On the validity of Smoluchowski's equation for cluster–cluster aggregation kinetics

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Large-scale computer simulations of cluster–cluster aggregation of particles undergoing Brownian motion have been performed to investigate the kinetic properties of the coagulation process. It is shown that the mean-field approach of the Smoluchowski equation accurately describes the kinetics if the fractal geometry of the clusters is taken into account. The kinetic rate kernels that enter into that equation are deduced explicitly from the simulations.

I. INTRODUCTION

There has recently been a great deal of interest in the computer simulation of aggregation phenomena.[1–9] Initially, the motivation of this work was to study the fractal geometry of the clusters that are produced, after the simpler particle–cluster aggregation model of Witten and Sander[1] had shown interesting nonclassical geometric behavior. It was found by Meakin[2] and Kolb, Botet, and Jullien[3] that the clusters formed by cluster–cluster aggregation are fractals with dimensionality $D_f \approx 1.75$ (for mass-independent diffusion coefficient, in three dimensional space), compared to $D_f \approx 2.5$ for the Witten Sander model, under the same conditions. In the much earlier work of Vold,[10] Sutherland and Goodarz-Nia,[11] and Medelia,[12] fractal aggregation clusters were produced from models that collided only pairs of particles, producing an ordered series of events but no well-defined time.

More recently, attention has turned to the kinetic properties, which physically are of importance. Viscek, and Family,[4] and Meakin, Viscek, and Family[5] have investigated the scaling properties of the distribution with respect to both size and time. Scaling properties allow the kinetic behavior to be classified with respect to other kinetic processes, but describe only the long-time behavior of the system. The kinetics, however, concern the complete time development of the cluster size distribution.

The classical understanding of aggregation kinetics is given by the Smoluchowski theory,[13] which follows from the assumption that the collisions are binary and that fluctuations in density are sufficiently small so that the collisions occur at random. The Smoluchowski equation is of universal use in the fields of colloid chemistry, aerosol dynamics, atmospheric science, etc., and is an obvious reference in interpreting the results of computer simulations of aggregation. Indeed, the simulations can serve as a means to test the validity of the mean field approach, and some work has been done in comparing results of computer simulations with the results of the mean-field Smoluchowski theory.

However, a simple comparison of the observed and predicted size distributions does not test the basic assumptions of the theory. The size distributions are only a coarse-grained reflection of the basic processes going on. Furthermore, since there is an adjustable rate matrix in the Smoluchowski equation, there is a great deal of freedom in the type of behavior that it can predict. Even if the Smoluchowski equation were found to predict the evolution of the size distribution correctly, it does not follow that the equation itself is valid or that it has any physical relevance.

The fundamental test of the applicability Smoluchowski theory is to show in detail that the underlying assumption is valid—that the rate of collision between two species is proportional to the product of their concentrations, even as the concentrations change. This test requires therefore that the collision histories are followed in detail. With current computers it is possible to collect a statistically sufficient amount of data to perform this test in a reasonable amount of time. We note that for a related model of particle trapping kinetics, Redner and Kang[14] have investigated the effects of the particle fluctuations and have shown that those fluctuations are important so that a mean-field equation is not valid for $d \leqslant 2$.

We note that such a measurement of the collision frequencies would be very difficult to do experimentally. The little experimental work that has been done on the validity of the Smoluchowski equation has been measurements of distributions and comparison with theory, and even this measurement is difficult.[15] Simulation of aggregation allows an explicit test of a theory that has been used for almost 70 years.

In this paper we report on the results of a computer test of cluster–cluster aggregation kinetics. We use some of the standard models of hard particles (cubes) on a cubical lattice, for which fractal and scaling properties have already been studied. We check both the collision rates and the evolution of the size distributions over the entire time period and investigate the relation of these results with the Smoluchowski theory.

Because the models we use lead to fractal aggregates, our study has a second aspect: how this fractal structure affects the kinetics. From the point of view of the Smoluchowski equation, the question translates into finding the form of the collision matrix when the clusters are fractal. The aggregation models we use are similar to smoke particle formation by Brownian coagulation, so the results of this

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study will lead to a better understanding of that process.

II. THE SMOLUCHOWSKI EQUATION

Here we make more explicit some of the essential features of this equation. From the assumption that the collisions are random and binary, it follows that the rate of aggregation of clusters of s units of mass (s-mers) with r-mers to form $(s+r)$-mers is proportional to the product of the concentrations of reactants

$$(\text{Rate})_{rs} = K_{rs}\, n_r\, n_s\,, \tag{1}$$

where n_s is the time dependent concentration (number per unit volume) of s-mers and the matrix K_{rs} is the collision matrix or kernel, a function of both the collision and aggregation processes. Smoluchowski's coagulation equation is then found by writing a population balance equation for the process described by Eq. (1), taking into account both the gains and losses due to collisions:

$$dn_s/dt = (1/2)\sum_{r=1}^{s-1} K_{r,s-r}\, n_r\, n_{s-r} - n_s \sum_{r=1}^{\infty} K_{s,r}\, n_r\,. \tag{2}$$

For particles undergoing Brownian motion, the solution of the diffusion equation implies that K_{sr} is given by[13]

$$K_{rs} = 4\pi R_{rs}\,[D(r) + D(s)]\,, \tag{3}$$

where R_{rs} is the effective cross-section radius for collisions between r-mers and s-mers, and $D(s)$ is the diffusion coefficient of an s-mer. For simple spherical particles where the radius of an s-mer, R_s, is proportional to $s^{1/3}$ (droplet coalescence), R_{sr} is proportional to $(s^{1/3} + r^{1/3})$, and by the Stokes–Einstein formula $D(s)$ is proportional to R_s^{-1}, resulting in a rate matrix[13]

$$K_{rs} = 2 + (s/r)^{1/3} + (r/s)^{1/3}\,. \tag{4}$$

An explicit solution of Eq. (2) has not been found for K_{rs} of the above form. If the above K_{rs} is approximated as a constant, independent of s and r, Eq. (2) can be solved explicitly for $n_s(t)$, yielding the complete time-dependent solution of this problem.

For the Brownian coagulation of particles that form fractals, the Smoluchowski equation will apply if the mean-field assumption is valid. For the collision kernel, one would expect that Eq. (3) applies with the cross-sectional radius replaced by the sum of the mean radii $R_r + R_s$ where, for a fractal,

$$R_s \simeq s^{\nu}\,. \tag{5}$$

Note that the exponent is the reciprocal of the fractal dimensionality D_f of the cluster. Thus, one would expect[16]

$$K_{rs} \propto (r^{\nu} + s^{\nu})\,[D(r) + D(s)] \tag{6}$$

since the basic diffusion mechanism is unchanged by the fractal properties. The diffusion coefficient will also depend upon radius, and we will consider two limiting cases of that dependence as discussed below.

III. DESCRIPTION OF COMPUTER SIMULATIONS

To answer the above questions we have carried out computer simulations of cluster–cluster aggregation in three dimensions. We considered between 4096 and 32 768 particles on cubic lattices of 80^3, 100^3, 128^3, and 133^3, most commonly 10 000 and 20 000 particles on 128^3 sites. Most of the simulations were carried out using an IBM 3081 computer. In order to reduce the effects of statistical fluctuations it was necessary to average the results from quite a large number of runs. Most of the results reported in this paper were obtained from simulations in which the effective total number of particles was $\simeq 10^7$. Particles occupying adjacent sites on the lattice were considered to be touching, so that the particles were effectively sticky cubes centered on the lattice points. First the particles were placed down randomly, subject only to the constraint that no two particles can occupy the same site. Consequently there were a small number of dimers, trimers, etc., besides the monomers, in the initial state.

In order to simulate the aggregation process clusters were selected at random and an attempt was made to move them in one of the six equally probable directions (also chosen randomly) on a cubic lattice. A random number (x) evenly distributed over the range $0 < x < 1$ was generated and the attempted move was made if x was smaller than s^{γ} (the cluster diffusion coefficient). After each attempted move the time (t) was incremented by $1/N$, where N is the total number of clusters in the system. Consequently time is measured in units of attempted moves per cluster. After each successful move the perimeter of the moved cluster is examined for contact with other clusters (via nearest neighbor occupancy). If two clusters contact each other, they are joined irreversible to form a larger rigid cluster. Occasionally a cluster will simultaneously contact more than one other cluster. In this event all of the contacting clusters are joined. The procedure outlined above is repeated many times during the course of a simulation.

The rate coefficients (K_{rs}) were determined by dividing the time into 100 time intervals and recording the number of "collisions" between clusters of size r and size s in each time interval. If a cluster of size r moves simultaneously into contact with several clusters of size $s_1, s_2, s_3, \ldots$, etc., the collision is recorded as individual $rs_1, rs_2, rs_3, \ldots$, etc. collisions.

By accepting an attempted move with probability proportional to s^{γ}, we are effectively choosing the diffusion coefficient as

$$D(s) \propto s^{\gamma} \tag{7}$$

because the motion of a particle (the displacement) is proportional to its diffusion coefficient. We considered the $\gamma = 0$, -1, and in a few cases, $\gamma = 1$. In those cases where $\gamma > 0$, an attempted move for the cluster is accepted with a probability $s^{\gamma}/s_{\max}^{\gamma}$ where $s_{\max}^{\gamma}$ is the maximum cluster size and the time (t) is incremented by $1/(ns_{\max}^{\gamma})$ after each *attempted* move.

These choices for γ represent some limiting cases which bound the expected behavior of the diffusion coefficient. For spherical particles, $D(i)$ is proportional to $i^{-1/3}$ ($\gamma = -1/3$). If the Stokes–Einstein formula were assumed to remain valid for a fractal, with the radius replaced by the radius of gyration, then by Eq. (5) above we would have $\gamma = -1/D_f$. Note that we cannot actually determine the value of γ from a simulation, and the value of D_f for the clusters depends upon that choice of γ. Thus we choose model forms of the diffu-

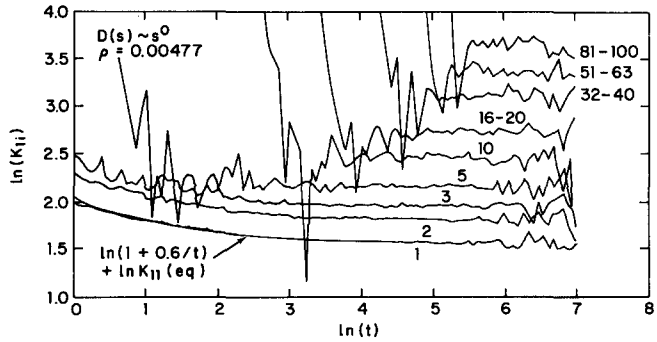

FIG. 1. The measured effective collision rate K_{1s} for $\gamma = 0$, averaged over 483 simulations of 10 000 particles on a lattice of 128^3 sites.

sion coefficient.

The "real" time, t, introduced above, is related to the "computer" time (the actual number of trials), T, by

$$t = \sum_{i=1}^{T} 1/N_i \approx 1/V \int_0^T dT'/M_0 , \tag{8}$$

where M_0 is the zeroth moment of the cluster size distribution, so that VM_0 represents the total number of clusters. Thus, t increases by unity when all particles have attempted to move once, on the average.

In the following sections, we describe and analyze in detail the results of the computer simulations. We consider the case of size-independent diffusion, $D(s) = 1$ (or $\gamma = 0$), in greatest detail, since this model is a natural one for computer simulation; all clusters are chosen for movement with equal probability.

IV. THE VALIDITY OF THE MEAN-FIELD ASSUMPTION

We investigated the validity of the mean-field assumption by measuring the concentrations of the species, n_i = number of i mers/total number of lattice points, and the rate of collision of pairs over various time intervals, to find the apparent K_{sr}:

K_{sr} = (Rate of collision between s mers and r mers)

$$/(n_s\, n_r) . \tag{9}$$

Verification of the mean-field assumption can be accomplished by showing that this quantity is independent of time (except for short times as discussed below).

Figure 1 shows the results for the effective K_{1s} (for the case $\gamma = 0$) for 483 runs of 10 000 particles on a 128^3 lattice. Data is presented for particle sizes $s = 1, 2, 3, 5, 10$, 16–20 (combined), 32–40, 51–63, and 81–100, as a function of t on a log–log scale. The large fluctuations for small and large times reflect the small number of clusters present at those times. In the middle region, where a sufficient number of particles are present so that the fluctuations are small, the K_{1s} can be seen to be well defined and nearly constant with time except for the increase for small times.

The small-time enhancement of the aggregation rate is an effect of the initial distribution; particles placed down randomly will frequently be close together, and will aggregate more quickly. As the close pairs are deleted, the diffusive flux falls to a steady-state value of K_{sr}. For a system of spheres uniformly distributed in space, diffusion equation predicts that Eq. (3) should be enhanced by the multiplicative factor[13]

$$1 + R / [\pi D t]^{1/2} . \tag{10}$$

We would expect the same behavior to occur for hard cubes. Indeed, the small time behavior of K_{11} can be well fit by Eq. (10) if the numerical factor $R/[\pi D]^{1/2}$ is taken to be 0.6, as the plot of this function in Fig. 1 shows. (Note, that both the length scale and D in our problem is 1.) Evidently, the regime where the coagulation kernels become nearly time independent is only approached toward the end of our simulation. In of our simulation. In order for the coagulation kernel to be nearly constant during the coagulation process, the density should be sufficiently low so that $t \approx 1000$ (i.e., each cluster moves roughly 1000 times) before a significant amount of aggregation takes place. The transient effect on the collision rates for higher s and r will be smaller than that for K_{11}, because most of these larger clusters are formed in a reaction—few, if any, exist initially—and it is the uniform initial distribution which causes the transient behavior. Indeed, the curves of K_{12}, K_{13}, etc., in Fig. 1 show less time dependence than that of K_{11}. Below we will show that the *overall* effect of the transient behavior is also less than that for K_{11}.

Thus, because the reaction rates have been shown to be proportional to the concentrations and time independent, except for the expected initial enhancement, it follows that the mean-field behavior is shown in these simulations.

V. THE FORM OF K_{rs}

To study the behavior or K_{rs} as a function of r and s, we calculated the average values of the apparent coagulation kernels, averaging the curves like those in Fig. 1 over all time where significant data exists. The results are shown in Fig. 2(a) for r and s in the range 1–100. As the size of a cluster increases, there is evidently a gradual increase in the rate of aggregation.

For $\gamma = 0$, Eq. (6) predicts, simply $K_{rs} \approx r^\nu + s^\nu$, and other studies[17] have shown that $\nu \approx 1/1.75 \approx 0.6$ for clusters formed by this process. Thus, we expect K_{rs} to be given by

$$K_{rs} = K (r^{0.6} + s^{0.6}) , \tag{11}$$

where K is a constant. In Fig. 2(b), this function is plotted and indeed it appears to agree with the observed K_{rs}. The value of K is found to be ≈ 3.0.

For $\gamma = -1$ (diffusion coefficient inversely proportional to the mass), much different behavior in the rate was seen, as shown in Fig. 3(a) for a run of 814 simulations of 20 000 particles on a 128^3 lattice. Here the small particles move more frequently and thus have a higher aggregation rate. Figure 3(b) shows, rather strikingly, that such behavior is well fit by

$$K_{rs} = (3.0)\,(r^{0.6} + s^{0.6})\,(r^{-1} + s^{-1}) \tag{12}$$

as predicted by Eq. (6).

VI. ASYMPTOTIC BEHAVIOR

In this section we discuss the use of the asymptotic behavior of the distribution to study the kinetics. Viscek and

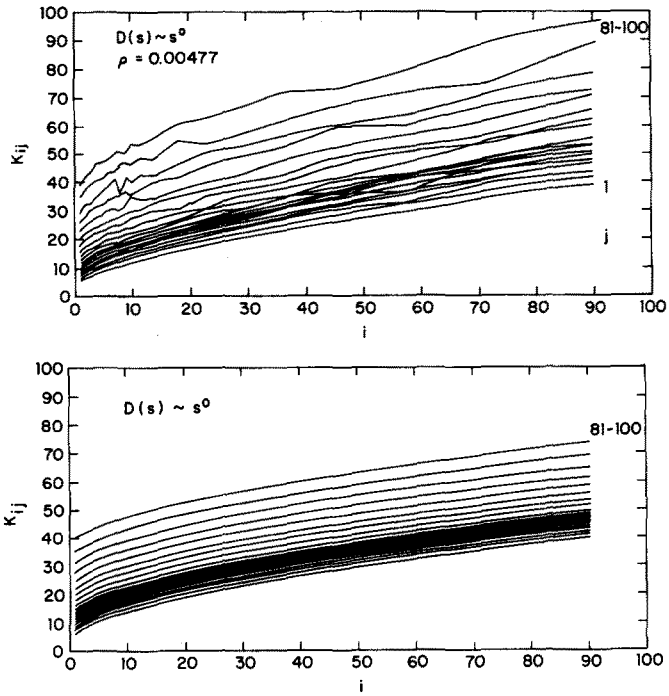

FIG. 2. (a) The time-averaged values of K_{rs} for the simulations of Fig. 1. (b) The behavior predicted by Eq. (11) with $K = 2.5$.

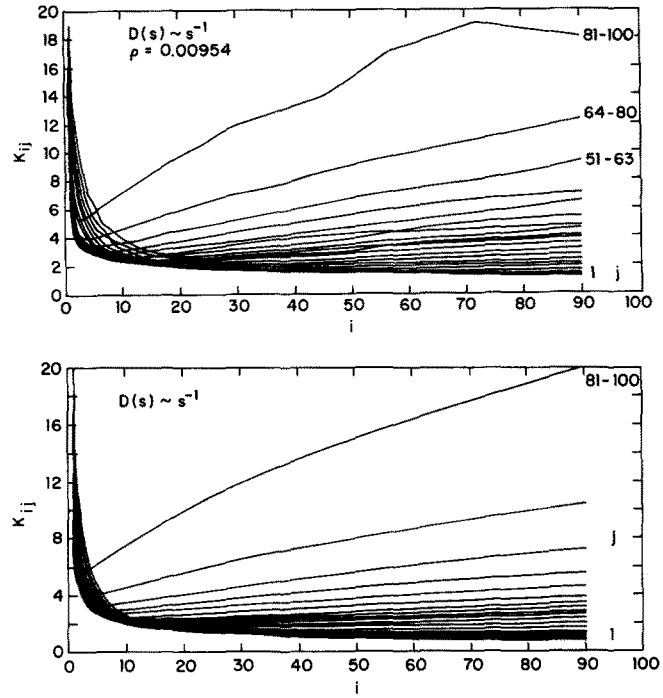

FIG. 3. (a) The average K_{rs} for $\gamma = -1$, for 814 simulations of 20 000 particles on a lattice of 128^3 sites. (b) The behavior predicted by Eq. (12).

Family,[4] Kolb[6], and Botet and Jullien[18] have characterized the long time behavior of n_s by an expression of the form

$$n_s \approx t^{-w} s^{-\tau} f(s/t^z), \tag{13}$$

where $f(x) \to$ const as $x \to 0$ and $f(x) \to 0$ for x large, and where, by mass conservation, the exponents satisfy $w = z(2-\tau)$. Equation (13) implies that the moments $M_i = \Sigma s^i n_s$ satisfy[4]

$$M_i \sim \begin{cases} t^{z(i-1)} & \tau < 1+i \\ t^{-w} & \tau \geqslant 1+i \end{cases} \tag{14}$$

as $t \to \infty$. The scaling of the Smoluchowski equation has also been studied in detail. Most of the known solutions of Eq. (2) satisfy Eq. (13), the exceptions being some special cases such as $K_{rs} = r + s$, where the long time behavior is exponential in time. For those regular solutions, the exponents w, τ, and z can be related to properties of the coagulation kernel. For example, for kernels of the form $K_{rs} = r^\mu s^{\theta-\mu} + s^\mu r^{\theta-\mu}$, with $\theta < 1$, z is given by

$$z = 1/(1-\theta), \tag{15}$$

which follows immediately by inserting Eq. (14) into the equation for the time evolution of the moments [which follows directly from Eq. (2)]. More generally, for K_{rs} composed of any combination of terms of powers of r and s with a homogeneity of θ, [$K(\theta i, \theta j) = \lambda^\theta K(i,j)$], Eq. (15) holds. Essentially, z tells how the size of the largest cluster grows with time; therefore, that growth rate depends only upon the homogeneity of the kernel. As $\theta \to 1$, $z \to \infty$ and the system approaches a situation where gelation occurs in a finite time.

For kernels of the form (6) we have $\theta = \nu + \gamma$ and therefore expect

$$z = 1/(1-\nu-\gamma). \tag{16}$$

The value of w, and thus of τ, will depend somewhat more upon the details of the form of K_{rs}. For $K_{rs} = r^\theta + s^\theta$, $0 < \theta < 1$, Leyvraz[19] has shown that w is given by

$$w = (2-\theta)/(2-2\theta), \quad \tau = 1 + \theta/2. \tag{17}$$

For $K_{rs} = r^\mu s^{\theta-\mu} + s^\mu r^{\theta-\mu}$, with $0 < \mu < 1$, $0 < \theta < 1$,

$$w = 1, \quad \tau = 1 + \theta, \tag{18}$$

Thus the asymptotic exponents w, τ, and z, can be used to verify a particular form of the coagulation kernel K_{rs}, and find the values of a parameter such as θ in the examples above.

To investigate the asymptotic properties of our simulations, we have plotted ln M_0 and ln M_2 vs ln t in Fig. 4, for 483 simulations of 10 000 particles on a lattice of 128^3, with $\gamma = 0$. It can be seen from these plots that the asymptotic behavior is only approached near the end of our simulations. According to Eq. (14), these moments should have the asymptotic behavior $M_0 \approx t^{-w}$ and $M_2 \approx t^z$ [since $1 < \tau < 2$]. The asymptotic slopes in Fig. 4 give $w \approx 1.8$ and $z \approx 3.4$, implying $\nu \approx 0.6$ and $\nu \approx 0.7$, respectively. However, because the asymptotic behavior is barely reached, its analysis is not accurate for these simulations. The time could not be extended further here because a single, large cluster is formed. For longer times, lower densities, and larger lattices, are needed.

When γ is decreased, the asymptotic region becomes more easily accessible. For $\gamma = -1$, the plots of Fig. 5 show M_0 and M_2 as a function of time, for the run of 474 simulations of 10 000 particles a 128^3 lattice. The slopes give $w = 0.74$ and $z = 0.75$. The latter implies by Eq. (15) that $\theta = -0.33$ and by Eq. (16) that $\nu = 0.66$ or $D_f = 1.5$. In the simulations of Meakin, Viscek, and Family,[5] a wider range

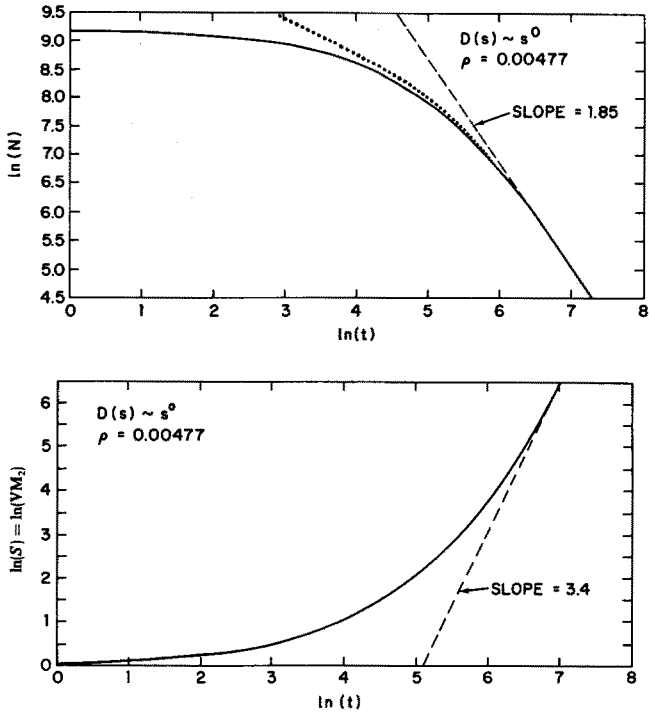

FIG. 4. $\ln N = \ln (V M_0)$, and $\ln S = \ln (V M_2)$, as a function of $\ln t$, for the mass independent simulations of Fig. 1, showing the approach to the asymptotic behavior.

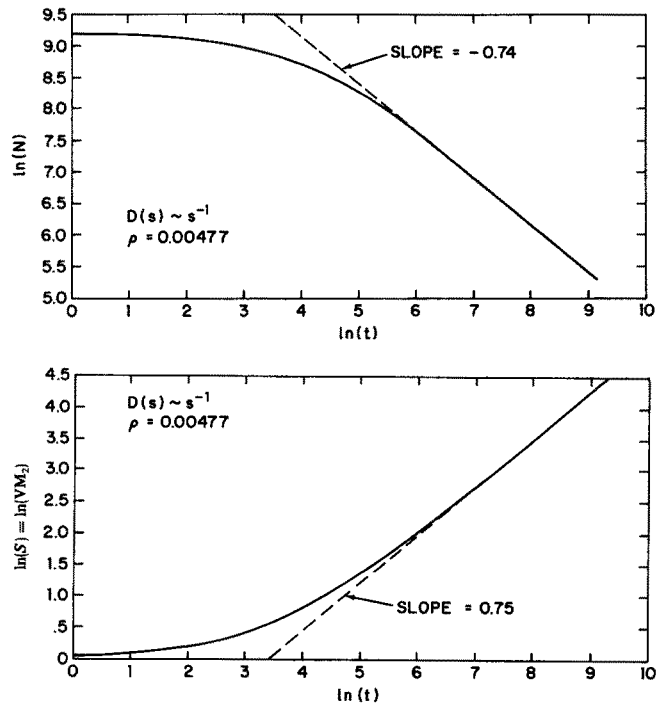

FIG. 5. The asymptotic behavior of the mass-dependent model with $\gamma = -1$; 474 simulations of 10 000 particles on 128^3 lattice sites.

of γ's have been studied, and the time has been carried further when possible. The values of z and w are consistent with the relations (16) and (18) above.

VII. THE COMPLETE TIME BEHAVIOR

We will study the complete time dependence for the case of $\gamma = 0$, and see how well the simulation results can be described by the Smoluchowski equation with K_{rs} of the form

$$K_{rs} = K(r^\theta + s^\theta) \tag{19}$$

as predicted by Eq. (6) and consistent with the measurements of the effective K_{rs} for small r and s. In Eq. (19), K is an overall rate constant and remains to be determined along with θ.

The above K_{rs} belongs to a class of kernels $K_{rs} = f(r) + f(s)$ [where $f(s)$ is any function of s growing less rapidly than s], which can be solved explicitly for $n_s/M_0 (s = 1, 2, 3, \ldots)$ as a function of the "computer" time T introduced in Eq. (8). For $s = 1$, the result is simply[20]

$$n_1/M_0 = \exp(-KT) \tag{20}$$

independent of θ. Checking whether this is obtained is a good test that $f(r) + f(s)$ is followed, since for other forms of the kernel, in particular the product $K_{rs} = f(r)f(s)$, the behavior of n_1/M_0 is not given by Eq. (20). The plot of Fig. 6 of $\ln n_1/M_0$ vs T, for the simulation of $\gamma = 0$, shows the predicted linear behavior strikingly. Its slope implies $K_{rs} \approx (2.4)$ (lattice spacing)^3/(unit time), consistent with the previous result. The small deviation at very short times can be attributed to the short-time enhancement of the aggregation rate discussed above. Note that the enhancement is of a shorter duration than that of K_{11}. The deviation in Fig. 6 at large times can be attributed to the finite size effects. Note that the corresponding plot for $\gamma = -1$ is definitely not linear, as expected.

With the form of Eq. (19) thus verified, all that remains is to find θ. A convenient place to look is the moments, which contain information from the complete distribution. For the kernel Eq. (19), it follows Eq. (2) that the time evolution of M_0 is given by, $dM_0/dt = -K M_0 M_\theta$, implying

$$\frac{1}{M_\theta}\frac{d \ln M_0}{dt} = -K. \tag{21}$$

A plot of the quantity on the left-hand side above, for the results of our simulations, is shown in Fig. 7, for various values of θ. For short times, there is a general decrease (note the negative scale) consistent with the decrease seen in K. For long times, constancy is reached if θ is chosen to be $\approx 0.6 - 0.7$, as found before.

As a final check that the complete time behavior can be

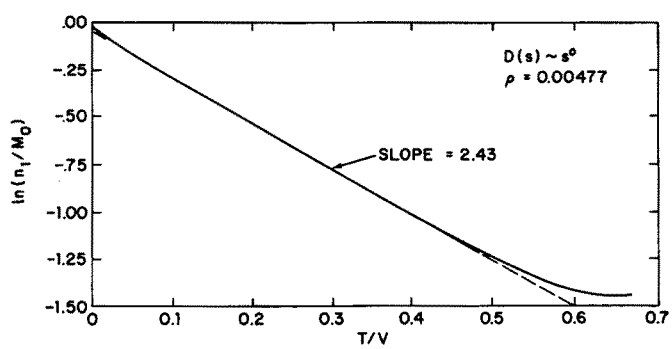

FIG. 6. $\ln n_1/M_0$ vs computer time T for $\gamma = 0$ (predicted to be a straight line with slope $-K$) where $v = 128^3$.

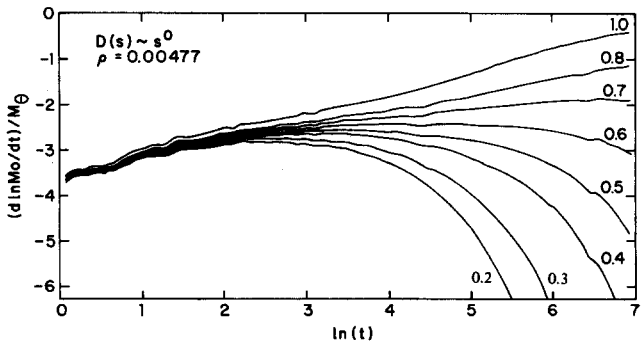

FIG. 7. Plots of $(1/M_\theta)(d \ln M_0/dt)$ vs $\ln t$ for various θ. The prediction of zero slope is confirmed for $\theta \approx 0.65$.

fit by Eq. (11) we consider the explicit behavior of $M_0(T)$. A direct numerical series solution of Eq. (2), for K_{rs} given by Eq. (11), yields

$$\ln [M_0(t)/M_0(0)] = -Kt + 0.242\,17(Kt)^2 - 0.078\,61(Kt)^3 + \ldots , \quad (22)$$

which describes the complete time behavior of M_0 given in Fig. 4(a).

VIII. FURTHER REMARKS AND CONCLUSIONS

Simulations similar to those described above were carried out at several different (larger) particle concentrations. We found that the effective rate constants (K_{rs}) were concentration dependent (particularly for the larger cluster sizes). Most of our simulations were carried out at the lowest practical concentrations. As the particle concentration is lowered, the simulations require more computer time and more simulations must be averaged to reduce statistical fluctuations. A comparison of the results obtained from simulations carried out at several different concentrations indicate that (except for large clusters at long times) our simulations were carried out under conditions which closely approximate the zero concentration limit. We have shown that the mean-field Smoluchowski equation is appropriate for describing the behavior of cluster–cluster aggregation simulations. Since these simulations closely model the essential features of Brownian aggregation, it follows that for that physical problem, the mean-field approach is valid.

We have shown that the kernel K_{rs} follows the prediction of the diffusion equation (6). When $\gamma = 0$ (mass independent diffusion coefficient) $\theta \approx 0.65$ ($D_f \approx 1.5$), slightly higher than expected from measurements of D_f. The overall rate constant K was consistently found to be ≈ 3.0 (lattice spacing)^3/(unit time), a result of the expected order of magnitude, since the for spherical particles in a continuum, $K = 4\pi$.

The short-time enhancement of the aggregation rate was also found to follow the prediction of the diffusion equation. The enhancement for K_{11} did not die out until the later stages of the simulation, while the net enhancement of the overall aggregation rate was of somewhat less duration. To make the time dependence of the coagulation rate less important, lower densities (to allow larger times) should be used, but would lead to a presently impractical amount of computer time. Perhaps this transient behavior can be minimized by making the initial state not completely random, but more like what is approached after aggregation takes place, where the particles are generally far apart (close pairs are less likely).

The asymptotic behavior of the moments is consistent with the expected behavior of K_{rs}; however, it was shown that the asymptotic behavior was only approached near the end of the simulation, so the results were not very clear. The asymptotic behavior is also less sensitive to the details of the kernel; for example, z depends only upon the homogeneity. Thus, the verification of the K_{rs} came from a more detailed study of the kinetics.

In the cases of mass-dependent diffusion coefficient with $\gamma = -1$, the apparent behavior of K_{rs} was found to be consistent with the prediction of Eq. (12). The homogeneity of Eq. (12) is $\theta - 1 \approx -0.3$. The measurement of z by Meakin, Viscek, and Family[5] verify this result, according to Eq. (15). While we did not carry out a detailed analysis of the time behavior in this case, there is every indication that Eq. (2) is well followed.

In closing, we note that while we have shown the mean-field Smoluchowski equation to be appropriate to describe aggregation of particles which form fractal clusters, the actual kernel needed in the equation can only be determined knowing those fractal properties which must be found from a measurement or computer simulation. There is no method of finding the fractal properties from the mean field theory directly. Once these properties are known however, the kernel can be guessed, and the entire description of the kinetics then follows Smoluchowski.

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