Fractal Dimensions of Aggregates Determined from Steady-State Size Distributions

Qing Jiang and Bruce E. Logan*

Environmental Engineering Program, Department of Civil Engineering, University of Arizona, Tucson, Arizona 85721

Aggregates formed by Brownian motion, shear coagulation, and differential sedimentation have fractal geometries. In order to model coagulation of fractal aggregates, we have derived a set of collision functions containing a fractal dimension for use in a general coagulation equation. These collision functions predict greater collision frequencies than models based on aggregates with Euclidean properties. Assuming only one mechanism of aggregate formation is dominant for a range of particle sizes, we also incorporated a fractal dimension in a dimensional analysis of steady-state particle-size distributions. Using particle-size distributions observed in marine systems, we calculated that aggregates formed by shear coagulation had fractal dimensions greater than 2.4, whereas aggregates formed from differential sedimentation had lower fractal dimensions in the range of 1.6–2.3. Reported fractal dimensions for many biological aggregates from bioreactors and marine systems are in the range expected for differential sedimentation. Fractal dimensions of inorganic colloidal aggregates are in the range expected for aggregation by Brownian motion and shear coagulation.

Introduction

Recent studies indicate coagulation can be an important mechanism of particle removal in lakes (1, 2) and oceans (3). In freshwater systems, collision efficiencies are low (≈0.001–0.1), and coagulation is strongly influenced by surface chemistry of the particles (4). In marine systems, large aggregates have been shown to have high sticking efficiencies (5). In the deep ocean, McCave (6, 7) predicted that low particle concentrations would result in slow coagulation rates except under specific conditions where particle concentrations are much higher, such as benthic boundary layers and near ocean outfalls (8, 9). Algal blooms have also been observed to rapidly flocculate forming large amorphous aggregates up to 20 mm in size (10). A coagulation model developed by Jackson (3) was used to show that diatom aggregates can be formed by shear and differential sedimentation, but he hypothesized that these types of aggregates are only formed in the absence of grazing. Aggregates can also be produced in the ocean from feeding webs and other material produced by small animals, such as fecal pellets (10).

Coagulation has been modeled through two approaches: by solving a general dynamic equation describing coagulation or by developing solutions for coagulation based on a dimensional analysis. A simplified equation for coagulation by the first approach (11) is

\[
\frac{dn(v)}{dt} = \frac{1}{2} \int_0^v \beta(\bar{v}, v) n(\bar{v}) n(v-\bar{v}) \, d\bar{v} - \int_0^v \beta(v, \bar{v}) n(v) n(\bar{v}) \, d\bar{v}
\]

where \( n(v) \, dv \) is the number concentration of flocs in the volume interval \( v \) to \( v + dv \). The first term on the right-hand side of the equation describes coagulation of similar flocs to form flocs of size \( v \), and the second term represents the loss of flocs of volume \( v \) through collision with other flocs. Numerical solutions have been provided by several researchers for hydrosol dynamics (12, 13), but none of these solutions have been verified with experimental data.

A second approach to describe particle sizes during coagulation was used by Hunt (8, 14) and McCave (6, 7). This approach is based on a dimensional analysis of particle-size distributions and requires four assumptions: (1) floc-size distributions are in a steady state, with a constant source of particles, which coagulate through the size distribution to form aggregates that are removed through sedimentation; (2) only one coagulation mechanism (Brownian, fluid shear, differential settling) is dominant at a given particle size; (3) particle sticking efficiency is constant and independent of particle size; (4) each mechanism can be characterized by a single parameter. Theoretical predictions were verified by analyzing particle-size distributions of clay particles (<2 μm) undergoing Brownian and shear coagulation in seawater (8) and compared with marine particle-size distributions (14).

The premise of both coagulation models is that aggregates formed during coagulation are composed of particles evenly spaced and uniformly distributed in spherical aggregates. However, it is now known that aggregates formed by Brownian motion have fractal structures (15–18). Therefore, the density of fractal aggregates is not constant, and the properties of fractal aggregates, such as mass and encased volume, do not dimensionally scale according to the mathematics of Euclidean geometry. For example, the number of particles, \( N \), in an aggregate of uniformly distributed spherical monomers (19) is

\[
N = \left( \frac{\xi}{\xi_0} \right)^3 \left( \frac{d}{d_0} \right)^3
\]

where the superscript \( * \) is used to denote variables based on Euclidean geometry, \( \xi \) is a packing factor, \( d \) is the aggregate diameter, \( d_0 \) is the diameter of primary particles composing the aggregate, and \( \xi \) and \( \xi_0 \) are shape factors of the aggregate and primary particles. An analogous expression for the number of particles in an aggregate for fractal aggregates cannot be directly developed, since for a fractal aggregate

\[
N = \xi^{D/3} \left( \frac{l}{l_0} \right)^D
\]

where \( \psi = \xi / \xi_0 \), \( l \) is the characteristic length of a fractal aggregate, here defined as the longest aggregate length, \( l_0 \) is the length of primary particles in the aggregate, and \( D \) is the fractal dimension. Comparison of eqs 2 and 4 shows that \( D = 3 \) for Euclidean objects. However, aggregates formed from metal colloids, soot, aerosols, silica, and polystyrene (18, 20) have fractal, or noninteger, dimensions significantly less than 3.

Since aggregates are fractal and have nonuniform properties, both of the above coagulation theories need to be revised to include the fractal geometry of the aggregates. In this paper we derive a set of collision frequency func-
tions that incorporate fractal dimensions of aggregates and show that collision rates for fractal aggregates are greater than rates for Euclidean aggregates. We also demonstrate that fractal dimensions affect steady-state size distributions in marine systems.

Methods

Characteristics of Fractal Aggregates. In order to describe coagulation by use of fractal geometry, the properties of the fractal aggregates must be cast in terms of fractal dimensions. These properties, such as mass, volume, density, porosity, and settling velocity affect particle collisions and, therefore, coagulation rate. Below, we derive equations for fractal aggregates based on relationships used for Euclidean objects.

(a) Aggregate Mass. If we assume that aggregates are composed of spherical particles with diameter \(d_o\) and density \(\rho_o\), the mass of each primary particle, \(m_o\), is

\[
m_o = \rho_o d_o^3
\]

The mass of an aggregate, \(m\), is the product of the number and mass of primary particles or, for a Euclidean aggregate, is

\[
m = \rho_o d^3
\]

For a fractal aggregate, we define the mass of the primary particle as

\[
m_o = \rho_o d_o^3
\]

Combining eqs 4 and 7, we obtain for fractal aggregates

\[
m = \rho_o \rho D^3 \xi d_D^3
\]

(b) Aggregate Volume. The volume of an aggregate can be defined in two ways: as an encased volume or as an occupied or solid volume. According to the first definition, the volume of an aggregate is calculated as the spherical volume that encases the aggregate, or \(\frac{d}{\xi}d_o^3\). For a fractal aggregate, we can similarly calculate this volume substituting \(d\) for \(d_o\), or

\[
v_o = \frac{d}{\xi}d_D^3
\]

The solid volume of the aggregate, \(v_o\), is calculated as the total volume occupied by all primary particles in the aggregate. The difference between the encased volume, \(v_o\), and the solid volume, \(v\), is that the former includes both the volume of particles and the volume of the pores. The solid volume for a fractal aggregate is related to its mass by \(m = \rho_o v_o\), or by using eq 8

\[
v = \rho_o \frac{D^3 \xi d_D^3}{(1/\xi)^{D-3}}
\]

As eq 10 shows, \(v\) does not scale to an integer power of 3, as assumed in previous models (8, 14). These changes affect the relationships between aggregate characteristics such as density, porosity, and settling velocity.

(c) Aggregate Density. The density of an aggregate is defined as the total mass of primary particles in the aggregate per encased volume, or \(\rho = m/v_o\) for Euclidean aggregates, and \(\rho = m/v\) for fractal aggregates. Using this definition and eq 8, the fractal density, \(\rho\), is

\[
\rho = \rho_o \rho O \frac{D^3 \xi d_D^3}{(1/\xi)^{D-3}}
\]

Since density is a function of aggregate size, and usually decreases with the size of the aggregate, the collision of two aggregates produces an aggregate of a larger encased volume than the sum of two original aggregate volumes.

(d) Aggregate Porosity. The porosity of a fractal aggregate, \(\epsilon\), can be expressed in terms of the encased and solid volume as

\[
\epsilon = 1 - \frac{v}{v_o}
\]

From the definition of \(v\) and \(v_o\), eq 12 becomes

\[
\epsilon = 1 - \frac{\rho D^3 (\xi d_D^3 (1/\xi)^{D-3}}{\rho O}
\]

(e) Settling Velocity. Relationships to describe the settling velocity of impermeable spheres are based on a force balance on a settling aggregate (21), or

\[
U(\rho_o - \rho_w)g = \frac{1}{2} A \rho_o d_D U^2
\]

where \(\rho_o\) is the bulk aggregate density, which includes the mass of both primary particles and liquid in the encased aggregate volume, \(\rho_w\) is the fluid density, \(g\) is the gravitational constant, \(A\) is the projected surface area of the aggregate perpendicular to the direction of settling, \(C_D\) is a drag coefficient, and \(U\) is the aggregate settling velocity. The bulk aggregate density can be obtained from the identity

\[
(\rho_o - \rho_w) = (1 - \epsilon)(\rho_o - \rho_w)
\]

which is valid for either fractal or Euclidean objects. In order to specify a similar relationship for the settling velocity of fractal aggregates, three assumptions are necessary. First, on the basis of the analysis contained in Logan and Hunt (22), it is assumed that the advective flow through the highly porous aggregate does not significantly affect settling velocity. Second, the projected surface area is assumed to be a function of an additional fractal dimension defined as

\[
A = \xi d_D^3 (1/\xi)^D
\]

where \(\xi\) is the shape factor and \(D_2\) is the fractal dimension that relate aggregate size to projected area in two dimensions. The area defined by the two-dimensional fractal dimension, \(D_2\), is not equal to an encased area, \(A_o\), for the same reasons that the fractal volume is not equal to the encased volume. Third, the empirical expression for the drag coefficient for spheres (23)

\[
C_D = \frac{24}{Re} + \frac{6}{(1 + \sqrt{Re})} + 0.4
\]

where the Reynolds number, \(Re = U d/\nu\), is assumed valid for fractal aggregates, and \(\nu\) is the fluid kinematic viscosity. An analysis by Aldredge and Gotschalk (10) on marine snow aggregates, which are known to be fractal (24), suggests that the above empirical drag coefficient does not accurately predict settling velocities at larger Reynolds numbers (Re > 1). However, Aldredge and Gotschalk were unable to derive a more accurate expression. In order to use this expression in the current scaling relationships, we approximate the drag coefficient in eq 17 as a power law function in terms of a Reynolds number (Re = U/l/\nu) for a fractal aggregate as

\[
C_D = aRe^b
\]

where \(a\) and \(b\) are determined for different ranges of Reynolds numbers from eq 17. For Re < 0.1, \(a = 24.0\) and \(b = 1.0\); for 0.1 < Re < 10, \(a = 29.03\) and \(b = 0.871\); and for 10 < Re < 100, \(a = 14.15\) and \(b = 0.547\). As shown in Figure 1, the power law function is within 10% of values calculated from eq 17.

Substituting eqs 10, 16, and 18 into an analogous expression of eq 14, we obtain for fractal aggregates

\[
U = \left[ \frac{2\xi d_D (\rho_o - \rho_w) \rho O \rho O \xi d_D^3 (1/\xi)^D d_D^2}{\rho_9 d_D^2 \rho O + \rho_9 d_D^2 \rho O \rho O \xi d_D^3 (1/\xi)^D d_D^2} \right]^{1/(2-b)}
\]

If the aggregate is Euclidean, i.e., a sphere with \(D = 3\), and \(Re << 1\), eq 19 reduces to Stokes law. For fractal aggregates, \(D_2\) must be less than or equal to 2. As discussed by
Meakin (17), if \( D \) is less than 2, then \( D_2 = D \); when \( D \) is greater than 2, \( D_2 = 2 \).

**Collision Frequency Functions.** Coagulation of particles occurs by three coagulation mechanisms: Brownian motion, shear and differential sedimentation. Collision frequency functions for fractal aggregates can be derived for each coagulation mechanism by using size-volume relationships. In this analysis, we assume that collision frequency functions, expressed as a function of the size of the aggregate, are valid for fractal aggregates of size \( l \) or Euclidean aggregates of size \( d \). Therefore, the collision frequency functions for fractal aggregates can be written by replacing aggregate diameter, \( d \), with the aggregate length, \( l \).

The collision frequency function for Brownian motion, \( \beta_B \), based on Smoluchowski's equation and Einstein's relationship, is

\[
\beta_B(l, l) = \frac{(2kT/3\mu)(l + l)^2}{(l + l)^3}
\]

where \( k \) is the Boltzmann constant, \( T \) is absolute temperature, and \( \mu \) is the fluid viscosity.

The collision frequency for shear coagulation \( (11) \) is

\[
\beta_{sh}(l, l) = \frac{(G/6)(l + l)^3}{(l + l)^3}
\]

where \( G \) is the shear fluid rate.

The third coagulation mechanism, differential sedimentation, occurs when a faster settling floc overtakes and collides with a slower settling floc. The collision frequency for differential sedimentation is the collision cross section times the difference in the floc settling velocities, assuming a constant floc density

\[
\beta_d(d, d) = \frac{4}{25}\left[(d + d)^2 - (d + d)^2\right]
\]

For fractal aggregates, we use the settling velocity in eq 19 and replace the aggregate diameter with the aggregate length, \( l \), to obtain

\[
\beta_d(l, l) = \frac{4}{25}\left[(l + l)^2 - (l + l)^2\right]1^{(d-b)}(l + l)^3 \times
\]

\[
\left[1^{(d-b)} - (l + l)^2 - l((l + l)^2 - (l + l)^2)\right]
\]

The collision frequency equations for fractal aggregates can be expressed in terms of solid volume. These collision functions are

\[
\beta_B(u_i, u_j) = \frac{2kT}{3\mu}u_i^{1/(D)} + u_j^{1/(D)}(u_i^{1/D} + u_j^{1/D})^3
\]

\[
\beta_{sh}(u_i, u_j) = \frac{\pi}{4}\left[\frac{2g}{a_0}((\rho_0 - \rho_w)^{1/2})\right]1^{(d-b)}(l + l)^3 \times
\]

\[
\left[1^{(d-b)} - (l + l)^2 - l((l + l)^2 - (l + l)^2)\right]
\]

where \( u_i \) is the volume of primary particles in the aggregate. These equations do not include correction factors suggested by others (7, 13) to reduce collisions between dissimilar-sized particles.

**Dimensional Analysis.** The assumption of a dynamic steady state used in a dimensional analysis implies that there is a continuous source of primary particles that coagulate through the size distribution to form aggregates that are removed through sedimentation \((11, 25, 26)\). Thus, larger aggregates undergoing coagulation by shear or differential sedimentation would primarily be produced by aggregates formed by Brownian coagulation of the smallest (submicron) particles. In marine systems, however, particles can be produced de novo that are on the same order in size as aggregates produced from Brownian coagulation. A dimensional analysis also requires the four assumptions made by Hunt \((14)\), as described in the Introduction. These assumptions and limitations may not be critical factors in the current calculations since previous research by Hunt \((14)\) has shown that a dimensional analysis does result in steady-state size distributions in agreement with observations. In the current analysis, we modify relationships used in a dimensional analysis to include size—mass relationships based on fractal geometry.

In our analysis we define \( n(u) \) as a continuous function describing the number of aggregates per volume of fluid per solid volume interval, in units of \( L^{-3} \), where \( L \) is a fluid—length unit and \( t \) is the aggregate—length unit. For a steady-state size distribution, Hunt \((14)\) defined \( E (R L^{-3} a^{-1}) \) as the steady-state particle volume flux through the size distribution. In our analysis, we define a fractal solid volume flux, denoted by \( E \), which has the same dimensions as \( E \).

The characteristic parameters for each coagulation mechanism, based on fractal geometry, are

\[
K_B = kT/\mu \quad [L^3 t^{-1}]
\]

\[
K_{sh} = G\nu 1^{-3/(D-D)} \quad [L^3 t^{-D} a^{-1}]
\]

\[
K_d = \left[\frac{g^{1/b}((\rho_0 - \rho_w)^{1/2})}{\mu w}^2\right]^{1/(d-b)}(l + l)^3 \times
\]

\[
\left[1^{(d-b)} - (l + l)^2 - l((l + l)^2 - (l + l)^2)\right]
\]

where \( K_B \), \( K_{sh} \), and \( K_d \) are the characteristic parameters for Brownian, shear motion, and differential sedimentation, respectively, which are obtained from the collision frequency functions \((eqs 24–26)\), except the independent variables are not included.

The size distribution has the functional form of

\[
n(u) = n(v, E, K_B, K_{sh}, K_d)
\]

By selecting a size interval where only one coagulation mechanism is dominant, eq 28 becomes an expression of four variables and three units \((l, L, t, \text{and } E)\). Using the Buckingham \(\pi\) theorem, we can obtain a size—distribution function for each coagulation mechanism as

\[
n(u) = A_B \left(\frac{E}{K_B}\right)^{1/2} u^{-3/(D)}
\]
\[ n(\nu) = A_{ab}(\frac{E}{K_{ab}})^{1/2} \nu^{-(3/2)[1+(1/D)]} \] (30)

\[ n(\nu) = A_{da}(\frac{E}{K_{da}})^{1/2} \nu^{-(3/2)-(1/2D)[1+(1+2D-D_{pa})/(2-b)]} \] (31)

where \( A_{B} \), \( A_{ab} \), and \( A_{da} \) are dimensionless constants that must be experimentally determined.

The size distribution function, \( n(l) \), is a continuous function describing the number of aggregates per volume fluid per flocc length interval. The relationship between \( n(\nu) \) and \( n(l) \) is

\[ n(l) = n(\nu) \frac{dl}{d\nu} \] (32)

and by taking the derivative of eq 10, we determine

\[ \frac{dl}{d\nu} = \frac{\nu^{D/3} \xi_{0}^{1+D}}{\nu_{0}^{3-D} D!} \] (33)

Combining eqs 32 and 33, we obtain

\[ n(l) = \nu^{D/3} \xi_{0}^{1-D} \frac{\nu_{0}^{3-D} D!}{D-1} n(\nu) \] (34)

Using eq 34 in eqs 29–31, the size-distribution functions based on \( n(l) \) are

Brownian

\[ n(l) = A_{B}^d (\frac{E}{K_{B}})^{1/2} l^{-(1/2)\{1+(1/D)\}} \] (35)

Shear

\[ n(l) = A_{ab} (\frac{E}{K_{ab}})^{1/2} l^{-(1/2)(D+5)} \] (36)

Differential Sedimentation

\[ n(l) = A_{da}^d (\frac{E}{K_{da}})^{1/2} l^{-(1/2)(1+2D-D_{pa})/(2-b)} \] (37)

where \( A_{B}^d \), \( A_{ab} ^d \), and \( A_{da}^d \) are functions of \( l_{0} \) and \( D \). The size-distribution functions \( n(l) \) and \( n(\nu) \) are summarized in Table I.

**Results**

**Effect of Fractal Structures on Collision Rates.**

When fractal dimensions are included in expressions for collision frequency functions and when packing and shape factors for Euclidean and fractal objects are equal, particles are predicted to collide more frequently than when \( D = 3 \). This occurs because the size of the fractal aggregate increases faster during coagulation than aggregates with constant size-mass relationships. In Figure 2 we plot collision frequencies for coagulation via Brownian, shear, and differential sedimentation (for \( Re \ll 1 \)) as a function of aggregate size for different fractal dimensions. Collision frequencies are calculated as a ratio of collision frequencies at fractal dimensions of 1.5, 2, and 2.5 versus collision frequencies at \( D = 3 \). As the fractal dimension decreases, the collision frequency of fractal aggregates is larger than for Euclidean aggregates. For example, during shear coagulation, aggregates with a fractal dimension of 1.5 could collide 774 times as frequently as aggregates with a fractal dimension of 3. For floccs with the same solid volume, collision frequencies could be up to 8.4 and 91 times as large as predicted from conventional models for coagulation by Brownian and differential sedimentation. A constant porosity could be chosen to make coagulation rates equal to Euclidean and fractal aggregates, but the magnitude of the porosity would be variable for different fractal dimensions.

**Fractal Dimensions from Size Distribution Functions.**

The equations derived for the fractal size distributions, \( n(\nu) \), based on coagulation by Brownian motion, shear, and differential sedimentation (Table I) are identical with those previously presented (8, 14) if the fractal dimension in each size-distribution equation is set equal to a Euclidean value of 3 and \( Re \ll 1 \).

Hunt (14) compared steady-state size distributions from marine systems with his predicted relationships based on a dimensional analysis. In this study, we can make an analogous comparison of size distributions with our dimensional analysis based on fractal aggregates. The fractal
Table I. Size Distribution Functions for Fractal Aggregates

<table>
<thead>
<tr>
<th>coagulation mechanism</th>
<th>( n(v) )</th>
<th>( A' )</th>
<th>( n(l) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownian</td>
<td>( A_B \left( \frac{E}{K_B} \right)^{1/2} ) ( u^{-3/2} )</td>
<td>( A_B D_1^{1/2} \left( \frac{D}{D_1} \right)^{3-D} )</td>
<td>( A_B \left( \frac{E}{K_B} \right)^{1/2} ) ( \frac{1}{(1+D/3)^{3/2}} )</td>
</tr>
<tr>
<td>shear</td>
<td>( A_{sh} \left( \frac{E}{K_{sh}} \right)^{1/2} ) ( u^{-(2/3)(1+(1/D))} )</td>
<td>( A_{sh} D_1^{1/2} \left( \frac{D}{D_1} \right)^{3-D} )</td>
<td>( A_{sh} \left( \frac{E}{K_{sh}} \right)^{1/2} ) ( \frac{1}{(1+D/3)^{3/2}} )</td>
</tr>
<tr>
<td>differential</td>
<td>( A_{ds} \left( \frac{E}{K_{ds}} \right)^{1/2} ) ( u^{-(2/3)-1+(1/2D)(1+2+D-D_1/(2-D_1))} )</td>
<td>( A_{ds} D_1^{1/2} \left( \frac{D}{D_1} \right)^{3-D} )</td>
<td>( A_{ds} \left( \frac{E}{K_{ds}} \right)^{1/2} ) ( \frac{1}{(1+D/3)^{3/2}} )</td>
</tr>
<tr>
<td>sedimentation</td>
<td>( u^{-(2/3)-1+(1/2D)(1+2+D-D_1/(2-D_1))} )</td>
<td>( u^{-(2/3)-1+(1/2D)(1+2+D-D_1/(2-D_1))} )</td>
<td>( u^{-(2/3)-1+(1/2D)(1+2+D-D_1/(2-D_1))} )</td>
</tr>
</tbody>
</table>

Table II. Fractal Dimensions and Slopes Determined from Dimensional Analysis of Steady-State Size Distributions in Marine Systems

<table>
<thead>
<tr>
<th></th>
<th>Brownian</th>
<th>shear</th>
<th>differential sedimentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>size range, ( \mu m )</td>
<td>&lt;2</td>
<td>2–40</td>
<td>&gt;40</td>
</tr>
<tr>
<td>slope [ \log n(l) \text{ vs } \log l ]</td>
<td>(- \left( \frac{1+D}{2} \right) )</td>
<td>(- \frac{D+5}{2} )</td>
<td>(- \frac{1}{2} \left[ 3+D+\frac{2+D-D_1}{2-b} \right] )</td>
</tr>
<tr>
<td>predicted in this work</td>
<td>(-\frac{5}{2} )</td>
<td>(-4 )</td>
<td>(-\frac{9}{2} )</td>
</tr>
<tr>
<td>predicted by Hunt (14)</td>
<td>(-2.65 )</td>
<td>(-3.7 \text{ to } -4.4 )</td>
<td>(-4.65, -5.2, -5.3 )</td>
</tr>
<tr>
<td>observed</td>
<td>(-3 )</td>
<td>(-\frac{3}{2} \left( 1+\frac{1}{D} \right) )</td>
<td>(-\frac{3}{2} \frac{1}{2D} (1+\frac{2+D-D_1}{2-b}) )</td>
</tr>
<tr>
<td>size range, ( \mu m )</td>
<td>(-\frac{2}{3} )</td>
<td>(-\frac{13}{6} )</td>
<td>(-\frac{2}{6} )</td>
</tr>
<tr>
<td>slope [ \log n(v) \text{ vs } \log v ]</td>
<td>(-\frac{2}{3} )</td>
<td>(-2 )</td>
<td>(-\frac{13}{6} )</td>
</tr>
<tr>
<td>predicted in this work</td>
<td>(-1.9 \text{ to } -2.13 )</td>
<td>(-2.22, -2.40, -2.43 )</td>
<td>(-2.4, -2.75 )</td>
</tr>
<tr>
<td>observed</td>
<td>2.4–3.75</td>
<td>1.61–2.31</td>
<td>2.4–3.75</td>
</tr>
<tr>
<td>fractal dimension</td>
<td></td>
<td></td>
<td>2.4–3.75</td>
</tr>
</tbody>
</table>

The dimension in eqs 30 and 31 can be obtained from the slope in a plot of \( \log n(v) \) versus \( \log v \). Hunt used data available in the literature to calculate several such slopes. These size distributions were originally obtained by using particle counters for marine particles larger than 2 \( \mu m \), and from direct microscopic observation for smaller sized particles. Although size distributions are reported in terms of aggregate diameter, \( d_p \), particle counters (resistance type) measure the volume occupied by the primary particles comprising the aggregate (i.e., \( v \) not \( v_a \)); \( d_p \) is the equivalent spherical diameter based on instrument calibration with solid spheres. As a result of this calibration procedure, aggregate size, \( l \), is underestimated. However, aggregate size data \( n(l) \) reported in ref 14 can be converted back into solid volume \( n(v) \) with the equation

\[
\sigma_v = \frac{(s_v - 2)}{3}
\]

(38)

where \( s_v \) is the slope based on the particle-volume log-log plots, and \( s_l \) is a slope based on the particle-length log-log plots. This equation can be verified by either comparing equations presented in ref 8 with ref 14, or for fractal aggregates, comparing eqs 29–31 with 35–37.

The observed and predicted slopes of log-log plots of size distributions as reported by Hunt (14) and calculated here are shown in Table II. The size range over which each coagulation mechanism operates is assumed to be the same as determined by Hunt (14). From the range of reported slopes for particles assumed to be produced by shear coagulation, we calculate fractal dimensions of 2.4–3.75 for aggregates developed from shear coagulation; however, it is unlikely that \( D \) is greater than 3. Several factors may help explain the magnitude of this fractal dimension. First, the size range calculated for aggregates formed by shear coagulation (2–40 \( \mu m \)) is typical of non-aggregated particles in the water column, such as phytoplankton. Since particle counters do not distinguish between amorphous aggregates and solid particles, it may be that some particles analyzed in the shear coagulation size range are not aggregates, but microorganisms such as single-celled phytoplankton with Euclidean, and not fractal, structures. A second source of error is the sensitivity of the magnitude of the fractal dimension to the slope. For example, fractal dimensions in a wide range of 1 < \( D < 3 \) produce slopes in the narrow range of 2.17–2.5. Third, many marine aggregates contain actively growing microorganisms (27), resulting in aggregates formed by growth of cells already in the aggregate, and not by coagulation of unattached particles.

For particles assumed to be produced by differential sedimentation, slopes of -2.22 to -2.53 were calculated for fractal size distributions by using slopes of -4.65 and -5.2 reported by Hunt (Table II). A third set of data also reported by Hunt (14) indicated a slope of -5.6, but our examination of the data reported by Faist (28) provided a slope of -5.3. Using slopes of -4.65, -5.2, and -5.3, we obtained fractal dimensions in the range of 2.31, 1.67, and 1.61. All Reynolds numbers were less than 0.1 independent of our assumed value of \( D_p \), resulting in \( b = 1 \). The assumption that \( D_p = D_0 \) when \( D \) is less than 2 increased the calculated fractal dimension. If we assumed that \( D_p = 2 \), we would calculate fractal dimensions of 1.28 and 1.15, for slopes of -5.2 and -5.3, respectively.

Only a single slope of -2.65 was reported by Hunt (14) for small aggregates (<2 \( \mu m \)) assumed to form by Brownian
coagulation. However, a fractal dimension cannot be calculated from a dimensional analysis for aggregates formed from Brownian motion since $D$ does not appear in the final expression for the slope calculated by using eq 29 (Table II) based on aggregate volume.

Discussion

There is now substantial evidence that aggregates formed from coagulation processes possess fractal structures (15-18, 29). As a result, existing coagulation models based on Euclidean scaling relationships must be modified to account for the scaling properties of fractal aggregates. Collision functions based on fractal geometry (Table I) indicate more frequent collisions between fractal aggregates ($D < 3$) than Euclidean objects ($D = 3$). Fractal aggregates have a larger size, and therefore a greater collision probability, than aggregates assumed to have a constant porosity.

Using a dimensional analysis based on a fractal scaling relationship, we calculated fractal dimensions of aggregates formed in marine systems. For aggregates formed from differential sedimentation and shear coagulation, we determined $1.61 \leq D \leq 2.31$ and $2.4 \leq D \leq 3.75$, respectively. Fractal dimensions could not be calculated for aggregates formed by Brownian motion by use of the dimensional analysis since $D$ did not appear in the final dimensional analysis based on aggregate volume (eq 29). However, computer simulations describing colloidal aggregate have shown that aggregates formed through the collision of clusters (cluster–cluster) have fractal dimensions of either 1.8 or 2.2 (18). These simulations have been experimentally verified by measurement of the fractal dimensions of a variety of colloidal aggregates formed by Brownian motion (18). The two different values of the fractal dimension occur as a function of different particle stickiness. Particles that stick immediately upon contact with other particles cannot penetrate the aggregate since they collide with particles on the aggregate exterior and stick. Aggregates formed from these particles are classified as “diffusion limited” and have fractal dimensions of $D = 1.8$. As the collision probability approaches zero, however, particles may collide many times before sticking; these cells can penetrate the aggregate, increasing the aggregate density. These aggregates are referred to as “reaction limited”, with $D = 2.2$ (18). Since different types of aggregates have different values of $D$, fractal classification of aggregates formed by Brownian motion identifies both the aggregate formation mechanism as well as the collision efficiency of cells composing the aggregate.

The different ranges of the fractal dimensions presented in Table III indicate that different values of the fractal dimension occur as a result of different coagulation mechanisms. Conversely, this suggests that the magnitude of the fractal dimension for a collection of aggregates could be a useful reference for identifying a coagulation mechanism. Although the fractal dimensions determined for coagulation by Brownian motion ($1.8 \leq D \leq 2.2$) and differential sedimentation ($1.61 \leq D \leq 2.31$) overlap, it is unlikely that we would need to distinguish between aggregates formed by these two different coagulation mechanisms. Aggregate formation by Brownian motion is likely to be dominant only for small particles, on the order of 1 $\mu$m or less (7). Therefore, these two coagulation mechanisms are easily distinguished by the absolute aggregate size. The fractal dimensions of aggregates formed by shear coagulation ($D \geq 2.4$) are larger than those determined for the other two coagulation mechanisms, suggesting that shear coagulation produces denser aggregates than other coagulation mechanisms. However, it is not clear that all particles measured in the 2–40-$\mu$m size distribution were aggregates produced by coagulation since this size range includes solid particles such as single-celled phytoplankton. Thus, it may be that most particles analyzed in this size range in marine systems are not aggregates, but other objects with Euclidean, and not fractal, structures. Additional information, which could be obtained through direct observation via photographs, is necessary to clarify the types of particles present in the 2–40-$\mu$m size distributions.

The fractal dimensions determined by Lin et al. (18) for coagulation by Brownian motion and the fractal dimensions for coagulation by shear and differential sedimentation are compared to reported fractal dimensions of a variety of organic and inorganic aggregates in Table III. On the basis of eq 4, Logan and Wilkinson (29) determined the fractal dimension of $3.0 \pm 0.4$ for macroscopic aggregates (0.4–1.4 mm) of Zoogloeas ramigera grown in a laboratory benchtop fermentor. This fractal dimension is within the range of values calculated from marine distributions for aggregates formed by shear coagulation. However, when bacterial aggregates were developed in rotating test tubes, Z. ramigera aggregates had a fractal dimension of $1.8 \pm 0.3$. The fractal dimension obtained for the rotating tube aggregates is smaller than the range of fractal dimensions indicated for shear coagulation. The results of the dimensional analysis imply that aggregates formed in the rotating tubes were not formed by shear coagulation, but by differential sedimentation. Since these aggregates settled to the bottom of the rotating tubes during culture growth and coagulation, this conclusion is reasonable.

To our knowledge, there are no reports of fractal dimensions of aggregates formed by differential sedimentation that have been generated either through computer simulations or through experiments. However, Logan and

---

**Table III. Fractal Dimensions of Various Types of Aggregates**

<table>
<thead>
<tr>
<th>Type of Aggregate</th>
<th>Fractal Dimension</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownian motion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diffusion limited</td>
<td>1.8</td>
<td>18</td>
</tr>
<tr>
<td>reaction limited</td>
<td>2.2</td>
<td>18</td>
</tr>
<tr>
<td>Differential Sedimentation</td>
<td>2.4–3.75</td>
<td>a</td>
</tr>
<tr>
<td>Zoogloeas ramigera</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rotating tubes</td>
<td>1.8±0.03</td>
<td>29</td>
</tr>
<tr>
<td>benchtop bioreactor</td>
<td>3.0±0.04</td>
<td>29</td>
</tr>
<tr>
<td>Marine Snow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>general</td>
<td>1.26±0.06</td>
<td>24</td>
</tr>
<tr>
<td>general</td>
<td>1.39±0.15</td>
<td>24</td>
</tr>
<tr>
<td>diatom aggregates</td>
<td>1.52±0.19</td>
<td>24</td>
</tr>
<tr>
<td>Activated Sludge</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>1.44–1.49</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>1.55–2.0</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>1.70–2.07</td>
<td>31</td>
</tr>
<tr>
<td>Inorganic Aggregates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>alum</td>
<td>1.59–1.97</td>
<td>31</td>
</tr>
<tr>
<td>alum</td>
<td>2.30–2.32</td>
<td>31</td>
</tr>
<tr>
<td>clay–iron</td>
<td>1.92</td>
<td>31</td>
</tr>
<tr>
<td>clay–magnesium</td>
<td>1.91</td>
<td>31</td>
</tr>
<tr>
<td>ferric</td>
<td>2.61–2.81</td>
<td>31</td>
</tr>
</tbody>
</table>

*This study.*
Wilkinson (24) estimated fractal dimensions of marine snow aggregates assumed to be formed by differential sedimentation using in situ data reported by others (10, 30). They obtained fractal dimensions of 1.39 ± 0.15 from size-porosity data and 1.26 ± 0.26 from settling velocity data, for marine snow aggregates 0.4–20 mm in length. They also calculated a fractal dimension of 1.52 ± 0.19 for diatom aggregates using data on the number of diatoms per aggregate, for aggregates 7–20 mm in length. The magnitude of these fractal dimensions obtained from in situ studies is within the range predicted by the fractal size distribution analysis for aggregates formed from differential sedimentation.

Li and Gancarczyk (31) determined fractal dimensions for a variety of aggregates formed in water and wastewater treatment processes. Inorganic flocs have higher fractal dimensions in the range of 1.59–2.65. The primary particles forming these inorganic aggregates are colloidal (<1 μm), so we would expect these aggregates to be formed by either Brownian motion or shear coagulation. The clay flocs have fractal dimensions in the Brownian motion range of 1.9–2.2, but the fractal dimensions for alum flocs span the range of values for shear and Brownian motion. The ferric aggregates are in the range indicated for shear coagulation. Activated sludge flocs had fractal dimensions ranging from 1.4 to 2.07 (Table III). Since these flocs are very large, this suggests formation by differential sedimentation. Activated sludge flocs containing a large number of filamentous microorganisms have a lower fractal dimension of 1.0 (24).

In general, the fractal dimensions of biological aggregates obtained from natural and engineered environments (1.0–1.5) are smaller than other fractal dimensions determined for inorganic colloidal aggregates. Part of the reason for fractal dimensions below values of 1.61–2.31 determined here may be due to different scaling relationships used to relate settling velocity to aggregate size. Li and Gancarczyk (31) assumed that \( v \sim D_{2}^{-1} \). Although Logan and Wilkinson used \( v \sim D_{2}^{-1+b} \), they assumed \( D_{2} = 2 \), which reduced their expression to the same as that of Li and Gancarczyk. In the present study, we have used \( v \sim D_{2}^{-1+b} \). If \( D < 2 \) and we can assume \( D_{2} = D \), then settling velocity is only a function of the power law relationship and is not a function of the fractal dimension. Therefore, at \( Re > 1 \), aggregate settling velocities are most sensitive to values of \( b \). For example, marine snow aggregates analyzed by Logan and Wilkinson (24) had a fractal dimension of \( D = 1.39 \pm 0.15 \) determined from size-porosity data, and Reynolds numbers in the range of 0.1–10 (10). In this range, \( b = 0.87 \), and we would expect that \( v \sim D_{2}^{-0.87} \). It was observed that \( v \sim D_{2}^{-0.5} \). These differences could either be due to different values of \( D_{2} \) than assumed here or errors introduced by using drag coefficients developed for spheres for nonspherical fractal aggregates. From size-projected area data (32), \( D_{2} = 1.46 \pm 0.16 \). Within a standard error, \( D_{2} = D_{c} \) since \( D_{c} = 1.39 \pm 0.15 \). Therefore, the differences in observed and calculated relationships between size and settling velocity are probably a result of our assumption of the drag coefficient for these aggregates.

The collision functions derived by using fractal relationships are only a first step in modifying coagulation theory to incorporate fractal geometry. Existing collision models predict a very low probability of collisions between dissimilar-sized spheres in marine systems (7). However, collisions between dissimilar-sized aggregates are probably more likely for fractal aggregates than spheres. The larger cross-sectional area and branches of a fractal aggregate not only allow for increased collisions between colliding particles, but the open- branched structure of a fractal will permit advective flow through the aggregate, resulting in collisions between aggregates that would not occur if the aggregates were constrained to follow streamlines that did not cross the aggregate surface. The effect of fractal geometry on flow-through porous objects is an emerging field with important implications for coagulation theory.

Conclusions

Coagulation equations and a self-similar size-distribution analysis used to describe coagulation can be modified to incorporate the fractal geometry of aggregates. We have proposed a set of collision functions containing a fractal dimension that can be used in the general coagulation equation. Through the use of a fractal size distribution analysis, we have calculated that aggregates formed by shear coagulation should have fractal dimensions greater than 2.4, whereas aggregates formed from differential sedimentation would have lower fractal dimensions in the range of 1.6–2.3. Most biological aggregates from engineered bioreactors and marine systems have fractal dimensions in the range expected for differential sedimentation. Fractal dimensions of inorganic and colloidal aggregates were in the range expected for aggregation by Brownian motion and shear coagulation.

Acknowledgments

We thank James R. Hunt, Charles R. O’Melia, William Becker, and Kwok-Keung Au for many helpful comments made during their review of an earlier manuscript.

Literature Cited


(32) Aldredge, A. L. University of California, Santa Barbara, unpublished.
(33) Adler, P. M. *J. Colloid Interface Sci.* 1981, 81, 531–535.

Received for review March 4, 1991. Revised manuscript received June 17, 1991. Accepted June 26, 1991. Funding for this research was provided through ONR Contracts N00014-88-K0387 and 423G004-01.