clusters is given by the zeroth moment, M_0 , and if its equilibrium value is called N_0 , they found that

$$N_0 = M_1 s_0^{-1} \int_0^\infty \phi(x) dx. \quad [10]$$

Since growth when $t \ll t_0$ is characterized by $s \sim t^z$ with $z = (1 - \lambda)^{-1}$, and breakup when $t \ll t_0$ is characterized by $s \sim t^{z'}$ with $z' = -(\alpha + 1)^{-1}$, an exponent relation exists between the exponents describing growth, breakup, and equilibrium,

$$1/y = 1/z + 1/z'. \quad [11]$$

Finally, it was shown that for small deviations from equilibrium, $\delta = |s - s_0|/s_0 \ll 1$, the system relaxes back to equilibrium exponentially as

$$s - s_0 \sim e^{-t/y t_0}. \quad [12]$$

Meakin and Ernst developed the important result that the scaling distribution has two different forms in an aggregation-fragmentation system. The first form appears early in the system evolution in the aggregation dominated regime and is identical to the usual scaling ansatz found for pure aggregation systems, Eq. [2]. The second form appears late in the sys-

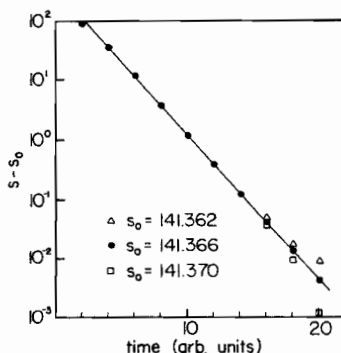


FIG. 3. Demonstration of the exponential approach with time to equilibrium for the mean size. The optimized equilibrium size s_0 was picked from the most linear curve. The decay constant is $y t_0$. The kernel combination for this example is $K(i, j) = (i + j)^{0.3}$ and $F(i, j) = 1$.

tem evolution as the system approaches equilibrium and has the same form as Eq. [2] but the function $\phi(x)$ is different. A characteristic time dividing these two regimes was found to obey

$$\tau(k) \sim k^{-x}. \quad [13]$$

In Eq. [13], k measures the relative strength of the fragmentation and aggregation kernels, presumably $k = k_f/k_c$ in our notation, and the "new" exponent is $x = y/z = (1 - \lambda)y$ (not to be confused with the variable $x = k/s$ in Eq. [2]). They were then critical of the use by Sorensen *et al.* of the scaling ansatz in Eq. [2] since this should not apply at all time.

It is noteworthy, however, that despite the approximation incurred by Sorensen *et al.* by use of the scaling ansatz Eq. [2] for all time, the characteristic time separating the evolving and equilibrium regimes is obtained correctly. In fact, the characteristic time $\tau(k)$ is our t_0 in Eq. [8] above. Furthermore, the exponent x is not new, it is the exponent for k_f also in Eq. [8]. If $k = k_f/k_c$, then Eq. [8] suggests that the Meakin and Ernst result, Eq. [13], is incomplete, and there are two exponents, one for k_f and one for k_c , needed to describe the scaling of the characteristic time $\tau(k) = t_0$.

To see this we redo the scaling argument

used by Meakin and Ernst to obtain Eq. [13]. Now, however, we pass from a *fragmentation* dominated regime, obtained by starting with a mean size much greater than equilibrium, to the *equilibrium* regime. Then, following Meakin and Ernst we assume a characteristic time $\tau(k_c)$ which increases as $\tau(k_c) \sim k_c^{-x'}$ for $k_c \rightarrow 0$. For $t \gg \tau(k_c)$ the process is at equilibrium, for $t \ll \tau(k_c)$ the process is essentially irreversible fragmentation. This implies the following scaling form for the mean cluster size:

$$s(t, k_c) \sim k_c^y \psi(T); T = t/\tau(k_c) = tk_c^{x'}. \quad [14]$$

To match the behavior of irreversible fragmentation as $k_c \rightarrow 0$, the function ψ must decrease algebraically, $\psi(T) \sim T^{z'}$ where $z' = -(\alpha + 1)^{-1}$, and must be independent of k_c , implying $y = z'x'$. Thus $x' = y/z' = -(\alpha + 1)y$ which is the exponent given in Eq. [8]. Thus it seems the complete picture involves *three* regimes, aggregation and equilibrium dominated regimes, as told by Meakin and Ernst, and a fragmentation dominated regime as well. The theory shows explicitly that whereas s_0 is symmetric in k_c and k_f , i.e., is only a function of their ratio, t_0 is not symmetric, but rather has different dependencies

TABLE I
Comparison between Numerical Calculation and Analytical Theory

$K(i, j)$	$F(i, j)$	y^{-1}	s_0			t_0		
			Numerical	Theory	Error (%)	Numerical	Theory	Error (%)
1	1	2	63.5	63.25	0.4	0.0665	0.0633	5
1	4	2	31.7	31.6	0.3	0.0332	0.0316	5
0.25	1	2	32.0	31.6	1.3	0.136	0.126	8
$(i + j)^{0.1}$	1	1.9	80.6	81.6	-1.2	0.054	0.049	10
$(i + j)^{0.3}$	1	1.7	141.4	148.6	-4.8	0.030	0.027	11
$(i + j)^{0.5}$	1	1.5	288	317.5	-9.3	0.0136	0.0126	8
1	$(i + j)^{0.1}$	2.1	51.	50.2	1.6	0.055	0.050	10
1	$(i + j)^{0.3}$	2.3	35.4	33.6	5.4	0.044	0.034	30
$(i + j)^{0.1}$	$(i + j)^{0.1}$	2	63.3	63.25	0.08	0.043	0.039	10
$(i + j)^{0.3}$	$(i + j)^{0.3}$	2	63.25	63.25	0	—	—	—
$(ij)^{0.3/2}$	1	1.7	121.3	121.3	0	—	—	—
$(ij)^{0.6/2}$	1	1.4	307	310.3	-1.1	—	—	—

on k_c and k_f , contrary to the Meakin and Ernst assumption.

The central problem with the work of Sorensen *et al.* is the use of the scaling ansatz, Eq. [2]. The work of Meakin and Ernst demonstrated that the concepts of scaling must be modified and Eq. [2] does not hold throughout the process as it evolves from either aggregation or fragmentation dominated to the equilibrium regime. Vigil and Ziff's (9) accurate comment that the parameters a and b are not constants, as is necessary for the rigorous application of Eq. [4], is no doubt a consequence of this scaling ansatz. Yet Eq. [4] works to yield the proper exponents for the characteristic size and time and to give the correct stability regimes. It is then relevant to ask how well the other analytic predictions hold. To answer this question we have used numerical methods to solve Eq. [1]. We find the predictions of Sorensen *et al.* work very well. We then suggest why this is so.

III. NUMERICAL METHOD

Equation [1] is an infinite set of coupled, nonlinear first-order differential equations. We approached the solution to this equation in two ways. The first was to follow the evolution of the population and the mean size with time

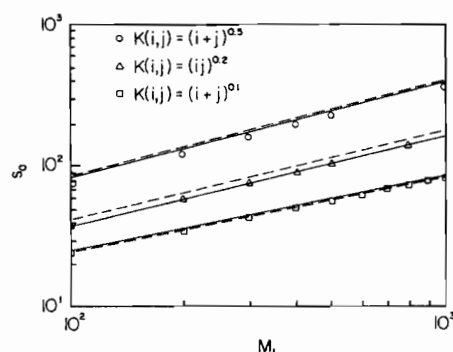


FIG. 4. Mean equilibrium size versus the first moment for three kernel combinations. Dashed lines are a first approximation theoretical fit and solid lines are a second (and better) approximation theoretical fit to Eq. [7] as described in the text.

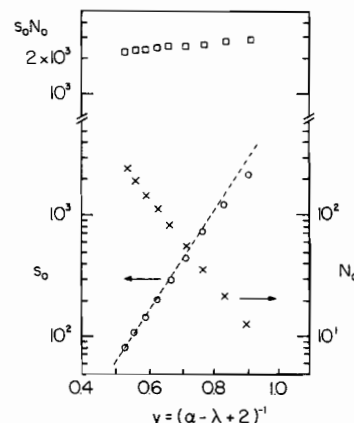


FIG. 5. Equilibrium mean size, s_0 (\circ), equilibrium number of clusters, N_0 (\times), and their product (\square) as a function of the exponent $y = (\alpha - \lambda + 2)^{-1}$ for $K(i, j) = (i + j)^\lambda$ and $F(i, j) = 1$. Dashed line is a first approximation theoretical to Eq. [7] as described in the text.

by integrating the system of equations. The second was to solve directly for the equilibrium state which the system would reach after long evolution time.

Equation [1] was cut to a finite number of equations by setting a limit to the maximum value k can have in the sums of Eq. [1]. This k_{\max} was usually 1000 but when $s_0 \geq k_{\max}/5$, as it was for larger λ , we found this truncation caused errors in s_0 and increased k_{\max} until no variation in s_0 was seen.

In most cases we watched the temporal evolution of the size distribution $n_k(t)$ with a starting distribution of 1000 monomers. We also solved the case of $F = K = (i + j)^{0.1}$ starting from a broad seminormal distribution (truncated for $k \leq 0$), and the case of $K = 1$, $F = 4$ starting with twenty-five 40-mers. The last two cases were to observe the approach to equilibrium from a fragmentation dominated regime.

Our numerical method was to integrate Eq. [1] using both the central difference and the fourth order Runge-Kutta method with variable time step (12). The time step was varied to ensure that we calculated in a regime with results independent of the time step. We recorded the size distribution $n_k(t)$ for $1 \leq k$

$\leq k_{\max}$ as a function of time. We also calculated and recorded the time dependencies of the zeroth, first, and second moments of the size distribution, M_0 , M_1 , and M_2 . M_1 should be a constant and this constancy was a check of our calculations. We pushed the integration procedure until the mean size, $s = M_2/M_1$, approached equilibrium. Our step size was quite small at the beginning of integration, then it increased gradually to accelerate the procedure.

Another program was written to deal directly with the equilibrium situation. After long evolution time, a steady state should be obtained, thus the left hand side of the Smoluchowski Equation [1] is zero for all k , i.e., $n_k = 0$. This enabled us to express any given n_k as a function of all the other n_k 's. With any reasonable initial distribution, we could algebraically iterate and update the population until we reached convergence, i.e., the mean size and the population did not substantially change. Although we could not watch the temporal evolution of $n_k(t)$ and its moments with this method, it was a fast routine that could be used to jump directly to equilibrium.

IV. RESULTS AND DISCUSSION

A. General Equilibrium

Figure 1 displays the evolution of the mean size versus time in reduced variables s/s_0 and t/t_0 as determined from our numerical solution of Eq. [1]. One can qualitatively see the aggregation dominated and equilibrium regimes for $t/t_0 < 1$ and > 1 , respectively. The increasing curvature with increasing λ at small times is the result of $s \sim t^z$ with $z = (1 - \lambda)^{-1}$ expected when aggregation dominates. Another example of the approach to equilibrium is given in Fig. 2, where n_k for a variety of k 's is displayed as a function of time for the kernel combination $K(i, j) = (i + j)^{0.1}$ and $F(i, j) = (i + j)^{0.1}$. The initial distribution was all monomers, $k = 1$, hence one sees $n_1(t)$ fall monotonically with time, $n_k(t)$ for $k < s_0$ all show maxima, and $n_k(t)$ for $k > s_0$ all increase monotonically with time.

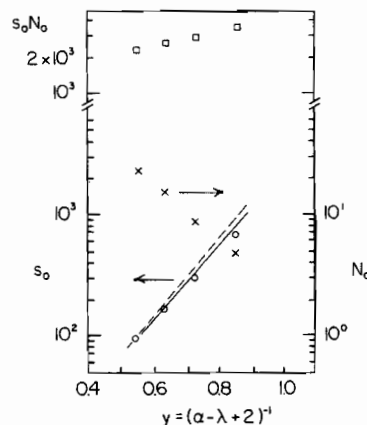


FIG. 6. Equilibrium mean size, s_0 (○) equilibrium number of clusters, N_0 (×), and their product (□) as a function of the exponent $y = (\alpha - \lambda + 2)^{-1}$ for $K(i, j) = (ij)^{1/2}$ and $F(i, j) = 1$. Dashed line is a first approximation theoretical fit and solid line is a second (and better) approximation theoretical fit to Eq. [7] as described in the text.

The values of s_0 and t_0 used to obtain the plots in Fig. 1 were determined by analysis of the approach to equilibrium which should be exponential as described by Eq. [12]. An example of this is given in Fig. 3 where we plot $s - s_0$ versus t semilogarithmically. Straight lines are obtained supporting Eq. [12] and the best fits to the straight lines yield s_0 and yt_0 . Values for s_0 and t_0 for the variety of kernel combinations used are tabulated in Table I.

To compare these numerical values of s_0 and t_0 to theory, we use the analytical results Eqs. [7] and [8]. $M_1 = 1000$ in all these runs and k_c and k_f are determined from the kernels. The values for a and b could not be calculated analytically due to our ignorance of the analytic form of the size distribution n_k for arbitrary kernels. As we will show below, the scaling function is almost exponential, $\phi(x) = Be^{-\beta x}$, for kernels of the same homogeneity, $\lambda = \alpha$, and approximately so for other kernel combinations. The normalization condition that $M_1 = \sum k n_k$ and the use of $s = M_2/M_1$, Eq. [3], yield $B = 4$ and $\beta = 2$. Thus we use this along with $\Psi(x, y) = \Phi(x, y) = 1$ as a lowest-order approximation to calculate a and

b to allow for a comparison of theory to the numerical values. These theoretical values are also given in Table I.

Inspection of Table I shows good agreement, especially when $\lambda \simeq \alpha$. Systematic differences are seen, however. The equilibrium size is either smaller or larger than theory depending on whether $\lambda > \alpha$ or $\lambda < \alpha$, respectively. The characteristic time, t_0 , always deviates larger than theory. We cannot determine whether these deviations are due to the exponential approximation for n_k or the Vigil-Ziff (9) objection that a and b are inappropriate. It is most likely a combination of these two errors. Regardless of this, the deviations are small, especially for small λ and α , and we conclude that Eqs. [7] and [8] work in a satisfactory manner.

The values of s_0 and t_0 in Table I were determined from the time evolution study of $n_k(t)$. As described in our numerical procedure section, we also determined the asymptotic solutions for $n_k(t)$, s_0 and t_0 by solving the Smoluchowski equation, Eq. [1], with $n_k(t) = 0$ expected at equilibrium. This has allowed us to make a more far reaching test of theory versus numerical values in that we have allowed both γ , through λ , and M_1 to vary widely.

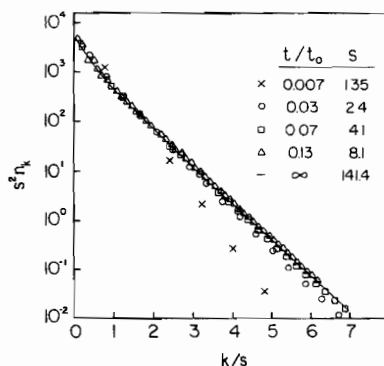


FIG. 7. Demonstration of how quickly the system develops a scaling form, $n_k \sim s^{-2} \phi(k/s)$. Also note how no evolution is seen between $t/t_0 = 0.13$ and ∞ on the scale of this graph. The kernel combination is $K(i, j) = (i + j)^{0.3}$, $F(i, j) = 1$.

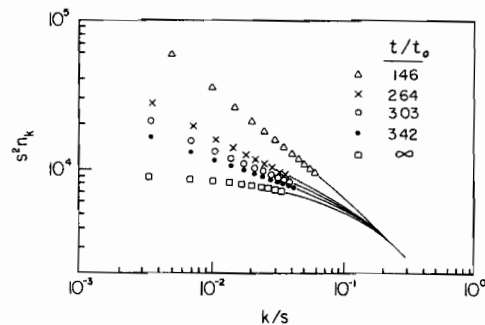


FIG. 8. Scaling plot showing small $x = k/s$ evolution as $t/t_0 \rightarrow \infty$. The kernel combination is $K(i, j) = (i + j)^{0.5}$, $F(i, j) = 1$.

Figure 4 shows s_0 as a function of M_1 for three different aggregation kernels combined with a constant fragmentation kernel $F(i, j) = 1$. The theoretical lines are calculated from Eq. [7]. Once again, approximation must be made when calculating the values a and b . We have made two levels of approximation in order to see the importance of the approximations. The lowest order approximation is to assume, as described above, that $n_k(t)$ is exponential in k and also that $\Phi(x, y) = \Psi(x, y) = 1$. The next order and better approximation is again to assume an exponential $n_k(t)$ but now use $\Phi(x, y)$ and $\Psi(x, y)$ equal to their actual values. The integral in Eq. [5] could not be solved exactly for sum kernels of the form $(x + y)^\lambda$ but suitable approximations were used. Figure 4 demonstrates good agreement between theory and the numerical values especially when the better approximation is used, although results using the lower order approximation are not bad.

Figures 5 and 6 show both s_0 and N_0 and their product as functions of $\gamma = (\alpha - \lambda + 2)^{-1}$ for combinations of $F(i, j) = 1$ and sum and product aggregation kernels, respectively. Once again two levels of approximation were used in calculating a and b which were involved in calculating s_0 . Again good agreement is seen for s_0 , better for the better approximation. Deviation of theory and numerical values increase with increasing γ , however, and we will show below this is most likely a

result of an increasing difference of $n_k(t)$ from exponential. Also note that theory and numerical values cross at $y = \frac{1}{2}$ which can correspond to $\alpha = \lambda = 0$, a combination known to yield an exponential $n_k(t)$.

The product $s_0 N_0$ is also shown in Figs. 5 and 6 and it is not a constant as forecast by Sorensen *et al.* For $\alpha = \lambda = 0$, $n_k = M_1 s^{-2} \phi(x) = 4 M_1 s^{-2} e^{-2k/s}$ (see above). Thus by Eq. [10], $s_0 N_0 = 2 M_1 = 2000$ for $\alpha = \lambda = 0$ or $y = \frac{1}{2}$. This value appears true for the numerical results at $y = \frac{1}{2}$ in Figs. 5 and 6 as well. For $y > \frac{1}{2}$, however, $s_0 N_0 > 2000$ and not a constant. This is due to the nonconstancy of $\int_0^\infty \phi(x) dx$ as y varies; we find the shape of $\phi(x)$ is a function of K and F . If we had taken $s = M_1/M_0$ instead of M_2/M_1 , then the product of $N_0 s_0$ would have remained constant.

B. Scaling

We first demonstrate how quickly scaling is established by Eq. [1] after an initial size distribution composed solely of monomers $n_k(0) = M_1 \delta_{k,1}$. This is done by plotting $s^2 n_k(t)$ versus k/s . We will take a general attitude that scaling is indicated when such plots fall on the same curve.

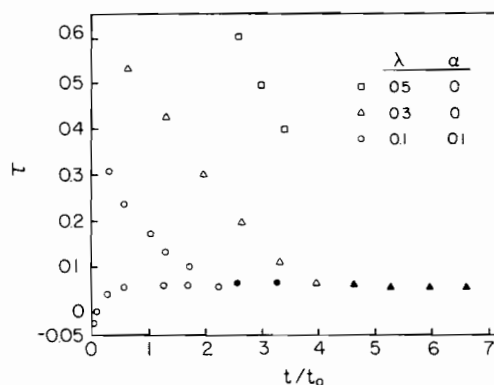


FIG. 9. The exponent τ vs. reduced time t/t_0 . All systems evolve to $\tau \approx 0.05$ but this value is a residual value representing the limiting slope of the scaling plot $s^2 n_k$ vs. k/s which is always slightly negative (to yield $\tau > 0$). Solid points indicate τ determined when only the first two points on a log-log scaling plot could fit to a straight line. Data represented by the circles started monodisperse but with the initial size greater than the equilibrium mean size.

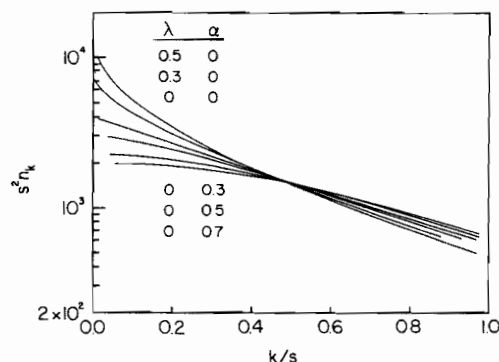


FIG. 10. Scaling plot for a variety of kernel combinations of the form $k(i, j) = (i + j)^\lambda$, $F(i, j) = (i + j)^\alpha$. For $k/s \geq 1$ all curves are linear, hence n_k is exponential, and for $k/s \ll 1$ have $\tau \approx 0$.

Figure 7 is such a scaling graph plotted semilogarithmically for the kernel combination $K(i, j) = (i + j)^{0.3}$, $F(i, j) = 1$. One sees that very soon, relative to t_0 , after $t = 0$ the different time plots fall on nearly the same curve to indicate an approximate scaling is achieved. This approximate scaling at small t/t_0 is very important in the analysis of Eq. [1] as performed by Sorensen *et al.* notwithstanding the objections of Meakin and Ernst. Use of the scaling ansatz, Eq. [2], at early times after a very nonscaling start is justified as a good approximation by Fig. 7.

We find in general that the size distribution does continue to evolve past $t/t_0 > 1$, although it is not readily apparent in Fig. 7 because the evolution continues only for $k/s \ll 1$. To illustrate this we plot $s^2 n_k(t)$ vs. k/s on a double-log scale for a similar kernel combination, $K(i, j) = (i + j)^{0.5}$, $F(i, j) = 1$ in Fig. 8. Here for $k/s < 0.3$ we see the size distribution continues to evolve past $t/t_0 \approx 1$. Not shown in the graph is the nonevolving exponential tail for $k/s > 0.3$ which was readily apparent in Fig. 7. For $k/s < 0.3$ the double-log graphs are straight lines implying the power law $n_k \sim k^{-\tau}$ in this region. The exponent τ decreases with time.

In pure aggregation systems, i.e., $F(i, j) = 0$, power law behavior for n_k is expected for sum kernels with $\tau \leq 1 + \lambda$ (13). Thus we may

interpret the declining τ with time as another manifestation of the crossover from aggregation dominated to equilibrium regimes as discussed by Meakin and Ernst. In fact, the kernel combinations which we have studied fit into their class (iii) category for which they predict $\tau = 0$ at infinite time. Figure 9 shows τ as a function of reduced time, t/t_0 , for a number of examples and indeed τ does approach zero at long time.

We can achieve the asymptotic $t/t_0 \rightarrow \infty$ size distribution with our second numerical analysis method wherein we set $\dot{n}_k(t) = 0$. Results for a variety of kernel combination are given in Fig. 10. Here we see a systematic trend with $\alpha - \lambda$. For $\alpha - \lambda = 0$ we find exponential $n_k(t)$ for all k including $k \rightarrow 0$. For $\alpha - \lambda < 0$, n_k increases rapidly as $k \rightarrow 0$ whereas for $\alpha - \lambda > 0$ the $k \rightarrow 0$ region is rounded below an exponential. For all $\alpha - \lambda$ the size distributions are exponential for $k/s \geq 1$.

We believe it is this quasiexponential behavior which allows the analytical results to have reasonable accuracy. As Vigil and Ziff (9) pointed out, a and b are constants for $K(i, j) = F(i, j) = 1$ and $\phi(x)$ exponential. Our numerical results show $\phi(x)$ is exponential for $k/s > 1$ for a variety of λ and α . We have also seen that this exponential behavior improves for $\lambda \simeq \alpha$. Meakin and Ernst were correct to object to the use of the scaling ansatz because the scaling function should evolve, but Figs. 7 and 8 demonstrate that the evolution from aggregation dominated to equilibrium regimes is confined to small k/s and hence may have little effect on integrals such as those involved in a and b . Certainly, the theory proves itself in the correct prediction of the exponents describing the dependencies on k_c and k_f of the equilibrium size and the characteristic time. It also properly describes stable and nonstable regimes. Finally, its predictions for the equilibrium size and characteristic time show reasonable agreement with the numerical results. Thus it seems that limitations placed into the theory, i.e., the evolution of the scaling and the indeterminacy of the constants a and b , are not severe.

V. SUMMARY

We have numerically solved the Smoluchowski rate equation including both aggregation and fragmentation kernels. The theoretical predictions of Sorensen *et al.* regarding equilibrium cluster sizes and characteristic time scales are found to hold. The size distribution was seen to quickly reach a scaling form and then slowly evolve at $k/s < 1$ as the system passed from an aggregation dominated to an equilibrium regime in accord with the predictions of Meakin and Ernst. The scaling function, $\phi(x)$, was well approximated by an exponential, and this and the small evolution of the cluster-size distribution as the system approached equilibrium were used to show that the approximations inherent in the theory do not severely hinder its usefulness.

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