On Aggregating Populations

Doraiswami Ramkrishna*

School of Chemical Engineering, Purdue University West Lafayette, Indiana 47907

The evolution of particle size distributions due to aggregation between particles is described generally by incorporating an aggregation frequency into a population balance equation. The frequency is derived by analyzing the relative motion between particles culminating in their physical contact and aggregation. The usual approach, originating from the pioneering work of Smoluchowski (Smoluchowski, M. Sitzungber. Math., Astron., Phys., Meteor. Mech. 1914, 123, 2381), is to view the relative motion between two particles and their aggregation in isolation from the population balance. The procedure is predicated on the assumption that the spatial homogeneity of the population (over some length scale, say, L) is disturbed by relative motion only in a neighborhood of length scale l that is small compared to L; furthermore, relative motion is assumed to occur at a rate sufficiently higher than the rate at which the population of particles diminishes by aggregation. This paper presents a mathematical perspective on this approach, examines the circumstances of its validity, and provides a remedial procedure when it is inadmissible with potential applications. Thus, this work identifies circumstances that permit the use of an aggregation frequency, together with a procedure for its calculation.

1. Introduction

Aggregation between particles is a common occurrence in the evolution of dispersed-phase systems in nature as well as in engineering. This phenomenon is of great scientific and engineering interest because of its profound consequences to the behavior of these systems. It has also been a subject of interest to Professor Reuel Shinwar,* and this author is pleased to contribute to a volume honoring an engineering scientist revered for his outstanding contributions to many diverse areas of chemical engineering. Since the work of Smoluchowski on aggregation by Brownian motion, extensions have appeared for aggregation frequencies for various other forms of relative motion, although these extensions still fall generally within the legacy contained in Smoluchowski’s pioneering effort. It is the objective of this paper to examine this legacy within a mathematical perspective, to deduce the conditions under which the assumptions made are valid, and to provide a remedy for when they are not. We begin by introducing the essential mathematical implements, the general population balance equation for the analysis of aggregation processes in terms of the size and spatial coordinates of particles, followed by a scaling analysis that reveals the assumptions implicit in Smoluchowski’s strategy. When the physical parameters of a problem do not support the implied assumptions, the general population balance equation in particle size (internal coordinate) and particle location (external coordinate) offers the proper description of the aggregation problem.

2. Particle Density Functions

We are concerned with spherical particles distributed in a flowing fluid in some physical domain. The particles are distinguished by their size (volume v) and their physical locations, which are described by their centroids’ coordinates, x, relative to some fixed origin.

Although adding particle velocity as an additional external coordinate contributes nothing to our conceptual burden, in view of the simplicity that accrues from specifying particle kinematics, this detail can be forsaken without concessions on generality. Thus, we let $f_1(v,x,t) dv dx$ be the probability that there exists a particle at time $t$ with its size (volume) between $v$ and $v + dv$ in spatial volume $dx$ about the point $x$. This density function is not a probability density because it is the expected number density of particles with volume $v$ at location $x$ and time $t$. It is therefore essential to define only one other density function associated with particle pairs, viz., $f_2(v,x',v',x,t)$, which is the expected number of pairs of particles, one with volume $v$ at location $x$ and the other with volume $v'$ at location $x'$; it is also true that this function represents the probability that there exist at time $t$ a particle with volume between $v$ and $v + dv$ in volume $dx$ about $x$ and a particle with volume between $v'$ and $v' + dv'$ in volume $dx'$ about $x'$. The probabilistic interpretations are most convenient for deriving the population balance equation.

3. Particle Motion

Next, we stipulate the particle kinematics to be given by the velocity $X(v,x,t)$ for a particle of volume $v$ at location $x$ at time $t$, which subsumes a number of different cases within the assumption that we neglect the detail of dynamics requiring an equation of motion for the particle. For a particle free of inertia and consequently moving with the local fluid velocity, the dependence on space and time is acquired from that of the fluid motion, and the dependence of the velocity on size is irrelevant. Of course, the issue of hydrodynamic interactions between particles is avoided by the assumption that the particle assumes the local convective motion of the fluid. The accounting of hydrodynamic

---

* E-mail: ramkrish@ecn.purdue.edu.
interactions calls for a detailed analysis such as that of Batchelor and Green, however. For a particle moving with its “terminal” velocity, the dependence on particle volume is a natural consequence, whereas the spatiotemporal dependence can be acquired possibly through the corresponding dependence of the force acting on the particle and the hindering effects due to neighboring particles. In what follows, we preclude only for convenience any process that changes the size of an isolated particle. Such “growth” terms introduce no complications but are excluded to prevent them from distracting the focus on the chief issue of aggregation. For the same reason, we have also chosen to exclude random motion (diffusion) of particles. The incorporation of random motion in population balances is readily accomplished by including a stochastic (Langevin) equation for the particle as shown by the author. We shall have more to say about this issue at a subsequent stage in this paper. Aggregation is assumed to occur instantly on two particles coming into contact. Two particles of volumes \( v \) (with radius \( \sqrt[3]{3v/\pi} \)) and \( \v' \) (radius \( \sqrt[3]{3\v'/4\pi} \)) will come into contact when their centroids are exactly apart by a distance equal to the sum of the particle radii. (By detailed considerations of the drainage of an intervening film separating two drops that have “collided”, the analysis of relative motion can be carried further to examine the circumstances of aggregation. The result of this analysis would be to produce an aggregation efficiency.) Thus, a particle of volume \( v \) at location \( x \) will be in contact with any particle that is located at the surface of the sphere whose center coincides with the center of the first particle and has the radius \( \rho(v,v') = (\sqrt[3]{3v/4\pi} + \sqrt[3]{3\v'/4\pi}) \) (see Figure 1). We denote the set of points on the sphere of radius \( \rho(v,v') \) with its center at \( x \) by \( S(x,v,v') \). In other words, particles on the surface of the foregoing sphere with coordinate \( x' \) must satisfy the relationship \( ||x - x'|| = \rho(v,v') \). It is also necessary to recognize that the configuration of two particles touching each other must emerge from their being previously away from each other and moving toward each other.

### 4. Aggregation Rate

Prior to the identification of the population balance equation, it is of interest to calculate the rate at which a particle of size \( v \) at location \( x \) aggregates with other particles of specified size. Clearly, particles distinctly apart from each other can aggregate only as a result of relative motion between them such that they move toward each other. This condition of having relative motion between a particle pair to occur such that the particles move toward each other is met by stipulating that the dot product of the unit vector in the direction of relative motion and the unit vector toward the center of the sphere \( S_x(v,v') \) be positive. From the discussion in section 3, it follows that the rate at which a particle of size \( v \) at location \( x \) aggregates with particles of size \( v' \) (without regard to location) is given by

\[
\int_{S_x(v,v')} dA \frac{X(x,v,t) - X(x,v',t)}{||x - x'||} f_2(v,v',v',x,t) \quad (4.1)
\]

where \( dA \) is a differential area element on the surface of the sphere \( S_x(v,v') \) and the set \( S_x(v,v') \) represents that part of the surface of the sphere \( S_x(v,v') \) on which the integrand in eq 4.1 is positive in order to ensure that the particles are moving toward each other. Alternatively, one can write

\[
S_x(v,v') = \{ r \in S_x(v,v') : -\frac{r}{r} [X(v,x+r,t) - X(v,x,t)] \geq 0 \} \quad (4.2)
\]

where we have used the definition \( r = ||r|| \). The biparticle density appears in eq 4.1 because the aggregation event in question can occur only if the appropriate pair of specified particle sizes actually exists. Equation 4.1, when multiplied by \( dt \), represents the probability that there is aggregation between a particle of size \( v \) located at \( x \) and a particle of size \( v' \) during the time interval between \( t \) and \( t + dt \). (If we had accounted for diffusion, eq 4.1 would have featured a relative diffusive flux term involving a (relative) diffusion coefficient and the (partial) gradient with respect to \( x \) (the coordinates of the particle of volume \( v \)) of the density function \( f_2(x) \).) The foregoing term is the rate at which actual contact is established between a particle of volume \( v \) located at \( x \) and a particle of volume \( v' \) somewhere on the surface of the sphere of radius \( \rho(v,v') \).

The preparation is now complete for the derivation of the population balance equation, except for one technical issue that has potential for some added complexity. This is the issue of locating the coordinates of the aggregate particle, which arises because the population balance is on particles of a particular size at a specified location. The physics of this process could be considerably complicated as the magnitude of the relative velocity between the two aggregating particles will play a role in determining the immediate location of the aggregate. The error introduced by locating the aggregate particle somewhere on the line joining the centroids (including that of one of the particles), however, is likely to be small as long as the particles themselves are small compared to the scale at which the number density is reasonably uniform. We shall thus ignore this detail in the discussion that follows.
5. Population Balance Equation

In order for us to identify the population balance equation, we need only to see how particle numbers change as a result of aggregation. We prefer, however, to use a probabilistic derivation of the equation as below. The focus is on particles of volume \( v \) at the specific location \( x \). Because experimental measurement of the number density is more appropriately viewed as volume-averaged over some local domain, say \( \Omega_v \), with \( x \) as its centroid and volume \( V_0 \) that is independent of location \( x \), it will be of interest to perform this volume averaging after the local equation has been obtained. We denote by \( \partial \Omega_v \) the bounding surface of the averaging domain \( \Omega_v \). This averaging volume must be sufficiently large to contain several particles.

On the basis of the probability interpretation of the monoparticle density function \( f_1(v,x;t) \), the derivation of the equation for this function must account for changes introduced by particle motion as well as by aggregation. Thus, the probability of locating at time \( t \) a particle of volume \( v \) at location \( x \) is through either of the following events an infinitesimal instant earlier: (i) finding a particle of volume \( v \) in the appropriate neighborhood that arrives without aggregating with another particle or (ii) finding two other particles of appropriate sizes (i.e., \( v \) and \( v' \)) and location aggregating to produce the particle in question. The population balance equation is now readily identified for the density function \( f_1(v,x;t) \) on the basis of a probabilistic derivation

\[
\frac{\partial f_1(v,x;t)}{\partial t} + \nabla \cdot [\mathbf{X}(v,x,t)f_1(v,x;t)] =
\]

\[
\frac{1}{2} \int_0^v dv' \int_{S_{v,v'}} dA \delta_r[\mathbf{X}(v',x,t) - \mathbf{X}(v,x+r,t)] f_2(v,v';v,x+r,t) -
\]

\[
\int_0^v dv' \int_{S_{v,v'}} dA \delta_r[\mathbf{X}(v',x+r,t) - \mathbf{X}(v,x+r,t)] f_2(v,v',v+x+r,t) +
\]

\[
\int_{S_{v,v'}} dA \delta_r[\mathbf{X}(v',x,t) - \mathbf{X}(v,x+r,t)] f_2(v,v',v+x+r,t) \tag{5.1}
\]

where we have replaced \( r/r \) by the unit vector \( \delta_r \).

Equation 5.1 is then the population balance equation of interest and must be solved subject to boundary and initial conditions that depend on the application. The fact that the right-hand side of the foregoing equation has the biparticle density makes the problem unclosed and impossible to solve without a suitable closure hypothesis. A common closure hypothesis is that of statistical independence between particles of different sizes and locations. However, we defer the introduction of this hypothesis to a later stage. For the present, we employ the rules of probability theory to write for the biparticle density

\[
f_2(v',v';x,t) = f_2(v',v';t) f_2(v,v';x,t) \tag{5.2}
\]

where \( f_2(v',v';t) \) is the biparticle density associated with locating, at time \( t \), a particle of volume \( v' \) at location \( x \) and another particle of volume \( v \), without regard to its location, in the averaging volume \( \Omega_v \); the function \( f_2(v',v';x,t) \) is the conditional density for the location \( (x') \) of a second particle (of volume \( v' \)) at instant \( t \) given that, at the same instant \( t \), a particle of size \( v \) has been located at \( x \) and a second particle of size \( v' \) exists somewhere in \( \Omega_v \). Substituting eq 5.2 into eq 5.1, we obtain

\[
\frac{\partial f(v,x;t)}{\partial t} + \nabla \cdot [\mathbf{X}(v,x,t)f_1(v,x;t)] =
\]

\[
\frac{1}{2} \int_0^v dv' f_2(v',v;v,v';t) \int_{S_{v,v'}} dA \delta_r[\mathbf{X}(v',x,t) - \mathbf{X}(v,x+r,t)] f_2(x,v+r,t;v,v';t) -
\]

\[
\int_0^v dv' f_2(v',v;v,x+r,t) \int_{S_{v,v'}} dA \delta_r[\mathbf{X}(v',x+r,t) - \mathbf{X}(v,x+r,t)] f_2(x,v+r,t;v,v';t) \tag{5.3}
\]

Toward preparation for the local volume-averaged version of eq 5.3, we now formally introduce the concept of local volume averaging. The local volume-averaged spatial density of the expected number density, denoted \( n(v,x,t) \), is defined by

\[
n(v,x,t) \equiv \langle f_1(v,x,t) \rangle = \frac{1}{V_0} \int_{\partial \Omega_v} f_1(v,x+r,t) dV_r \tag{5.4}
\]

where \( dV_r \) is an infinitesimal volume about \( x + r \) with \( x \) regarded as fixed. To volume average eq 5.3, we observe that volume averaging of a divergence [of an arbitrary vector field \( \mathbf{a}(x) \)] term leads to the following result

\[
\langle \nabla \cdot \mathbf{a}(x) \rangle = \nabla \cdot \mathbf{a}(x) = \frac{1}{V_0} \int_{\partial \Omega_v} \nabla \cdot \mathbf{a}(x + r) dV_r =
\]

\[
\frac{1}{V_0} \int_{\partial \Omega_v} dA \delta_r \mathbf{a}(x + r) \tag{5.5}
\]

where the term on the extreme right contains \( dA \) as an infinitesimal area on \( \partial \Omega_v \) and arises from the application of the divergence theorem. (The subscript on the gradient operator refers to the point with respect to which the gradient is evaluated holding all other coordinates constant. In understanding eq 5.5, one must recognize that \( \nabla_{x+r} = \nabla_x = \nabla_r \). We are now in a position to derive the local volume-averaged version of eq 5.3. However, it is now necessary to resolve the problem of closure associated with this equation with an assumption of statistical independence that was mentioned earlier.

The notion of statistical independence between the particle of volume \( v \) at location \( x \) and a particle of volume \( v' \) anywhere in the domain \( \Omega_v \) can now be written as

\[
f_2(v,v';x,t) = V_0 n(v',x,t) f_1(v,x,t) \tag{5.6}
\]

where we have implied through the use of eq 5.4 that the particles (of volume \( v \)) are anywhere in the domain \( \Omega_v \). Using eq 5.6, we obtain from eq 5.3 the following equation

\[
\frac{\partial f(v,x;t)}{\partial t} + \nabla \cdot [\mathbf{X}(v,x,t)f_1(v,x;t)] =
\]

\[
\frac{1}{2} \int_0^v dv' f_2(v',v;v,v';t) \int_{S_{v,v'}} dA \delta_r[\mathbf{X}(v',x,t) - \mathbf{X}(v,x+r,t)] f_2(x,v+r,t;v,v';t) -
\]

\[
\int_0^v dv' f_2(v',v;v,x+r,t) \int_{S_{v,v'}} dA \delta_r[\mathbf{X}(v',x+r,t) - \mathbf{X}(v,x+r,t)] f_2(x,v+r,t;v,v';t) \tag{5.7}
\]

Suppose, for the present, that we consider the special situation in which the particle velocity is independent of space and time. In other words, we assume that
\( \frac{\partial n(v,t)}{\partial t} + \nabla \cdot \mathbf{X}(v) n(v,t) = - \frac{1}{2} \int_{S_{x}(v)} dA \delta_{r} \cdot [\mathbf{X}(v) - \mathbf{X}(v')] p(r,t;v,v';t) - V_{0} \int_{0}^{\infty} dv' n(v,t) n(v,v') t_{S_{x}(v,v')} dA \delta_{r} \cdot [\mathbf{X}(v) - \mathbf{X}(v')] p(r,t;v,v';t) \) (5.8)

In arriving at eq 5.8, we have made use of eq 5.5. If, initially, the system is spatially homogeneous and if, thereafter, the net flow of particles across each averaging volume can be considered negligible, then the volume-averaged number density at any location \( x \) might be virtually independent of \( x \). Thus, we can replace \( n(v,x,t) \) by \( n(v,t) \). Consequently, the divergence term on the left-hand side of eq 5.8 can be neglected so that eq 5.8 becomes

\[ \frac{\partial n(v,t)}{\partial t} = - \frac{1}{2} \int_{S_{x}(v,v')} dA \delta_{r} \cdot [\mathbf{X}(v) - \mathbf{X}(v')] p(r,t;v,v';t) - V_{0} \int_{0}^{\infty} dv' n(v,t) n(v,v') t_{S_{x}(v,v')} dA \delta_{r} \cdot [\mathbf{X}(v) - \mathbf{X}(v')] p(r,t;v,v';t) \] (5.9)

If the particle population is uniformly distributed in space initially, then the relative motion between the particles might disturb the state of this uniformity in the neighborhood of each particle. If the averaging domain \( \Omega_{t} \) is such that the net flux across its boundary virtually vanishes, then the state of uniformity in the domain is left undisturbed. From eq 5.8, it follows that the aggregation frequency to be used in the population balance is to be defined as

\[ a(v,v';t) \equiv V_{0} \int_{S_{x}(v,v')} dA \delta_{r} \cdot [\mathbf{X}(v) - \mathbf{X}(v')] p(r,t;v,v';t) \] (5.10)

which suggests a time dependence that we shall address at a later stage. Expression 5.10 yields from eq 5.9 the well-known population balance equation for aggregating systems

\[ \frac{\partial n(v,t)}{\partial t} = - \int_{0}^{\infty} dv' n(v,t) n(v,v') a(v,v';t) - \int_{0}^{\infty} dv' n(v,t) n(v,v') t_{S_{x}(v,v')} dA \delta_{r} \cdot [\mathbf{X}(v) - \mathbf{X}(v')] p(r,t;v,v';t) \] (5.11)

6. Calculation of the Aggregation Frequency

The calculation of the aggregation frequency from expression 5.8, of course, requires knowledge of the function \( p(r,t;v,v';t) \). We view this circumstance (of two particles of volumes \( v \) and \( v' \) touching each other at time \( t \) as arising from the past over some time scale, say, \( T_{rm} \), during which no aggregation is possible. We picture the particle pair (of volumes \( v \) and \( v' \)) to be distinctly apart at some time (prior to the instant \( t \)) that lies between \( t \) and \( t \) - \( T_{rm} \). The tacit implication here is that the existence of the particles of volumes \( v \) and \( v' \) would have preceded in the interval (\( t \), \( t \) - \( T_{rm} \)), with the particles describing relative motion. This scenario is a consequence of envisaging a region \( \Omega_{t} \) in which relative motion is occurring free of aggregation during this (short) period! From the foregoing discussion, it should be evident that the aggregation event envisaged at time \( t \) could have resulted from the particle of volume \( v' \) being somewhere in \( \Omega_{t} \) at some appropriate instant of time on the order of \( T_{rm} \). Thus, the domain \( \Omega_{t} \) is, in fact, the domain that is swept by the particle by the motion of the particle of volume \( v' \) relative to that of the particle of volume \( v \) and moving toward it. In the present case (unlike the situation in diffusive relative motion), the relative motion must occur along the direction of the relative velocity vector. Because the relative velocity vector for the case in question does not depend on position, the path is necessarily rectilinear in the direction of motion. For example, if the particle motion is vertical, as in the case of gravitational settling (or creaming), the relative motion is also along the vertical direction. Regardless of such details, it is clear that one must traverse backward in a direction exactly opposite that of the relative velocity vector to obtain the relative position vector at instant (\( t \) - \( t \)), because this vector represents the image of \( r \) prior to \( t \). Now, given that the relative position vector at time \( t \) can be anywhere on the surface of the set \( S_{x}(v,v') \), its image must necessarily lie anywhere within a right circular cylinder with its axis along the relative velocity vector. Of course, for aggregation to occur, the relative velocity vector must be directed toward the surface of the sphere \( S_{x}(v,v') \). More clearly, the particle of volume \( v' \) must be in the foregoing cylinder on the side from which it moves toward the surface of the sphere \( S_{x}(v,v') \) for aggregation to occur with the particle of volume \( v \). (This scenario is well-known among researchers in this field except for its recasting in the framework under discussion.) The discussion here then identifies the domain \( \Omega_{t} \) as the right circular cylinder whose axis is along the direction of relative motion and whose radius is equal to that of the sphere \( S_{x}(v,v') \), i.e., \( \rho(v,v') \). Mathematically, the precise definition of \( \Omega_{t} \) for this case can be identified conveniently by orienting a spherical coordinate system with its center at \( x \) and a “vertical” axis along the direction of relative motion from which the azimuthal angle \( \theta \) is measured while the angle \( \phi \) is measured from some axis on the plane perpendicular to the vertical axis. Thus, we have

\[ \Omega_{t} = \left\{ 0 < z < 1; \cos^{-1} \frac{z}{\rho} < \theta < \cos^{-1} \frac{z}{\sqrt{\rho^{2} + \rho^{2}}} \right\} \] (6.1)

where \( l \equiv T_{rm} |\mathbf{X}(v) - \mathbf{X}(v')| \) represents the length scale of relative motion without aggregation. In the more general case where particle motion depends not only on particle size but also on position and time, the domain \( \Omega_{t} \) is no longer a right circular cylinder. Although we shall consider this case subsequently, we formalize below the results for the size-dependent aggregation frequency with no spatiotemporal dependence.

6.1. Particle-Size-Dependent Frequency with Spatiotemporal Uniformity. We now identify the fundamental assumptions connected with calculating the aggregation frequency identified in eq 5.10. We assume that the particles are distributed uniformly in \( \Omega_{t} \) throughout the period of this relative motion. Thus
where the uniform distribution implied by the expression on the right-hand side is, in fact, acquired from that at the "boundary" characterized by \( \tau = T_{rm} \). [Note that eq 6.2 is, in fact, invariant with \( \tau \) and that this invariance is a consequence of satisfying the partial differential equation \( i[p(\tau - x_0)] - \{X(v) - X(v')\}/v_0 = 0 \) that describes the relative motion of the two particles in the reverse preceding aggregation. If we had included relative (Fickian) diffusion with coefficient \( D_{rel} \), then we would have had to add the term \( v_0^2 \rho \) to the right-hand side of the foregoing equation. In this situation, one uses the steady-state solution of the partial differential equation for relative motion to calculate the aggregation rate.]

Thus, the aggregation frequency is determined by combining eqs 5.8 and 6.2 to obtain

\[
a_{rel}(v,v') = \int \delta_r(\mathbf{X}(v) - \mathbf{X}(v')) \cos \theta \, d\Sigma \:
\]

which is significantly free from any explicit time dependence on the right-hand side. If, further, we set \( \mathbf{X}(v) - \mathbf{X}(v') = \mathbf{X}_{rel} \), implying thereby that the magnitude of relative motion of the specific particle pair is \( \mathbf{X}_{rel} \) and that particle motion occurs along the direction \( \mathbf{k} \), we obtain

\[
a_{rel}(v,v) = \mathbf{X}_{rel} \int \delta_r(\mathbf{X}(v) - \mathbf{X}(v')) \cos \theta \, d\Sigma
\]

where \( \theta \) has been defined to be the angle between the local radius vector and the rectilinear direction of particle motion. In spherical coordinates, one has \( d\Sigma = 2\pi r v_0^2 \sin \theta \, dr \, d\theta \). Thus, the aggregation frequency for uniformly rectilinear particle motion (distinguished here by subscript \( 0 \)) becomes for this case

\[
a_{rel}(v,v) = \pi \rho(v,v)^2 \int \delta_r(\mathbf{X}(v) - \mathbf{X}(v')) \cos \theta \, d\Sigma
\]

which is the cylindrical volume described earlier. We have thus an aggregation frequency, independent of spatial and temporal coordinates, that is conveniently used in eq 5.11 to describe aggregation dynamics. The reader is referred to the classical paper of Smoluchowski\(^7\) for the original treatment of this problem. (The first term on the right-hand side of eq 6.12, which pertains to the relative motion of particles through shearing motion of the surrounding continuum, produces the same result as in eq 28 of Smoluchowski.\(^7\))

Of course, several other considerations could have been added here, such as particle diffusion and its joint occurrence with convective motion, multiple mechanisms of such relative motion, and so on. However, our objective here has been merely to provide a perspective on aggregation processes that is sufficient to consider the important case below of spatiotemporal nonuniformity that leads to aggregation frequencies that depend on space and time.

### 6.2 Aggregation Frequency with Spatiotemporal Dependence

We now return to the case where the particle motion depends not only on particle size but also on spatial coordinates as well as time. There are two important requirements for treating this situation.

The first is with respect to the transition to eq 5.7 from eq 5.8. In the volume averaging of eq 5.7, it is necessary to replace the particle velocities with

\[
\frac{\langle X(v,x,t) f_1(v,x,t) \rangle}{n(v,x,t)}
\]

in which we have retained the assumption that the probability distribution, \( p \), for the relative positions of two particles continues to be independent of the absolute position of the particle pair. If, further, it is assumed that the number density does not vary substantially from its volumed-averaged value (which requires that the averaging domain be chosen to be not overly large), then expression 6.6 becomes \( \langle X(v,x,t) \rangle \).

The second is the modification of eq 6.2. The path representing the reverse of the relative motion of the particle of volume \( v' \) is traced by solving the differential equation

\[
\frac{dx}{dr} = X(v,x,t-r) - X(v,x,t-r), \quad \text{at } r = 0, \ X = x + r
\]

Denoting the solution to this differential equation by \( X(v,x,t-r) \), eq 6.2 becomes

\[
p(r - X(v,x,t-r)) v' r, t = \frac{1}{v_0}, \quad 0 \leq \tau \leq T_{rm}
\]

which must be substituted into eq 5.10 as before to obtain an expression for the aggregation frequency. We now assume that the local particle velocity is given by the local fluid velocity plus the terminal velocity of the particle relative to the local fluid velocity and express this quantity as

\[
X(v,x,t) = u(x,t) + U(v)
\]

which expresses the spatiotemporal dependence of the absolute velocity of the particle as being entirely due to the local fluid velocity and the size dependence as arising only as a result of the terminal velocity relative to the fluid. The velocity of the particle of volume \( v' \) at \( x + r \) relative to that of the particle of volume \( v \) at \( x \) can then be written as

\[
X(v',x+r,t) - X(v,x,t) = u(x+r,t) - u(x,t) + U(v') - U(v)
\]

where we can take the particle velocity relative to the fluid, \( U(v) \), to be rectilinear along some direction \( \mathbf{k} \). If we let \( D \equiv \nabla v \) be the local velocity deformation tensor for the fluid phase, then from eq 6.10, we can write

\[
X(v,x+r,t) - X(v,x,t) = D \cdot r + X_{rel} \mathbf{k}
\]

In eq 6.11, we have, of course, neglected the higher-order terms in the Taylor expansion, given that the magnitude of \( r \) is small as a consequence of the particles being small. Substituting eq 6.11 into the expression for the aggregation frequency, we obtain

\[
a_{rel}(v,v) = -\rho(v,v) \int \delta_r(\mathbf{D} \cdot \delta_r) a_{rel}(v,v')
\]

where \( a_{rel}(v,v') \) is the same frequency as defined in eq 6.5 and the spatiotemporal dependence of the aggrega-
tion frequency is evident from that of the tensor \( \mathbf{D} \). The population balance equation for this case becomes
\[
\frac{\partial n(v, x; t)}{\partial t} + \nabla \cdot (\mathbf{X}(v, x; t)) n(v, x; t) = \\
1 \int_0^\infty dv' \ n(v-v', x; t) n(v', x; t) - \\
\int_0^\infty dv' \ n(v-v', x; t) n(v', x; t) 
\] (6.13)

7. Scaling Analysis of Relative Motion and Aggregation

The purpose of this section is to consider the issue of when the assumption of perfect local mixing can be justified at any stage of the aggregation process. The particles are considered to be initially well-mixed. If we assume that the rate of aggregation is negligibly small relative to the rate of particle motion, which is assumed to be solenoidal, then the application of the divergence theorem to the integral, over the averaging volume, of the term \( \nabla \cdot \mathbf{X}(v, x; t) \) yields the result that, at the initial instant, the net flow of particles across the boundary of the averaging volume is zero. (This arises from the fact that the surrounding fluid might be incompressible flow and the motion of the particle relative to the fluid is independent of position under the circumstances considered herein.) Thus, the initial uniformity of the particle distribution is perpetuated within the averaging volume. In order that aggregation within the averaging volume be considered negligible, we perform the following scaling analysis.

Recall that \( L \) is the length scale of the volume of mixing. We further let \( N_o \) be the characteristic number density; \( v_o \) be the characteristic particle size (which can be the average size in the prevailing distribution); \( X_o \) be the characteristic absolute particle velocity; \( \Delta U_o \equiv |U(v_o + \sigma_o) - U(v_o - \sigma_o)| \) (where \( \sigma_o \) is the standard deviation about the mean particle size) be the characteristic relative velocity between a particle pair; and \( u_o \) be the fluid’s characteristic velocity, which has a characteristic gradient of \( D_o \). The absolute velocity of the particle, \( X_o \), can then be estimated as \( u_o + U(v_o) \). The quantity \( \rho(v, v) \) can be deemed to have the characteristic value \( \rho_o \equiv v_o^{3/2} \). Then, the characteristic aggregation rate can be estimated as \( N_o (\rho_o^{3} D_o + \rho_o^{2} \Delta U_o) \), while the characteristic rate of particle motion over the averaging volume is given by \( X_o/L \). For the rate of aggregation to be negligible compared to the rate of particle motion, the ratio of these two expressions must be considerably smaller than 1. In other words, we must have
\[
N_o (\rho_o^{3} D_o + \rho_o^{2} \Delta U_o) \ll X_o/L 
\] (7.1)

Inequality 7.1 can be readily justified by direct scaling of the population balance in eq 6.13. Defining the following dimensionless variables (quantities with asterisks)
\[
v \equiv v/v_o, \quad X \equiv X/X_o, \quad t \equiv t L/X_o, \quad \mathbf{X} \equiv X(X, t) = \int_0^\infty n(v, x; t) L^{-3} dv x, \quad a \equiv (\rho_o^{3} D_o + \rho_o^{2} \Delta U_o) \sigma_o, \quad \nabla \equiv L^{-1} \nabla \nabla 
\] (7.2)

and substituting into the population balance in eq 6.13, one obtains the dimensionless equation
\[
\frac{\partial n^v(v, x^v; t^v)}{\partial t^v} + \nabla \cdot (\mathbf{X}^v(v, x^v; t^v)) n^v(v, x^v; t^v) = \\
\frac{N_o (\rho_o^{3} D_o + \rho_o^{2} \Delta U_o)}{X_o} \left[ \int_0^\infty dv' a^v(v, v'; x^v; t^v) n^v(v, x^v; t^v) - \\
\int_0^\infty dv' a^v(v, v'; x^v; t^v) n^v(v, x^v; t^v) \right] 
\] (7.3)

The terms on the left-hand side of eq 7.3 are both \( O(1) \), and the aggregation terms on the right-hand side contained within the square brackets are also \( O(1) \). Thus, for the right-hand side (i.e., the net aggregation rate) to be negligible, it becomes essential that the coefficient of the square brackets term must be much smaller than 1, which is, of course, the condition implied by inequality 7.1. Inequality 7.1 can be construed as a stipulation on the size of the averaging volume (i.e., the scale of uniformity).

As an example, consider a situation in which the volume fraction of the dispersed phase is \( 10^{-2} \) with 100 \( \mu m \) as the average particle size. The number density is then on the order of \( 10^{10}/m^3 \). For \( D_o = 10^{-5} \), inequality 7.1 shows that the length scale of the averaging volume must be considerably less than \( 10 \) \( cm \). The implication is that the well-mixed volume is rather small, on the order of \( 1 \) \( cm^3 \) or less. If the volume fraction of the dispersed phase is reduced to \( 10^{-4} \) with the same sized particles under the same hydrodynamic conditions, inequality eq 7.1 leads to \( L \ll 1000 \) \( cm \), so that the scale of uniformity might even be as large as \( 1 \) \( m \). On the other hand, if the shear rate is increased ten fold, we are faced with a requirement of \( L \ll 1 \) \( cm \) (although this is without changing other kinematic quantities), which has a very small scale of uniformity, on the order of the average particle size. Thus, no uniformity is to be expected in this situation.

Consider the circumstances under which no local volume of uniform distribution of particles is available. In this case, we can choose an averaging volume \( \Omega_x \) (provided, of course, that it exists as, for example, in the case of small fluid velocity gradients) in which the particle motion does not change significantly so that an aggregation frequency is available through eq 6.12. Then, the population balance of interest is as shown in eq 6.13. (Note, however, that, in this case, the volume-averaged particle motion is the same as the local particle motion.) However, if such an averaging volume does not exist, one is forced to consider the population balance equation in its original form, viz.
\[
\frac{\partial f_v(v, x; t)}{\partial t} + \nabla \cdot (\mathbf{X}(v, x; t)) f_v(v, x; t) = \\
1 \int_0^\infty dv' \ \int_{S(x, v)} dA \ \delta_{r'} \mathbf{X}(v, x; t) - \\
\mathbf{X}(v-v', x+r; t)) f_v(v, x; t) f_v(v-v', x+r; t) - \\
\int_0^\infty dv' \ \int_{S(x, v)} dA \ \delta_{r'} \mathbf{X}(v, x; t) - \\
\mathbf{X}(v+v'; x+r; t) f_v(v, x; t) f_v(v, x+r; t) 
\] (7.4)

where the statistical independence of eq 5.6 has been written for the particle pair with specific sizes \( v \) and \( v' \) and with specified locations \( x \) and \( x' \).
8. Scope of Applications

There has been considerable interest in recent times on the formulation and solution of population balance equations for aggregating systems in which spatial heterogeneity is an inherent feature. The birth and death functions have the potential to vary with position and time, and it has been the objective of this paper to address the formulation of equations for the same.

Spatial heterogeneity might arise because of heterogeneity in hydrodynamic flow conditions so that the fluid mechanics of the continuous phase becomes an integral part of the formulation. The presence of the particulate phase increases the complexity of this formulation because of the mutual interaction between the fluid and particle phases, on which quantitative understanding is only beginning to emerge. Thus, the population balance equation such as either eq 6.13 or eq 7.4 must, in fact, be coupled with the equation of motion for the continuous phase. This equation of motion must be spatially averaged to account for the effect of the particles on the fluid so that it is applicable everywhere in space.

In many applications, the particle populations could approach densities too high to permit the usual neglect of multibody interactions. Hindered motion of polydisperse particles becomes very significant under such circumstances. Although little exists in the literature by way of general result in this regard, the use of population balances to interpret experimental data on hindered motion has resulted in size-specific particle velocities from the recent work of Kumar et al. Moreover, in a doctoral thesis, it was shown that the data (obtained for slowly creaming polydisperse emulsions) thus obtained can be described by an extension of the Richardson–Zaki correlation to include polydispersity. Such an expression also provides for the exchange of momentum between the fluid and particle phases, so that the coupled equations for the motion of the continuous phase and the detailed population balance equation provide a complete description of the fluid mechanics of such a description accounting for flow-dependent aggregation effects. We consider below the creaming of an emulsion in a vertical cylinder as an interesting example of such a formulation.

8.1. Creaming of a Stored Emulsion. Consider a vertical cylinder in which an emulsion containing a distribution of particles is stored. The droplets in the emulsion are creaming (or settling), thereby inducing motion in the continuous phase and clearly providing a dynamic environment for a combination of gravity and shear-induced coalescence of the droplets. It is of interest to consider the formulation of this problem. We assume cylindrical coordinates with axisymmetry for both the fluid and particle phases, so that no dependence of the variables of interest on the azimuthal angle, which we denote here by \(\alpha\), need be considered. The aqueous continuous phase is described by the velocity field \(\mathbf{u}(r,z,t)\), which is spared for convenience from any distinctive notation to remind us of its volume-averaged status. This vector field satisfies the following continuity and momentum equations. The latter are written for the radial and vertical components neglecting inertial forces, as the induced flow is assumed to be very slow.

\[
\frac{1}{r} \frac{\partial}{\partial r} (ru_r) + \frac{\partial (ru_z)}{\partial z} = 0 \tag{8.1}
\]

\[
\frac{\partial (1-\Phi)u_r}{\partial t} = -(1-\Phi) \frac{1}{\rho} \frac{\partial p}{\partial r} + \nu (1-\Phi) \left( \frac{1}{r} \frac{\partial}{\partial r} (ru_r) \right) + \frac{\partial^2 u_r}{\partial z^2} - \frac{1}{\rho} \int_0^\infty dv \mathbf{K}(v,\{\phi_v\})[u_r - \langle X_r(v,r,z,t) \rangle] \tag{8.2}
\]

\[
\frac{\partial (1-\Phi)u_z}{\partial t} = -(1-\Phi) \frac{1}{\rho} \frac{\partial p}{\partial z} - g + \nu (1-\Phi) \left( \frac{1}{r} \frac{\partial}{\partial r} (ru_z) \right) + \frac{\partial^2 u_z}{\partial z^2} - \frac{1}{\rho} \int_0^\infty dv \mathbf{K}(v,\{\phi_v\})[u_z - \langle X_z(v,r,z,t) \rangle] \tag{8.3}
\]

where \(\phi_v\) is the size-specific volume fraction density and \(\Phi = \int_0^\infty \phi_v \, dv\) is the overall volume fraction of the dispersed phase, \(\mathbf{K}(v,\{\phi_v\})\), given by Piroq, is the coefficient of momentum interaction between the fluid and particle phases; and the notation \(\langle \phi_v \rangle\) is used to denote the fact that \(K\) is a functional of the size-specific volume fraction, \(\phi_v\), expressed by

\[
\mathbf{K}(v,\{\phi_v\}) = \frac{\phi_v(v) u_v}{2(3v/4\pi)^{1/2}} \exp \left[ -\int_0^\infty \phi_v(v) \alpha(v, v') \, dv' \right] \tag{8.4}
\]

in which \(\alpha(v,v')\) is an empirically determined function, replacing the “exponent” in the Richardson–Zaki correlation for monodispersed suspensions. In eq 8.4, the volume fraction is understood to depend on both spatial and temporal coordinates for the application under consideration. Equations 8.1–8.3 are coupled to the volume-averaged population balance in eq 6.13 or 7.4. The choice of the population balance equation depends on the domain of analysis as determined by inequality 7.1 in accord with the discussion in section 7. Where the emulsion shows high volume fractions of the dispersed phase, inequality 7.1 is jeopardized so that the required population balance equation is given by eq 7.4. However, during the initial stages of the dynamics, one expects smaller population densities, thus justifying the use of the population balance in eq 6.13. Because a volume-averaged population balance equation is implied in this case, it is essential that a volume-averaged volume fraction distribution be used in eq 8.4. Because of the nonlinearity of eq 8.4, it is necessary that the averaging volume be sufficiently small that higher-order fluctuations in the number density be negligible within it.

The boundary conditions to be satisfied with respect to \(r\) are rather straightforward. The fluid velocity must satisfy the no-slip boundary conditions at \(r = R\), where \(R\) is the radius of the cylindrical column; at \(r = 0\), we have \(u_r = 0\). The boundary conditions for the number density depend on whether diffusion (Brownian motion, shear-induced diffusion, and so on) is included. The zero-slope condition also holds for the number density in the presence of diffusion. The boundary conditions with respect to \(z\) are as follows: At \(z = 0\) (the base of the column), \(u = 0\); for a creaming emulsion, the number density must vanish at this boundary as well. At the other end, say, \(z = h\), a free interface might involve a surface tension boundary condition. When particle densities climb to high values, the analysis becomes
considerably more complicated, and the framework presented here becomes increasingly inapplicable.

Acknowledgment

This paper is dedicated to Professor Reuel Shinnar for his many outstanding contributions to Chemical Engineering.

Literature Cited


Received for review July 25, 2003
Revised manuscript received October 25, 2003
Accepted October 27, 2003
IE0340239