Aggregation frequencies of fractal aggregates

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The size-specific coagulation frequencies of fractal aggregates formed by the simulation of diffusion-limited cluster-cluster aggregation in two and three dimensions are determined from dynamic-scaling spectra by an inverse-problem approach. The four cases considered are two- and three-dimensional aggregation in which the cluster diffusivity is independent and dependent upon the mass of the cluster. The frequencies derived from this approach describe the transient simulation results very well, the predictions being better than those with the Smoluchowski Brownian-coagulation frequency [Phys. Z. 17, 557 (1916)] modified by scaling arguments in three dimensions. Furthermore, frequencies are obtained for two-dimensional aggregation for which physical models have been evasive. The validity of the mean-field equation with a time-independent homogeneous frequency is examined. It is found that the mean-field approximation is valid in the range of simulation results but progressively deteriorates with time. The power of the inverse-problem approach here lies in its yielding size-specific aggregation rates of particles whether or not physical models are available.

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I. INTRODUCTION

Aggregation is important in several areas of science and technology. It governs the properties of smoke and haze [1], food [2], emulsion polymerization [3], etc. Recently, experiments [4] and computer simulations [5] have shown that irreversible aggregation processes can lead to the formation of ramified fractal aggregates. In this paper the coagulation frequencies of these fractal clusters produced during computer simulations (the so-called diffusion-limited cluster-cluster aggregation simulations) are determined from the long-time asymptotic behavior of the transient size distributions (the self-similar or dynamic-scaling size spectra). The coagulation frequency is determined for aggregation occurring in two and three dimensions. The determination of the aggregation frequencies for these cases is the primary step in the understanding of the kinetics of these fractal-producing aggregation processes. The techniques for the extraction of coagulation frequencies outlined in this paper can be directly applied to other aggregation processes.

The kinetics of irreversible binary-aggregation processes in a spatially homogeneous medium may be described by [6]

\[
\frac{\partial n(m, t)}{\partial t} = \frac{1}{2} \int_0^m K(m - m', m') n(m - m', m', t) dm' - \int_0^\infty K(m, m') n_2(m, m', t) dm',
\]

where \(n(m, t)\) is the number density of clusters of mass \(m\) at time \(t\) normalized so that

\[
\int_0^\infty mn(m, t) dm = 1.
\]

\(n_2(m, m', t)\) is the joint density of pairs of aggregates of masses \(m\) and \(m'\) at time \(t\) and \(K(m, m')\) is the binary-agglomeration-frequency function. A convenient restatement of the above equation is

\[
\frac{\partial n(m, t)}{\partial t} = \frac{1}{2} \int_0^m K^*(m - m', m', ...) n(m - m', t) \times n(m', t) dm' - \int_0^\infty K^*(m, m', ...) n(m, t) n(m', t) dm',
\]

and

\[
K^*(i, j, ... ) = K(i, j) n_2(i, j, t) / n(i, t) n(j, t) \text{ and } K^* = K \text{ if }
\]

\[
n_2(m, m', t) = n(m, t) n(m', t),
\]

which is the mean-field or superposition closure hypothesis [6]. The dots in the arguments to \(K^*\) represent potential dependence of this effective agglomeration frequency on time or on the state of the entire population and not just on the specific particle pair.

Basically the above closure approximation is tantamount to neglecting any correlations in the pair density \(n_2(m, m', t)\) which may arise either due to slowness of spatial mixing which results in segregational or correlation effects [7] or due to the smallness of cluster populations [8]. The physics of the agglomeration process is embodied in the coagulation frequency function \(K(m, m')\), which depends on the nature of relative motion between the aggregates as well as the details of the reaction cross section. In situations where neither of the above is complicated, coagulation frequencies may be modeled by estimating the flux of particles of a specific mass at a sink particle. A classic example is the Brownian-coagulation frequency derived by Smoluchowski [9]. Coagulation frequencies for other situations have been discussed by several authors [10]. Recent studies, via computer simulation [5] and controlled experiments [4], have shown that...
aggregates formed during irreversible clustering processes are often not compact but rather are self-similar fractals. The complex geometry of these clusters makes an analysis of the anisotropic relative diffusion and the collision cross section difficult and as such the coagulation frequencies of fractal aggregates is largely unknown. Ziff, McGrady, and Meakin [11] have attempted to determine the agglomeration frequencies by observing individual coagulation events in computer simulations of aggregation processes. The same approach has been pursued by Debierre [12] to extract aggregation frequencies of diffusing linear polymer chains. This method is difficult with real agglomerating systems. Moreover, it is difficult to obtain reliable estimates of the frequencies over a large range of cluster sizes.

From a theoretical viewpoint, one may investigate the possibility of modifying the Brownian coagulation frequency of Smoluchowski [9]. For particles diffusing in a d dimensional Euclidean space (d > 2), this frequency is given by

\[ K(m, m') = k(m^{1/d} + m'^{1/d})^{d-2} [D(m) + D(m')], \]

where the first factor pertains to the collision or reaction cross section and the second is the sum of the diffusion coefficients of the two particulates. An intuitive approach employed by Ziff, McGrady, and Meakin [11] to derive an expression for the clustering frequency of self-similar aggregates retains the same structure of the above frequency but accounts for the structure of the aggregates by modifying the reaction cross section. This frequency is given by

\[ K(m, m') = k(m^{1/D_f} + m'^{1/D_f})^{d-2} [D(m) + D(m')] \]

for d > 2, where D_f is the fractal dimension of the clusters. While the ability of this frequency to predict transient spectra remains to be established, there are two main limitations of this approach. First, the diffusivity of anisotropic clusters is difficult to model. Second, calculating the collision cross section of the two clusters by replacing them by spheres of effective radii is only a good approximation if the clusters are of comparable masses. Clearly, when clusters are of very disparate masses, the smaller aggregate can interpenetrate the larger and as such the collision cross section is larger than that obtained by replacing the particulates by effective spheres.

The above discussion calls for an alternate approach to determine the binary-coagulating coefficients. In this paper, we determine coagulation frequencies of fractal aggregates from dynamic-scaling size spectra using an inverse-problem approach [13, 14]. Diffusion-limited cluster-cluster aggregation (CCA) simulations similar to those of other investigators [15] have been performed. The transient size spectra have been observed to exhibit dynamic scaling. These selfsimilar spectra have then been used as input to the inverse problem to derive the binary-coagulation frequency function. The frequencies obtained by the procedure are assessed based on their ability to describe transient size spectra.

II. SIMILARITY AND THE INVERSE PROBLEM

The objective of the inverse-problem approach is to identify the coagulation-frequency function from transient experimental size spectra of agglomerating systems. A detailed description of the approach and procedure is available elsewhere [14, 16]. In this paper we summarize the salient aspects of this methodology, which is applicable whenever the transient size spectra exhibit dynamic scaling or self-similar behavior. Under similarity or dynamic scaling conditions, the size spectra at large times may be conveniently represented by the scaling form

\[ n(m, t) = m^{-\theta} f(m/S(t)), \]

where S(t) is the weight average mass of the population at time t S(t) = \( \int_0^\infty m^2 n(m, t) \) d m; the exponent \( \theta \) has a value two because of mass conservation. Such a scaling behavior is typical of agglomerating systems investigated experimentally [1, 4, 14, 17] and by Monte Carlo simulation of aggregation processes [15]. This dynamic scaling behavior does not depend on the specific form of the initial size distribution and depends only on the nature of the agglomeration frequency. The inverse-problem approach aims at identifying the frequency function by imposing the self-consistency requirement that the agglomeration kernel should predict the observed dynamic scaling when input into the mean-field agglomeration Eq. (1). The inverse problem or self-consistent mean-field approach basically involves deriving an integral equation for the binary agglomeration frequency function in terms of the scaling size spectra by making a similarity transformation of Eq. (2) using Eq. (5).

We rewrite Eq. (2) as

\[ \frac{\partial F(m, t)}{\partial t} = - \int_0^m df'(m', t) \times \int_{-\infty}^\infty dF(m', t) \times K^*(m', m'', ...) / m'', \]

where F(m, t) is the cumulative mass fraction defined by

\[ F(m, t) = \int_0^m m'n(m', t) dm', \]

where mn(t) is the mass fraction density. The number density function has been chosen so that the

\[ \int_0^\infty m'n(m', t) dm' = 1. \]

The similarity transformation given by Eq. (5) implies that the cumulative mass fraction satisfy

\[ F(m, t) \rightarrow f(z), \quad z = m/S(t). \]

On using Eq. (7) in Eq. (6) and requiring similarity, we find that the agglomeration frequency quite generally has the form [14]

\[ K^*(m, m', ...) = S(t)^\lambda b(z, z'). \]

Further, we also obtain equations for the two quantities
specifying the agglomeration frequency, viz. the parameter \( \lambda \) and the bivariate function \( b(z, z') \). The parameter \( \lambda \) governs the growth of the average cluster mass according to

\[
S(t) = [A + (b)(1 - \lambda)]^{1/1-\lambda},
\]

where

\[
(b) = \int_0^\infty \int_0^\infty dx \, dy \, f'(x)f'(y)b(x, y).
\]

It may be readily identified by a fit of the experimental average size data to Eq. (9). Notice that \( b \) is the expected value of scaled aggregation frequency since \( f'(z) \) is a probability density function. The function \( b(z, z') \) is obtained by solving the integral equation

\[
z' f'(z)/b = \int_0^2 dz' \int_{z-z'}^\infty dz'' f'(z')f'(z'')b(z', z'')/z''.
\]

The numerical solution of the above requires regularizing techniques to mitigate the effects of sensitive behavior characteristic of integral equations of the first kind [18].

We now briefly discuss the scope of the methodology. The class of frequencies given by Eq. (8) includes homogeneous agglomeration kernels as a special case for which

\[
K(ax, ay) = a^2 K(x, y) \quad \forall a, x, y > 0.
\]

Such homogeneous frequencies have attracted considerable theoretical interest [3]. More generally, the class of frequencies considered here includes frequencies that may have implicit time dependence through dependence on the number density function [19–21]. Time-dependent frequencies are generally not desirable characterizations of such physical processes, but in the case when self-similarity arises, these frequencies can be easily characterized by a time-invariant function \( b(z, z') \) and the time evolution of the average cluster mass \( S(t) \). The evolution of the average cluster mass \( S(t) \) is characterized by the constants \( \lambda \) and \( b \) and an initial average cluster mass measurement during self-similarity and Eq. (9). Because of this easier characterization of the possible time dependence, the frequency obtained by the inverse problem is strictly valid only during self-similarity (if the obtained frequency shows moment dependence) because all the moments of the size distribution \( n(m, t) \) are related during self-similarity. For example, the real underlying effective frequency may depend on many moments of the size distribution before the development of self-similarity, but during self-similarity this dependence collapses to dependence on a single moment \( S(t) \). This frequency with the single moment dependence is the effective frequency which will be extracted by the inverse problem.

This time dependence could arise due to two reasons. First, the medium in which agglomeration occurs may be externally changed in time. Second and more interestingly, the mean-field assumption may break down. In such cases, the fluctuations in the joint number density of cluster pairs from the mean-field value can be reflected in a time dependent aggregation frequency. The solution from the inverse problem may then be used to define effective binary clustering coefficients denoted by \( K^*(m, m', ...) \) for CCA. The dots represent the potential dependence of this effective frequency on the number density function.

### III. CLUSTER-CLUSTER AGGREGATION SIMULATIONS

Cluster-cluster aggregation has been recognized as an adequate model for describing the formation of several self-similar objects in nature [22] such as silica particles, gold colloids, etc. We outline the interval of quiescence [23] method of simulation and show its equivalence to the method outlined in Ref. [15].

Central to this method is the concept of quiescence interval or waiting time defined as the random time duration between any two successive changes in the state of the system. In this case, a change in the state of the system occurs whenever some cluster moves and hence the quiescence interval is the time between two consecutive cluster jump events. The total transition rate at any instant of time is given by

\[
k = \sum_{i=1}^n D_i,
\]

where \( D_i \) is the diffusivity of cluster \( i \). Hence the probability that the waiting time is less than or equal to \( \Delta t \), \( F(\Delta t) \), is given by

\[
F(\Delta t) = 1 - \exp(-k\Delta t).
\]

The random quiescence time is then given by

\[
\Delta t = -\ln(1 - r_1)/k,
\]

where \( r_1 \) is a random number distributed uniformly over the interval \((0, 1)\). The time is incremented by \( \Delta t \) and the cluster which is moved after generating this waiting time is identified by another random variate \( r_2 \) distributed uniformly on the interval \((0, 1)\). Cluster \( j \) is moved if

\[
\frac{\sum_{i=1}^{j-1} D_i}{k} < r_2 \leq \frac{\sum_{i=1}^{j} D_i}{k}.
\]

The rest of the procedure is identical to that employed by other investigators [15]. The problem with this simulation strategy is the determination of which cluster is to move in a computationally slow procedure. Meakin [15] developed an equivalent simulation by discretizing time in smaller intervals than the interval of quiescence.

Basically the equivalent procedure developed by Meakin which is used for our simulations begins by randomly sprinkling a fixed number of monomers on a lattice with periodic boundary conditions. Attempts are made to move clusters after every time interval \( \Delta t = D_{\text{max}}N^{-1} \), where \( D_{\text{max}} \) is the maximum of mass-dependent diffusion coefficients of the \( N \) clusters present at any time. This is achieved by picking a cluster at random and moving it in randomly in one of the possible
directions if a random number \( r \) drawn from a uniform distribution on the unit interval satisfies the condition \( 0 < r < D/D_{\text{max}} \), where \( D \) is diffusivity of the chosen cluster. Subsequently, this cluster is examined for possible contacts with other clusters and the number of clusters \( N \) and cluster sizes are updated if such contacts occur. In this procedure time is measured in units of attempted moves per cluster.

All systems considered in this paper are very dilute. Simulations in two and three dimensions were performed on lattices of length scales \( L \) equal to 400 and 133, respectively. The initial number of monomers was 8000 in all cases. This corresponds to an occupation fraction of 0.08 and 0.0034 in two and three dimensions, respectively. Typically 100–300 sample pathways were used to obtain the size spectra at different times.

IV. AGGREGATION FREQUENCIES FROM INVERSE PROBLEM

The aggregation frequencies of diffusion-limited aggregation for four different cases were determined via the inverse-problem procedure outlined in Sec. II. The four cases of interest are (a) aggregation in two dimensions with mass-independent diffusivity, (b) aggregation in two dimensions with mass-dependent diffusivity, (c) aggregation in three dimensions with mass-independent diffusivity, and (d) aggregation in three dimensions with mass-dependent diffusivity. Mass-independent diffusivity is, of course, not realistic, but it is computationally simple to implement since all clusters have equal probability to move.

A. Two-dimensional

aggregation-mass-independent diffusivity

As alluded to by Eq. (3), Smoluchowski's approach for modeling the aggregation frequency does not apply in two dimensions and therefore the intuitive approach given by Eq. (4) is not useful. It has generally been believed that \( d = 2 \) is the upper critical dimension \( d_c \) for irreversible aggregation [7] (although some [24] believe that \( d_c \geq 2 \)). For \( d > d_c \) the mean-field description given by Eq. (2) with a time-independent frequency is valid for all times, whereas for \( d < d_c \) behavior different than that predicted by Eq. (2) with a time-independent frequency can be expected. Since \( d_c \geq 2 \), the effective frequency \( K^* \) determined by the inverse problem can be tested for implicit time dependence that would be an indicator that the closure hypothesis given by Eq. (1) is not valid. Wright and Ramkrishna [25] show that the upper critical dimension is not necessarily a useful concept when determining the validity of Eq. (1). They indicate that the expected number of clusters within a cell volume (the cell size is determined by the distance traveled by the slowest particles within the observation time scale and which may change with time) is the important parameter for the determination of the validity of Eq. (1). As the expected number of particles in a cell increases the validity of Eq. (1) increases.

The extracted agglomeration frequency can be examined for implicit time dependence through dependence on a moment of the distribution. If significant time dependence is observed, then we can conclude that the expected number of clusters in the cell is small and thus we are in the regime where Eq. (1) is not a useful approximation. This indicates the advantage of an inverse-problem approach for extracting this kinetic coefficient. The inverse-problem procedure extracts an effective aggregation frequency regardless of the validity of the mean-field closure approximation.

The transient size distributions obtained from the computer simulations are shown in Fig. 1(a). Figure 1(b) shows the self-similar size distribution obtained at large times. The inverse-problem approach outlined in Sec. II can be used to obtain the effective aggregation frequency. The evolution of the average cluster mass is given by Eq. (9) where \( b = 4.787 \times 10^{-2} \) and \( \lambda = 0.43 \). Figure 1(c) shows the function \( b(z, y) \) determined via the inverse problem. The qualitative features of the extracted frequency can easily be seen. The agglomeration frequency increases as either particle mass increases which reflects (i) the increase in the collision cross section available for aggregation as either particle mass increases, and (ii) the diffusion mechanism put into the computer simulations. Consider the agglomeration frequency in more detail. Let us look at the agglomeration frequency of a large particle (say \( z = 1 \)) with particles of varying mass. As the mass of the second particle increases from very small to about the same mass as the first particle, the agglomeration frequency remains approximately constant or increases slightly. This means that for an approximately constant collision cross section the agglomeration frequency is approximately constant. Thus the relative motion of the cluster is not affected by cluster mass, i.e., cluster diffusivity is constant.

The veracity of this determined frequency can be assessed based on its ability to predict transient size distributions. Figure 2 shows the predictions of the extracted frequency compared with the simulation results. The earliest time in Fig. 2 is used as the initial condition to the population balance equation [Eq. (2)] to predict the later size distributions. The obtained frequency predicts the distribution at the later times very well. Therefore this effective aggregation frequency can serve as a good characterization for two-dimensional diffusion-limited cluster-cluster aggregation after the transient size distribution has reached the self-similar distribution. The question on implicit time dependence will be answered in Sec. V.

B. Two-dimensional

aggregation-mass-dependent diffusivity

For this case, identical simulations were performed as previously done with the exception that the cluster diffusivity was made to depend on the cluster mass \( k \) as \( D_k = k^{-0.6944} \). The fractal dimension \( D_f \) for these clusters is approximately 1.44. The mass dependence of the cluster diffusivity was chosen so that \( D_k = k^{1/D_f} \). The transient size distributions for three times can be seen in
Fig. 1. Aggregation in two dimensions with mass-independent diffusivities. (a) Transient size spectra. (b) Scaling spectrum. (c) Function $b(z, z')$ from solution of inverse problem.

Fig. 2. Test of frequency derived from inverse problem. The simulation data are shown as points and the solution of the Smoluchowski equation using the inverse-problem frequency is shown by the solid lines. The data at the earliest time were used as the initial condition.

Fig. 3(a). The self-similar size distribution that is used by the inverse problem can be seen in Fig. 3(b). The evolution of the average size is given by Eq. (9) with $(b) = 6.215 \times 10^{-2}$ and $\lambda = -0.27$.

The extracted frequency can be seen in Fig. 3(c). The qualitative features of this extracted frequency can again easily be interpreted. Let us fix one of the particles to be very small (say $x \sim 0$) and let the mass of the other particle increase ($y \sim 0^+$). This represents the case where the particle pair diffusivity is approximately constant (the particle pair diffusivity is dominated by the small particle). The agglomeration frequency increases with increasing mass of the second particle which indicates that once again the collision cross section increases with increasing mass. If we fix the first particle at some large value (say $x = 1$) and increase the mass of the second particle ($y \sim 0^+$), the agglomeration frequency decreases precipitously. This indicates that for an approximately constant collision cross section the agglomeration frequency decreases. This is again an indication of the diffusion mechanism input to the computer simulation, i.e., diffusivities decrease with increasing particle mass.

The veracity of the extracted frequency can be determined based on its ability to predict the transient size distributions. Figure 4 shows the predictions of population balance equation with the extracted agglomeration frequency. The earliest time in the figure is used as the initial condition to predict the later time distributions. The predictions of the extracted frequency mimic the actual transient size distributions.

**C. Three-dimensional aggregation-mass-independent diffusivity**

Figure 5(a) shows the transient size distributions from Monte Carlo simulations of aggregation and the self-
similar size spectrum is depicted in Fig. 5(b). The parameter \( \lambda \) required to specify the aggregation frequency was obtained by fitting Eq. (9) to average mass \( S(t) \).

\[ \lambda = 0.59 \quad \text{and} \quad \langle b \rangle = 1.77 \times 10^{-2}. \]

The inverse-problem solution \( b(z, z') \) is shown in Fig. 5(c). The veracity of the frequency thus determined was evaluated by its ability to predict transient size spectra when used in Eq. (2). The data at the earliest time at which similarity behavior is observed were used as the initial condition. It is evident from Fig. 6 that the frequency predicts the data very well indeed.

Once again the qualitative features of the extracted frequency can be interpreted. The collision cross section increases with increasing particle mass as expected. The observation that large clusters agglomerate slightly better with clusters of increasing mass is indicative of the input diffusion mechanism.

D. Three-dimensional aggregation-mass-dependent diffusivity

In this case the particle diffusivity is assumed to depend on its mass as \( D_k = k^{-1/3} \), where \( D_f = 1.78 \) [22]. The transient size distributions can be found in Fig. 7(a). The similarity transformation is found in Fig. 7(b). The evolution of the average cluster mass is given by the evolution equation where \( \langle b \rangle = 1.80 \times 10^{-2} \) and \( \lambda = 0.05 \). The extracted frequency can be seen in Fig. 7(c). Figure 8 shows the predictions of the transient size distributions for the extracted frequency. The behavior of the aggregation frequency for fixed collision cross section \( y \sim 1, x \ll y \) decreases precipitously because of the mass dependence of the diffusion coefficient.
In this section, the extracted agglomeration frequencies will be approximated by suitable homogeneous functions for comparison with frequencies determined by other methods. First let the scaled aggregation frequency $b(x, y)$ have the following property:

$$b(x, y) = b(x^\mu y^\nu)$$  \hspace{1cm} (14)

for $y$ much greater than $x$. Also since we are approximating the extracted $b$ by a homogeneous function, we have

$$b(ax, ay) = a^{\mu+\nu} b(x, y).$$  \hspace{1cm} (15)

The asymptotic behavior of the self-similar size distributions near the origin (small $z$) from such frequencies have been examined [26, 16]. Only the general conclusions that aid our identification will be stated here. If $\mu < 0$, then the self-similar size distribution $f'(z)/z$ falls off exponentially fast to the origin as $z$ approaches zero. If $\mu \geq 0$, then the similarity distribution $f'(z)/z$ will become large as $z$ approaches zero. If $\mu > 0$, then the degree of singularity $\tau$ of the similarity distribution is

$$\tau = 1 + \mu + \nu. \hspace{1cm} (16)$$

If $\mu = 0$ then $\tau$ is a function of $\nu$ and $b$.

For two-dimensional aggregation with mass-independent diffusivities, the similarity distribution is singular with $\tau = 0.623$. From Fig. 1(c) it is clear that for one particle of small $z$ the agglomeration frequency increases for particles of increasing mass then $\nu \geq 0$ thus $\mu = 0$. The parameter $\nu$ can be determined by fitting the inverse problem result $b(0, y)$ vs $y$. The result is $\nu = 0.43$ and thus the degree of homogeneity ($\mu + \nu = 0.43$) in agree-
FIG. 7. Aggregation in three dimensions with mass-dependent diffusivities. (a) Transient size spectra. (b) Scaling spectrum. (c) Function $b(x, z')$ from solution of inverse problem.

FIG. 8. Test of frequency derived from inverse problem. The simulation data are shown as points and the solution of the Smoluchowski equation using the inverse problem frequency is shown by the solid lines. The data at the earliest time were used as the initial condition.

ment with the $\lambda$ determined from the evolution of the average cluster mass. An additional estimate of $\nu + \mu$ can be determined from fitting $b(y, y)$ vs $y$ (from the homogeneity relationship). In this case $\nu + \mu = 0.45$. Since $\lambda$ from the $S(t)$ evolution and $\mu + \nu$ determined from the inverse problem are the same, the aggregation frequency does not depend implicitly or explicitly on time. The simplest homogeneous frequency that has $\mu = 0$ and $\nu = 0.43$ is

$$b(x, y) = \bar{b}(x^{0.43} + y^{0.43}).$$

(17)

$\bar{b}$ can be determined by placing the above form of the aggregation frequency into Eq. (10); $\bar{b}$ was determined to be $4.759 \times 10^{-2}$. The usefulness of this homogeneous approximation can be evaluated based on the predictions of the transient size distributions from the aggregation frequency. These predictions can be seen in Fig. 9. This homogeneous frequency predicts the transient size distributions well. Therefore we can say that the aggregation frequency for this case is

$$K(m, m') = 4.759 \times 10^{-2} (m^{0.43} + m'^{0.43}).$$

(18)

Note that the number 0.43 is approximately equal to $1 - d - D_f$.

For two-dimensional aggregation with mass-dependent diffusivities a homogeneous approximation can also be found. The exponent $\mu$ must be less than zero since the $f'(z)/z$ falls to the origin as $z$ approaches zero. To determine the parameter $\mu$ let us look at the extracted frequency. Fix $y = 1$, fit $b(x, 1)$ vs $x$. As $x$ increases, $b(x, 1)$ decreases, giving a value of $\mu = -0.70$. We can fix $x = 0.05$ and fit $b(0.05, y)$ vs $y$ to determine $\nu$, which is estimated to be $\nu = 0.46$. The diagonal elements of $b(x, y)$ give an estimate of $\mu + \nu = -0.27$. These results and the previous case results intimate the form of $b(x, y)$ to be
\begin{equation}
b(x, y) = \bar{b}(x^{0.43} + y^{0.43})(x^{-0.70} + y^{-0.70}).
\end{equation}
\(\bar{b}\) was determined in a similar manner as the previous case. \(\bar{b} = 1.46 \times 10^{-2}\). The predictions of this frequency are shown in Fig. 10. The homogeneous approximation for the aggregation frequency is
\begin{equation}
K(m, m') = 1.46 \times 10^{-2}(m^{0.43} + m^{0.43}) \\
\times (m^{-1/D_1} + m'^{-1/D_1}).
\end{equation}

For three-dimensional aggregation with mass-independent diffusivities the similarity distribution is singular at the origin indicating that \(\mu = 0\). The degree of singularity \(\tau = 1.16\). For a fixed small value of \(x\), \(\nu\) is determined to be \(\nu = 0.59\), which indicates that \(\mu = 0\). The diagonal elements of \(b(x, y)\) give an estimate of \(\mu + \nu = 0.62\).

The simplest homogeneous function that matches these parameters is
\begin{equation}
b(x, y) = \bar{b}(x^{0.59} + y^{0.59}).
\end{equation}
\(\bar{b}\) was determined as before to be \(\bar{b} = 9.66 \times 10^{-3}\). The predictions of this frequency are shown in Fig. 11. Since this is a homogeneous frequency
\begin{equation}
K(m, m') = 9.66 \times 10^{-3}(m^{0.59} + m^{0.59}).
\end{equation}
The similarity distribution \(f'(z)/z\) falls to the origin as \(z\) approaches zero; therefore \(\mu < 0\) for three-dimensional aggregation with mass-dependent diffusivities. For fixed large \(y\), \(b(x, y)\) vs \(x\) gives an estimate of \(\mu = -0.545\). For fixed small \(x\), \(b(x, y)\) vs \(y\) gives \(\nu = 0.62\). \(b(x, x)\) vs \(x\) gives an estimate of \(\mu + \nu = 0.05\). The homogeneous

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig9}
\caption{Test of homogeneous approximation of extracted frequency for the two-dimensional aggregation with mass-independent diffusivities [Eq. (17)].}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig10}
\caption{Test of homogeneous approximation of extracted frequency for the two-dimensional aggregation with mass-dependent diffusivities [Eq. (19)].}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig11}
\caption{Test of homogeneous approximation of extracted frequency for the three-dimensional aggregation with mass-independent diffusivities [Eq. (21)].}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig12}
\caption{Test of homogeneous approximation of extracted frequency for the three-dimensional aggregation with mass-dependent diffusivities [Eq. (23)].}
\end{figure}
approximation is
\[ b(x, y) = \bar{b}(x^{0.59} + y^{0.59})(x^{-0.54} + y^{-0.54}). \]  
(23)

\( \bar{b} \) was determined to be \( 4.10 \times 10^{-3} \). Figure 12 shows that this frequency adequately predicts the transient size distributions. Since \( \mu + \nu = \lambda \), the aggregation frequency may be written as
\[ K(m, m') = 4.10 \times 10^{-3}(m^{0.59} + m'^{0.59}) \times (m^{-0.54} + m'^{-0.54}). \]  
(24)

In summary, the aggregation frequency in two dimensions can be written as
\[ K(m, m') = k(m^{0.43} + m'^{0.43})[D(m) + D(m')], \]  
(25)

where the premultiplicative constant \( k \) is a function of the diffusion mechanism. In three dimensions,
\[ K(m, m') = k(m^{0.59} + m'^{0.59})[D(m) + D(m')], \]  
(26)

where again the premultiplicative constant is a function of the diffusion mechanism.

VI. COMPARISON OF RESULTS WITH LITERATURE

Ziff [27] approximates the aggregation frequency for size-independent diffusivity in two dimensions to be a constant. Our simulation results do not support this claim. A constant frequency cannot describe the singularity of the similarity size spectrum \( f'(z)/z \) seen in the simulations. Also, a constant \( K(m, m') \) predicts \( S(t) \) would grow linearly with time; instead we see that \( S(t)^{0.57} \) grows linearly with time. Also the homogeneous approximation for this case shows that the frequency is a monotonically increasing function as the mass of either particle increases.

In three dimensions, Ziff, McGrady, and Meakin [11] give a model frequency based upon Smoluchowki's arguments:
\[ K(m, m') = c(m^{1/D_f} + m'^{1/D_f})[D(m) + D(m')]. \]  
(27)

If we use the premultiplicative constant suggested by Ziff, McGrady, and Meakin, then the prediction of transient size distributions is possible. Figure 13 shows the predictions of this model frequency for mass-independent diffusion and Fig. 14 shows the predictions for mass-dependent diffusivities. As can be seen, the homogeneous approximations given in Sec. V predict the transient size distributions with greater accuracy. It should be noted, however, that Ziff, McGrady, and Meakin also determined the aggregation frequency via counting agglomeration events. In that case, the determined frequency was identical to Eq. (27) with the exponent \( 1/D_f \) replaced by 0.6, which is closer to our exponent value of 0.59.

VII. VALIDITY OF MEAN-FIELD APPROXIMATION

The expected number of clusters in a cell is the important parameter in determining the validity of the mean-field or superposition closure hypothesis [25]. As the expected number \( \langle N \rangle \) increases the validity of the approximation increases and thus as \( \langle N \rangle \) decreases the validity decreases. Reference [25] gives an expression for \( \langle N \rangle \) as a function of diffusion mechanism \( \alpha \) and the various agglomeration parameters \( \tau, \lambda, \) and \( \bar{b} \):
\[ \langle N \rangle = B \left( \frac{D}{\bar{b}} \right)^{d/(d+2)} S(t)^x(d), \]  
(28)

where \( B \) is a constant, \( D \) is the base diffusion coefficient, and
\[ x(d) = \frac{d}{d+2} \left( 1 - \alpha - \frac{2}{d} \right) \]  
(29)
if $\tau < 1$ or

$$\chi(d) = \frac{d}{d + 2} \left( 1 - \alpha - \lambda - \frac{2(2 - \tau)}{d} \right)$$ (30)

if $\tau \geq 1$. Obviously, if $\chi(d)$ is negative, the expected number of clusters in a cell decreases and the closure assumption worsens. $\chi$ can be calculated for the four cases considered above. For two-dimensional aggregation $\chi = -0.215$ and $-0.212$ for mass-independent and mass-dependent diffusivities, respectively. For three-dimensional aggregation $\chi(d) = -0.089$ and $-0.167$ for mass-independent and mass-dependent diffusion, respectively. Since all the $\chi$'s are negative, we can expect that from an uncorrelated initial condition, after a sufficient time, the mean-field approximation will break down. We noticed from Sec. VI that the aggregation frequency determined via the inverse problem could be approximated by homogeneous functions with degrees of homogeneity equal to the $S(t)$ growth exponent $\lambda$. This fact indicates that no significant time dependence of the aggregation frequency was observed. Our simulations have not yet reached the region where the mean-field equation will falter. If we look at the range of $S(t)$ in the simulations presented above, we see that the average cluster mass grows to about 250 at the largest. If we determine the ratio of the initial expected number of clusters in a cell to the final number of clusters in a cell we see that the maximum ratio is 3.2. This relatively small decrease in the expected number of clusters in a cell occurs even though massive agglomeration has taken place. Evidently, from our initial conditions a threefold decrease in the expected number of particles in a cell does not yet make correlations between particles important.

VIII. SUMMARY

Binary-aggregation frequencies of fractal aggregates formed in irreversible coagulation processes are difficult to model due to anisotropic diffusion of clusters and the complicated collision cross sections. An added difficulty for aggregation on surfaces is the possibility of spatial correlations in particle pair densities leading to break down of the mean-field approximation. In this paper, aggregation frequencies of fractal clusters formed during computer simulations of diffusion limited CCA have been determined by an inverse problem approach. This approach makes the mean-field model of coagulation kinetics self-consistent by giving a prescription to determine the binary-aggregation coefficients from asymptotic dynamic-scaling size spectra. The dynamic-scaling behavior is independent of the initial size distribution at the onset of the agglomeration process and should reflect then the properties of the aggregation frequency.

Spatial simulations of diffusion-limited CCA have been performed in two and three dimensions using mass-independent and mass-dependent diffusivities. The transient size spectra have been shown to exhibit self-similar behavior. The dynamic scaling spectra have been used to identify aggregation coefficients via the inverse problem approach expounded in Sec. II. The basic qualitative results are that the aggregation cross section increases with increasing mass of either particle in two and three dimensions. Quantitatively, the aggregation frequency can be approximated as

$$K(m, m') = k(m^\beta + m'^\beta)[D(m) + D(m')]$$

where the premultiplicative constant is a function of the spatial dimension and the diffusion mechanism. $\beta = 0.43$ in two dimensions and 0.59 in three dimensions.

It was also found that the mean-field or superposition closure hypothesis is valid over the range of the simulation results. However, it is shown that the validity of the approximation is decreasing with time, but at a fairly slow rate.

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AGGREGATION FREQUENCIES OF FRACTAL AGGREGATES


[19] For example, Wang and Friedlander (see Refs. [20, 21]) determined an analytic self-similar size distribution for one moment-dependent coagulation frequency. They [22] also proposed that Brownian coagulation in a shear flow field could show self-similar behavior if the mean free path showed a certain moment dependence. Kang and Redner [7] proposed a time-dependent effective agglomeration frequency for $d < 2$, but then indicated that their agglomeration simulations did not show that behavior. Wright et al. [14] numerically solved Eq. (2) for various moment-dependent coagulation frequencies and found that they could indeed yield self-similar behavior.


FIG. 1. Aggregation in two dimensions with mass-independent diffusivities. (a) Transient size spectra. (b) Scaling spectrum. (c) Function $b(z, z')$ from solution of inverse problem.
FIG. 3. Aggregation in two dimensions with mass-dependent diffusivities. (a) Transient size spectra. (b) Scaling spectrum. (c) Function $b(z, z')$ from solution of inverse problem.
FIG. 5. Aggregation in three dimensions with mass independent diffusivities. (a) Transient size spectra. (b) Scaling spectrum. (c) Function $b(z, z')$ from solution of inverse problem.
FIG. 7. Aggregation in three dimensions with mass dependent diffusivities. (a) Transient size spectra. (b) Scaling spectrum. (c) Function $b(z, z')$ from solution of inverse problem.