New Discretization Procedure for the Agglomeration Equation

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A new discretization procedure for the agglomeration equation is presented. The intrinsic problems caused by discretization of the particle-size distribution are mitigated by using proper probability functions. Thus, the new discretized equation predicts the same total number of particles as its continuous counterpart and guarantees conservation of mass. This general method can correctly predict any two properties simultaneously and is not limited to number and mass. Simulation results with various agglomeration kernels show that the new method provides significant improvements over the conventional discretization method. Furthermore, the new method allows the user to choose equal-size intervals or geometric-size intervals with any geometric ratio to cover the particle-size range. In addition to flexibility, the latter feature leads to better accuracy in particle-size distribution predictions.

Introduction

Population balance equations (PBEs) are widely used for modeling particulate systems in which the particle-size distribution (PSD) changes due to nucleation, growth, dissolution, agglomeration, and breakage. In this article, we focus on a special form of the PBE, the *agglomeration equation.* The phenomenon of agglomeration or coalescence is prevalent in the chemical processing industry. Examples of equipment units in which agglomeration plays a significant role include crystallizers, aerosol reactors, liquid–liquid extractors, fluidized beds, porous emulsion coalescers, and demisters. In order to better design such units and characterize the particulates in all these units in a chemical plant, it is necessary to solve the agglomeration equation in process simulations. The *discretized PBEs* are preferred to the *continuous PBEs* in these efforts. Thus, N_i, the number of particles per unit volume of slurry or per unit mass of powder in size interval i is used in the place of a continuous number density function, $n(v)$, to describe the PSD of the particle population. As discussed in detail elsewhere (Hill and Ng, 1995), one of the reasons for this preference is that once discretized, the population balance is a set of differential equations for N_i. Without the explicit dependence on size, the agglomeration equation can be integrated using standard algorithms. The trade-off, however, is that loss of mass cannot be prevented at long times due to intrinsic discretization problems to be discussed below. We present in this article a new discretized agglomeration equation, which guarantees conservation of mass and predicts the same total number of particles as its continuous counterpart. The discussion focuses on batch processes; however, the method is equally valid for a system with inflow and outflow of particles.

Literature Review

Detailed reviews of population balance equations in general (Ramkrishna, 1985) and the agglomeration equation in particular (Drake, 1972) are available. The agglomeration equation on a volume basis for a batch system is

$$\frac{\partial n(v)}{\partial t}=\frac{1}{2}\int_0^v a(v-\epsilon,\ \epsilon)n(v-\epsilon)n(\epsilon)d\epsilon - n(v)\int_0^\infty a(v,\ \epsilon)n(\epsilon)d\epsilon, \quad (1)$$

where $a(v, \epsilon)$ is the coalescence kernel for agglomeration between particles of volume v and ϵ. It states that the rate of change of the number of particles between volumes v and $v+d_v$, $n(v)\ dv$, is the net result of generation due to agglomeration of two particles with a combined volume of v, and loss of particles of size v by agglomeration with particles of

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any size. The following three kernels are often encountered in the literature: a_0, $a_0(v+\epsilon)$, and $a_0 v\epsilon$. Thus, we have a constant kernel, a linear kernel, and a product kernel, respectively.

Moments are frequently used in describing a PSD. The jth moment of the number density function is defined as

$$m_j = \int_0^\infty v^j n(v)dv. \tag{2}$$

The zeroth moment corresponds to the total number of particles, and the first moment is the total particle volume. One can show by integrating Eq. 1 with respect to v that the time derivative of the first moment is zero for all three kernels. This is expected because of volume conservation. The corresponding expressions for the zeroth moment depend on the functional form of the coalescence kernel. For example, it can be readily shown that

$$\frac{dm_0}{dt} = -\frac{1}{2}a_0 m_0^2 \tag{3}$$

$$\frac{dm_0}{dt} = -a_0 m_0 m_1 \tag{4}$$

and

$$\frac{dm_0}{dt} = -\frac{1}{2}a_0 m_1^2 \tag{5}$$

for the constant, linear, and product kernels, respectively.

Conventional discretized agglomeration equation

In the *conventional discretized agglomeration equation*, the integral signs of the continuous equation are replaced by summation signs, and each continuous function is replaced with a corresponding discretized function. Thus, for each size interval of the discretized PSD, an average particle size is used to represent all other sizes in that interval. That is, the following equation is used:

$$\frac{dN_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} a_{j,i-j}N_j N_{i-j} - N_i \sum_{j=1}^{\infty} a_{i,j}N_j. \tag{6}$$

Obviously, Eq. 6 is an approximation of Eq. 1 for systems such as liquid–liquid dispersions, where liquid drop sizes change continuously. However, it is exact for a system consisting of particles, each of which can be considered to be an aggregate of unit-size particles of the smallest possible size (Ramabhadran et al., 1976). Hidy (1965) and Hidy and Lilly (1965) provided numerical solutions to Eq. 6 in this context.

Moments for discretized PSDs can be similarly defined by using summation in Eq. 2. The jth moment is

$$m_j = \sum_{i=1}^{\infty} \bar{v}_i^j N_i. \tag{7}$$

Here, $\bar{v}_i$ is any representative size for interval i. The arithmetic mean of the largest size (v_i) and smallest size (v_{i-1}) in interval i is chosen for use in the derivations below, that is,

$$\bar{v}_i = \frac{v_i + v_{i-1}}{2}. \tag{8}$$

The discretized coalescence kernels also use the arithmetic mean volumes. For example, the following expression is used for the linear kernel:

$$a_{ij} = a_0(\bar{v}_i + \bar{v}_j). \tag{9}$$

Since the continuous distribution has a nonuniform distribution of particles across a size interval, the actual average particle volume may be greater or less than the arithmetic mean. At a later stage, it will be shown that other definitions for $\bar{v}_i$ can be used in the derivations.

Intrinsic problems of discretization

To illustrate the two intrinsic problems of discretization, let us consider a discretized PSD with equal-size intervals (Figure 1). The intervals are numbered consecutively with the first interval containing particles of size ranging from v_0 (= 0) to v_1, v_1 to v_2 (= $2v_1$), and so on. Let us assume v_1 equals 1 mm^3 and focus on interval 5 with particle sizes ranging from 4 to 5 mm^3. When a particle of size 0.2 mm^3 from interval 1 agglomerates with a particle of size 4.2 mm^3 from interval 5, N_5 is automatically reduced by 1 because of the last term in Eq. 6. Actually, N_5 does not decrease because the child particle of volume 4.4 mm^3 belongs to the same interval. This error would cause an artificial loss in the total volume of particles. Now consider the agglomeration of a particle of size

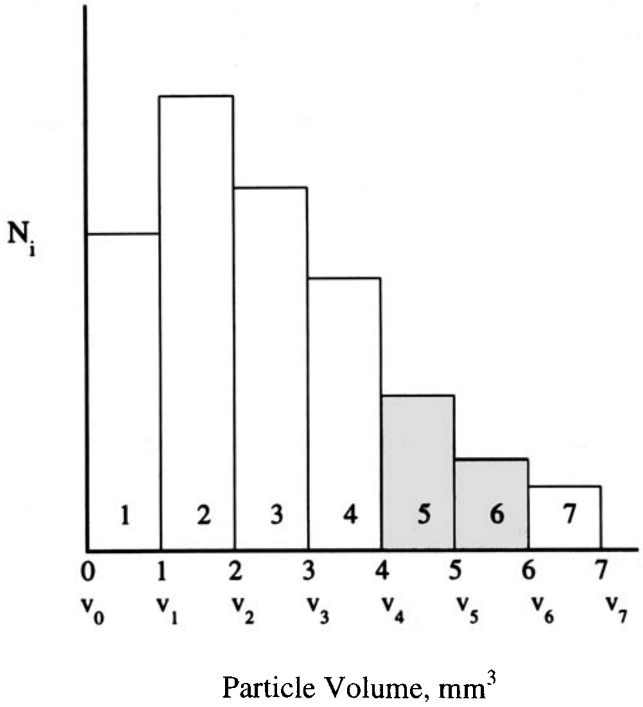


Figure 1. Equal-size intervals.

1.2 mm^3 from interval 2 with a particle of size 2.2 mm^3 from interval 3, N_5 is automatically increased by 1 because of the first righthand side (RHS) term in Eq. 6. However, the child particle of volume 3.4 mm^3 actually ends up in interval 4. Misplacing the child particle in a higher interval by Eq. 6 would result in an artificial gain in the total volume of particles.

Other discretization methods

A number of discretized equations have been proposed to mitigate the intrinsic discretization problems in the conventional discretized equation. Gelbard and Seinfeld (1980) and Gelbard et al. (1980) developed a sectional method that correctly predicts a single property such as the total particle number or volume. Landgrebe and Pratsinis (1990) extended this method to include chemical reactions. Sastry and Gaschignard (1981) developed two discretized equations: one predicts the total number of particles, and the other equation predicts mass. These methods can be used for equal-size intervals ($v_{i+1} - v_i$ = a constant) or for geometric-size intervals ($v_{i+1} = rv_i$) with a geometric ratio of r. However, a single discretized equation that would lead to both number and mass is not available.

Hounslow et al. (1988) and Hounslow (1990) considered a crystallizer with nucleation, growth, and coalescence. The discretized PBE was formulated in such a way that the total number of particles is not altered due to the discretization step, and the total volume of particles is conserved. However, the method is limited to geometric-size intervals with a geometric ratio of 2. Only very recently did a method for $r = 2^{1/q}$ where q is an integer ≥ 1 become available (Litster et al., 1995). In the simulation of crystallization with agglomeration, Marchal et al. (1988) modeled agglomeration between size intervals as a chemical reaction between species. However, the intrinsic problems of discretization were not considered. Hogg (1992) pointed out one of the intrinsic discretization problems—the total particle volume may not be conserved. Most relevant to this article is the work of Hill and Ng (1995), in which conservation of the number and volume of particles was achieved for the breakage equation by using proper probability functions. Here, we use a similar approach for discretizing the agglomeration equation. The new agglomeration equation can be used for equal-size intervals and geometric-size intervals with any geometric ratio.

New Discretization Method

Only binary agglomeration where two particles agglomerate to form a larger particle is considered. The following development leads to a single set of discretized equations for equal-size intervals, one equation for each size interval. For geometric-size intervals, the discretized equations change with the geometric ratio. There is a new set for each of the following geometric ratio ranges: $r \geq 2$, $1.618 \leq r < 2$, $1.4656 \leq r < 1.618$, $1.414 \leq r < 1.4656$, and so on. The reason for requiring different equation sets will become clear as we proceed further.

Equal intervals

The new agglomeration equation for equal intervals is developed based on two observations. The first observation is that when two particles from the same interval or two different intervals agglomerate, the child particle must fall into two adjacent intervals. Consider the particles in intervals 2 and 4 ranging in size from v_1 to $2v_1$ and from $3v_1$ to $4v_1$, respectively. Agglomeration between particles in these two intervals produces child particles ranging in size from $4v_1$ to $6v_1$. That is, the child particles fall into intervals 5 and 6, which are highlighted in Figure 1. Now consider the situation in reverse: What are the interval interactions that would result in a child particle in interval 5? We propose the following:

$$\frac{dN_5}{dt} = \frac{1}{4} \sum_{j=1}^{5} a_{6-j,j} N_{6-j} N_j. \tag{10}$$

Equation 10 states that a child particle in interval 5 can result from agglomeration of particles from intervals 1 and 5, and 2 and 4, and 3 and 3. One-half (1/2) of the one-fourth (1/4) prefactor is due to double counting in the summation. The other half (1/2) accounts for the fact that only half of the child particles fall into interval 5; the rest fall into interval 6.

The second observation is that the child particles formed in an interval may come from two sets of interval interactions. One set produces particles in intervals 5 and 6, while the other set produces particles in intervals 4 and 5. For interval 5, the first set is accounted for in Eq. 10. The second set includes interactions between particles from intervals 1 and 4 and intervals 2 and 3. Thus, the following additional birth term is required:

$$\frac{dN_5}{dt} = \frac{1}{4} \sum_{j=1}^{4} a_{5-j,j} N_{5-j} N_j. \tag{11}$$

To account for the loss of particles from interval 5, we have

$$\frac{dN_5}{dt} = -N_5 \sum_{j=1}^{\infty} a_{5,j} N_j. \tag{12}$$

Equation 12 presumes that all particles in interval 5 that agglomerate with another particle leave interval 5. It is possible for a particle from interval 5 to combine with a particle from interval 1 to form a child particle in interval 5. However, this possibility has already been accounted for in Eq. 10, which provides the proper correction to Eq. 12.

Generalization for any interval i yields

$$\frac{dN_i}{dt} = \frac{1}{4} \sum_{j=1}^{i-1} a_{i-j,j} N_{i-j} N_j + \frac{1}{4} \sum_{j=1}^{i} a_{i-j+1,j} N_{i-j+1} N_j - N_i \sum_{j=1}^{\infty} a_{i,j} N_j. \tag{13}$$

The zeroth and first moments of Eq. 13 are determined using Eq. 7. It can be shown that for all three coalescence kernels considered, the time derivative of the first moment is equal to zero for the discretized PSD. That is, mass is conserved. The time derivative of the zeroth moment is

$$\frac{d}{dt} m_0 = -\frac{1}{2} \sum_{i=1}^{\infty} N_i \sum_{j=1}^{\infty} a_{i,j} N_j. \tag{14}$$

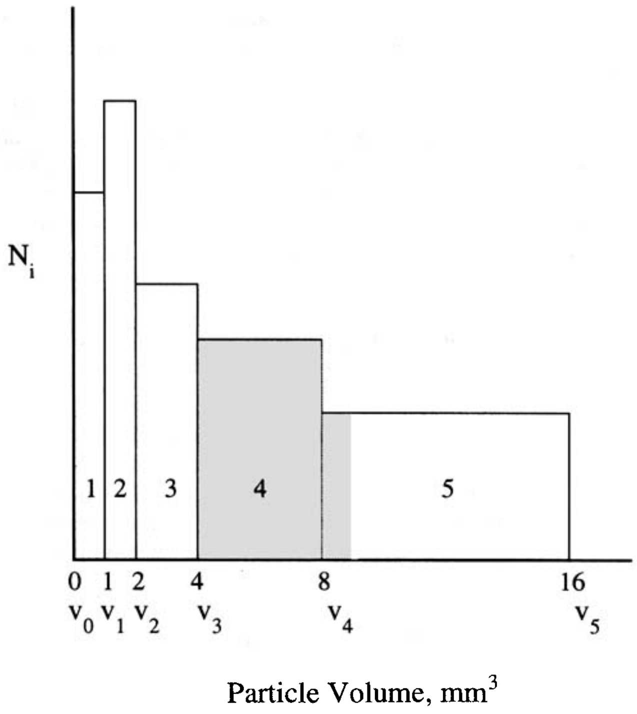


Figure 2. Geometric-size intervals with a ratio of 2.

The exact form of Eq. 14 depends on the functional form of the coalescence kernel. It can be shown that it reproduces the analytical results given in Eqs. 3 to 5. Actually, all other discretized equations to be developed below yield Eq. 14. They also conserve mass and reproduce the same zeroth moments, Eqs. 3 to 5, as the continuous agglomeration equation.

Geometric-size intervals: $r \geq 2$

As for equal intervals, the new discretized agglomeration equation for geometric-size intervals is developed based on a number of observations. Let us consider intervals with a geometric ratio of 2 (Figure 2) and let us focus on interval 5. For binary agglomeration, the larger one of the two parent particles must be at least half the size of the smallest particle in interval 5. That is, since a particle must be at least 8 mm^3 to be in interval 5, the larger parent particle must be at least 4 mm^3. Only particles from intervals 4 and 5 satisfy this requirement. Therefore, one birth term includes interactions between interval 4 and other intervals, while a second term includes interactions between interval 5 and other intervals. Thus, we have

$$\frac{dN_5}{dt} = N_4 \sum_{j=1}^{3} a_{4,j} N_j C_{4,j,5} + N_5 \sum_{j=1}^{4} a_{5,j} N_j D_{5,j,5}. \quad (15)$$

Here, C and D are two different probability functions.

In an interaction between two intervals, the resulting child particles are distributed over 2 adjacent intervals, $k-1$ and k. For example, when interval 1 interacts with interval 4, the child particles range in size from 4 to 9 mm^3, as highlighted in Figure 2, and are in intervals 4 and 5. The first RHS term in Eq. 15 reflects the fact that combining interval 4 with a lower interval causes the child particles to fall into intervals 4 and 5. Since not all of the child particles fall into interval 5, $C_{4,j,5}$ predicts the fraction of child particles, resulting from agglomeration of particles in intervals 4 and j, that fall into interval 5. Likewise, the second term reflects the fact that combining interval 5 with a lower interval causes the child particles to fall into intervals 5 and 6. To account for the fraction of child particles falling into interval 5, $D_{5,j,5}$ is used. In general, $C_{i,j,k}$ indicates the fraction of child particles that fall into the upper interval, k, from an interaction between particles in intervals i and j, while $D_{i,j,k-1}$ indicates the fraction of child particles that fall into the lower interval $k-1$.

When parent particles belonging to the same interval interact with each other, the term must be multiplied by one-half to avoid double counting. These terms are given by

$$\frac{dN_5}{dt} = \frac{1}{2} a_{4,4} N_4^2 C_{4,4,5} + \frac{1}{2} a_{5,5} N_5^2 D_{5,5,5}. \quad (16)$$

For $r = 2$, an inspection of Figure 2 shows that $D_{5,5,5}$ is zero. However, in the general case where $r > 2$, $D_{5,5,5}$ is greater than zero.

We can now generalize these observations for any interval. To form a particle in interval i by binary agglomeration, the two parent particles must have a combined volume greater than v_{i-1}. For this to be true, the larger one of the two particles must have a volume that is greater than half of v_{i-1}. When $r \geq 2$, only particles from intervals $i-1$ and larger satisfy this requirement. Since the parent particles cannot be from an interval larger than i, the larger parent particle must be from interval $i-1$ or interval i. A particle from any of the smaller intervals may combine with a particle in interval $i-1$ or i to form a particle in interval i.

Two particles from interval $i-1$ may coalesce with each other or two particles from interval i may coalesce with each other to form a particle in interval i. If one particle from interval i is labeled A and another particle is labeled B, then the term $a_{ii} N_i N_i$ counts the interaction between particles A and B twice. For such intrainterval interactions, the term must be multiplied by one-half to avoid double counting.

A discretized equation that takes these considerations into account is

$$\begin{aligned}\frac{dN_i}{dt} &= N_{i-1} \sum_{j=1}^{i-2} a_{i-1,j} N_j C_{i-1,j,i} + N_i \sum_{j=1}^{i-1} a_{i,j} N_j D_{i,j,i} \\ &\quad + \frac{1}{2} a_{i-1,i-1} N_{i-1}^2 C_{i-1,i-1,i} + \frac{1}{2} a_{i,i} N_i^2 D_{i,i,i}, \\ &\quad - N_i \sum_{j=1}^{\infty} a_{i,j} N_j. \quad (17)\end{aligned}$$

The last term presumes that every particle in i that agglomerates with another particle leaves interval i. This is corrected by the second and the fourth RHS terms. Together, the second, the fourth, and the fifth RHS terms account for the number of particles in i that leave the interval. The first and third RHS terms account for birth due to agglomeration in smaller size intervals.

The probability functions $C_{i,j,k}$ and $D_{i,j,k-1}$ can be determined as follows. Since $C_{i,j,k}$ and $D_{i,j,k-1}$ represent the fractions that fall into intervals k and $k-1$, respectively, the following constraint is imposed:

$$C_{i,j,k} + D_{i,j,k-1} = 1. \tag{18}$$

To conserve volume, the volume of the particles removed from intervals i and j must be equal to the volume of particles formed in intervals k and $k-1$. Therefore, the following equation must be true:

$$\bar{v}_i + \bar{v}_j = \bar{v}_k C_{i,j,k} + \bar{v}_{k-1} D_{i,j,k-1}. \tag{19}$$

Solving Eqs. 18 and 19 simultaneously yields

$$C_{i,j,k} = \frac{\bar{v}_i + \bar{v}_j - \bar{v}_{k-1}}{\bar{v}_k - \bar{v}_{k-1}} \tag{20}$$

and

$$D_{i,j,k-1} = \frac{\bar{v}_k - \bar{v}_i - \bar{v}_j}{\bar{v}_k - \bar{v}_{k-1}}. \tag{21}$$

If r is exactly equal to 2 and i is greater than one, a coalescence between interval i and itself yields no particles in interval i. Therefore, $D_{i,i,i}$ should be equal to zero and $C_{i,i,i+1}$ should be equal to one. An inspection of the preceding equations shows that these conditions are met.

Substituting $C_{i,j,k}$ and $D_{i,j,k-1}$ into Eq. 17 yields the following discretized equation:

$$\begin{aligned}\frac{dN_i}{dt} &= N_{i-1} \sum_{j=1}^{i-2} a_{i-1,j} N_j \left(\frac{\bar{v}_j}{\bar{v}_i - \bar{v}_{i-1}} \right) \\ &+ N_i \sum_{j=1}^{i-1} a_{i,j} N_j \left(\frac{\bar{v}_{i+1} - \bar{v}_i - \bar{v}_j}{\bar{v}_{i+1} - \bar{v}_i} \right) + \frac{1}{2} a_{i-1,i-1} N_{i-1}^2 \left(\frac{\bar{v}_{i-1}}{\bar{v}_i - \bar{v}_{i-1}} \right) \\ &+ \frac{1}{2} a_{i,i} N_i^2 \left(\frac{\bar{v}_{i+1} - 2\bar{v}_i}{\bar{v}_{i+1} - \bar{v}_i} \right) - N_i \sum_{j=1}^{\infty} a_{i,j} N_j. \end{aligned} \tag{22}$$

In summary, the observations which apply for $r \geq 2$ are as follows:

1. The death term assumes that any interaction of an interval with any other interval would remove particles from both intervals. Any child particles falling back into the parent particle interval are accounted for in the birth terms.
2. To form a particle in interval i, one parent particle must be from interval $i-1$ or interval i. In either case, any combination with a lower interval may produce particles in interval i.
3. Child particles may be formed in interval i by an intrainterval interaction in interval $i-1$.
4. Child particles may be formed in interval i by an intrainterval interaction in interval i.
5. With an intrainterval interaction in interval i, the number of child particles that fall back into i approaches zero as the geometric ratio decreases to two. With an intrainterval interaction in interval $i-1$, all of the child particles fall into i when the geometric ratio decreases to two.

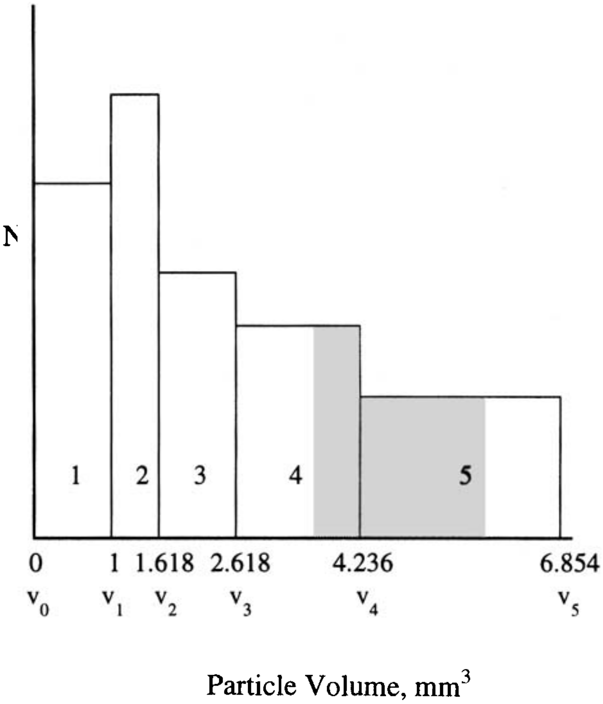


Figure 3. Geometric-size intervals with a ratio of 1.618.

Geometric-size intervals: 1.618 ≤ r < 2

An examination of intervals with a geometric ratio of 1.618 provides the rules for setting up the discretized equation (Figure 3). We consider below how particles may be produced in interval 5. If one of the parent particles is from interval 4, then a combination of interval 4 with any smaller interval may produce a child particle in interval 5. For example, when intervals 4 and 2 interact, the child particles range from 3.618 to 5.854 mm^3, as highlighted in Figure 3. Also, if one of the parent particles is from interval 5, then it may combine with a particle from any smaller interval to produce a particle in interval 5. For example, when particles from intervals 2 and 5 agglomerate, the child particles may range in size from to 5.236 to 8.472 mm^3. These two possibilities are modeled as:

$$\frac{dN_5}{dt} = N_4 \sum_{j=1}^{3} a_{4,j} N_j C_{4,j,5} + N_5 \sum_{j=1}^{4} a_{5,j} N_j D_{5,j,5}. \tag{23}$$

As before, C and D are probability functions to account for the fact that the child particles are spread over two adjacent intervals. The factors $C_{4,j,5}$ and $D_{5,j,5}$ indicate the fraction of child particles that fall into interval 5.

When interval 2 combines with itself, the largest possible child particle is 3.236 mm^3. Since this is not large enough to enter interval 5, there is no term for interval 2 interacting with itself. For the same reason, there is not a term for the first interval acting with itself. However, if interval 3 interacts with itself, it produces particles ranging from 3.236 to 5.236 mm^3. Therefore, there are some child particles formed in interval 5 from an intrainterval interaction in interval 3. Child particles in interval 5 may also be formed from an intrainterval interaction in interval 4. These two contributions are accounted for

$$\frac{dN_5}{dt} = \frac{1}{2} a_{3,3} N_3^2 C_{3,3,5} + \frac{1}{2} a_{4,4} N_4^2 D_{4,4,5}. \tag{24}$$

Again, the factor of one-half is used to avoid double counting. If there is an intrainterval interaction in interval 5, all of the child particles are too large to be included in interval 5. Therefore, this term is not included.

The preceding results can be generalized for any interval greater than 3:

$$\frac{dN_i}{dt} = N_{i-1} \sum_{j=1}^{i-2} a_{i-1,j} N_j C_{i-1,j,i} + N_i \sum_{j=1}^{i-1} a_{i,j} N_j D_{i,j,i} + \frac{1}{2} a_{i-2,i-2} N_{i-2}^2 C_{i-2,i-2,i} + \frac{1}{2} a_{i-1,i-1} N_{i-1}^2 D_{i-1,i-1,i} - N_i \sum_{j=1}^{\infty} a_{i,j} N_j, \tag{25}$$

where $C_{i,j,k}$ and $D_{i,j,k-1}$ can be determined as before. For all i and j where either i or j is greater than one, Eqs. 20 and 21 are used for $C_{i,j,k}$ and $D_{i,j,k-1}$. Equations for intervals 1, 2, and 3 require special treatment, which is discussed at at later stage.

The first RHS term of Eq. 25 indicates that interval $i-1$ may interact with any lower interval to form a particle in interval i. An interaction between intervals i and $i-1$ does not produce particles in interval i when $v_{i-1} + v_{i-2} \geq v_i$. This condition can be restated as $rv_{i-2} + v_{i-2} \geq r^2 v_{i-2}$ or $r^2 - r - 1 \leq 0$. In other words, when $r \leq 1.618$, no particles are produced in interval i from this interaction. Similarly, the second RHS term indicates that interval i may interact with any lower interval to produce a particle in interval i.

Intrainterval interactions in interval $i-2$ can produce particles in interval i. In general terms, the largest particle in interval $i-2$ has a volume of v_{i-2}, while the smallest particle in interval i has a volume of v_{i-1}. To produce a particle in interval i from two particles in interval $i-2$, the combined volume of the two particles in interval $i-2$ must be greater than the minimum particle volume in interval i. Mathematically, we must have $2v_{i-2} > v_{i-1}$, which can be simplified to $r < 2$. Likewise, to produce a particle in interval i from an interaction between intervals $i-2$ and $i-3$, we require $v_{i-2} + v_{i-3} \geq v_{i-1}$, which can be rearranged to $r^2 - r - 1 \leq 0$. Solving for r, we get $r \leq 1.618$. Therefore, for $r > 1.618$, there is no interaction between interval $i-2$ and a lower interval. Thus, for $2 > r \geq 1.618$, the term $a_{i-2,i-2} N_{i-2}^2$ is included and no term is included for the interaction of interval $i-2$ with a smaller interval. Similarly, the fourth term accounts for the intrainterval interactions in interval $i-1$.

As the geometric ratio approaches two, the number of particles formed in interval i from an intrainterval interaction in interval $i-2$ approaches zero. An examination of Figure 2 shows this to be true. Specifically, considering interval 5, the minimum particle size is greater than 8 mm^3 and the maximum particle size in interval 3 is 4 mm^3. Therefore, the other parent particle must be larger than 4 mm^3 and cannot come from interval 3. This limit is reflected in the equations for $C_{i,j,k}$ and $D_{i,j,k-1}$, and this is the reason for the absence of an $a_{i-2,i-2} N_{i-2}^2$ term in Eq. 22.

For all intervals other than interval 1, agglomeration between particles in interval i does not produce any particles in the same interval. An example of this is shown in Figure 3, where an agglomeration between particles in interval 2 produces particles only in intervals 3 and 4. The reason is that the smallest child particles formed by intrainterval agglomeration in interval i must be of size $2v_{i-1}$, but the largest particle in interval i is of size v_i or rv_{i-1}. As long as $2v_{i-1} > rv_{i-1}$ or $r < 2$, the child particles cannot fall back into interval i. The exception to this is interval 1 where $v_1 \neq rv_0$. Therefore, unlike Eq. 22, there is not an $a_{i,i} N_i N_i$ term in Eq. 25 for interval i.

The last term is the death term and it assumes that any interaction of an interval with any other interval removes particles from both intervals. Any child particles falling back into the parent particle interval are accounted for in the birth terms.

When particles agglomerate with each other in interval 1, they may produce particles in intervals 1, 2, and 3. In general terms, the particles formed may range in size from zero to $2v_1$, but the maximum particle size in interval 2 is rv_1. When $r < 2$, child particles may fall into intervals beyond interval 2; when $r \geq 2$, there are no particles formed beyond interval 2. As long as $v_3 \geq 2v_1$ or $r^2 \geq 2$, the child particles do not fall into any interval beyond interval 3. For this reason, there are special equations for the first three intervals, which differ from the general equation. The following set of discretized equations takes these observations into account:

For $i = 1$:

$$\frac{dN_1}{dt} = \frac{1}{2} a_{1,1} N_1^2 G_{1,1,1} - N_1 \sum_{j=1}^{\infty} a_{1,j} N_j. \tag{26}$$

For $i = 2$:

$$\frac{dN_2}{dt} = a_{2,1} N_2 N_1 D_{2,1,2} + \frac{1}{2} a_{1,1} N_1^2 F_{1,1,2} - N_2 \sum_{j=1}^{\infty} a_{2,j} N_j. \tag{27}$$

For $i = 3$:

$$\frac{dN_3}{dt} = a_{2,1} N_2 N_1 C_{2,1,3} + N_3 \sum_{j=1}^{2} a_{3,j} N_j D_{3,j,3} + \frac{1}{2} a_{1,1} N_1^2 E_{1,1,3} + \frac{1}{2} a_{2,2} N_2^2 D_{2,2,3} - N_3 \sum_{j=1}^{\infty} a_{3,j} N_j. \tag{28}$$

There is an $a_{1,1} N_1^2$ term in each of Eqs. 26 to 28; the other terms in these equations can be deduced from Eq. 25. The factors $E_{1,1,3}$, $F_{1,1,2}$, and $G_{1,1,1}$ are new probability functions which represent the fractions of particles produced in intervals 3, 2, and 1, respectively. This imposes the following constraint:

$$E_{1,1,3} + F_{1,1,2} + G_{1,1,1} = 1. \tag{29}$$

To conserve volume, the volume of the particles removed from intervals i and j must be equal to the volume of child particles formed in intervals 1, 2, and 3. Therefore, the following equation must be true:

$$2\bar{v}_1 = \bar{v}_3 E_{1,1,3} + \bar{v}_2 F_{1,1,2} + \bar{v}_1 G_{1,1,1}. \tag{30}$$

With two equations and three unknowns, one of the variables must be set arbitrarily. Since this interaction could produce particles ranging in size from zero to $2v_1$, as a first approximation, we assume that half of the particles would be smaller than v_1 and the other half would be larger. Solving Eqs. 29 and 30 simultaneously with $G_{1,1,1}$ equal to 0.5 yields

$$E_{1,1,3} = \frac{1.5\bar{v}_1 - 0.5\bar{v}_2}{\bar{v}_3 - \bar{v}_2} \tag{31}$$

and

$$F_{1,1,2} = \frac{0.5\bar{v}_3 - 1.5\bar{v}_1}{\bar{v}_3 - \bar{v}_2}. \tag{32}$$

As required, $E_{1,1,3}$ approaches zero and $F_{1,1,2}$ approaches one-half as the geometric ratio approaches two.

Substituting $C_{i,j,k}$, $D_{i,j,k-1}$, $E_{1,1,3}$, $F_{1,1,2}$, and $G_{1,1,1}$ into Eqs. 25 through 28 yields the following results:

For $i = 1$:

$$\frac{dN_1}{dt} = \frac{1}{4} a_{1,1} N_1^2 - N_1 \sum_{j=1}^{\infty} a_{1,j} N_j. \tag{33}$$

For $i = 2$:

$$\frac{dN_2}{dt} = a_{1,2} N_2 N_1 \frac{\bar{v}_3 - \bar{v}_2 - \bar{v}_1}{\bar{v}_3 - \bar{v}_2} + \frac{1}{2} a_{1,1} N_1^2 \frac{0.5\bar{v}_3 - 1.5\bar{v}_1}{\bar{v}_3 - \bar{v}_2} - N_2 \sum_{j=1}^{\infty} a_{2,j} N_j. \tag{34}$$

For $i = 3$:

$$\frac{dN_3}{dt} = a_{1,2} N_2 N_1 \frac{\bar{v}_1}{\bar{v}_3 - \bar{v}_2} + N_3 \sum_{j=1}^{2} a_{3,j} N_j \frac{\bar{v}_4 - \bar{v}_3 - \bar{v}_j}{\bar{v}_4 - \bar{v}_3} + \frac{1}{2} a_{1,1} N_1^2 \frac{1.5\bar{v}_1 - 0.5\bar{v}_2}{\bar{v}_3 - \bar{v}_2} + \frac{1}{2} a_{2,2} N_2^2 \frac{\bar{v}_4 - 2\bar{v}_2}{\bar{v}_4 - \bar{v}_3} - N_3 \sum_{j=1}^{\infty} a_{3,j} N_j. \tag{35}$$

For $i > 3$:

$$\frac{dN_i}{dt} = N_{i-1} \sum_{j=1}^{i-2} a_{i-1,j} N_j \frac{\bar{v}_j}{\bar{v}_i - \bar{v}_{i-1}} + N_i \sum_{j=1}^{i-1} a_{i,j} N_j \frac{\bar{v}_{i+1} - \bar{v}_i - \bar{v}_j}{\bar{v}_{i+1} - \bar{v}_i} + \frac{1}{2} a_{i-2,i-2} N_{i-2}^2 \frac{2\bar{v}_{i-2} - \bar{v}_{i-1}}{\bar{v}_i - \bar{v}_{i-1}} + \frac{1}{2} a_{i-1,i-1} N_{i-1}^2 \frac{\bar{v}_{i+1} - 2\bar{v}_{i-1}}{\bar{v}_{i+1} - \bar{v}_i} - N_i \sum_{j=1}^{\infty} a_{i,j} N_j. \tag{36}$$

In summary, observations 1 and 3 are still true, but observations 2, 4 and 5 no longer apply. Additional observations for these equations are:

6. For all intervals other than interval 1, agglomeration between particles in interval i does not produce any particles in the same interval. Therefore, except for interval 1, there is not an $a_{i,i} N_i N_i$ term in the equation for interval i.
7. To form a particle in interval i, one parent particle must be from interval $i-2$, $i-1$, or i. Agglomeration between particles in intervals $i-1$ or i with any smaller interval may form a particle in interval i.
8. Particles in interval $i-2$ cannot form particles in interval i if combined with particles from lower intervals, but there may be an intrainterval interaction to produce particles in interval i. For this reason, an $a_{i-2,i-2}\ N_{i-2}^2$ term is included.
9. As the geometric ratio approaches two, the number of particles formed in interval i from an intrainterval interaction in interval $i-2$ approaches zero.
10. An interaction between intervals i and $i-1$ produces particles in interval i. When $r \leq 1.618$, no particles are produced in interval i from this interaction.
11. When particles agglomerate with each other in interval 1, they may produce particles in intervals 1, 2, and 3.

Geometric-size intervals: 1.4656 ≤ r < 1.618

For this range of geometric ratios, observations 1, 3, 6, and 11 are valid. These and the following observations can be obtained by examining a figure with a geometric ratio of 1.4656 (Figure 4):

12. To form a particle in interval i, one parent particle must be from interval $i-2$, $i-1$, or i. Agglomeration between particles in interval $i-1$ with any smaller interval may form a particle in interval i.
13. For all intervals other than the first two intervals, agglomeration between particles in intervals i and $i-1$ does not produce any particles in interval i. However, an interaction between interval i and an interval smaller than $i-1$ produces particles in interval i.
14. Particles in interval $i-2$ cannot form particles in interval i if combined with particles from intervals smaller than $i-3$. It may have an intrainterval interaction to produce particles in interval i. As r approaches 1.618, the number of particles formed in interval i from intervals $i-2$ and $i-3$ approaches zero.
15. As the geometric ratio approaches 1.4656, the number of particles formed in interval i from intervals i and $i-2$ approaches zero.
16. When particles agglomerate between intervals 1 and 2, they may produce particles in intervals 2, 3, and 4. As the

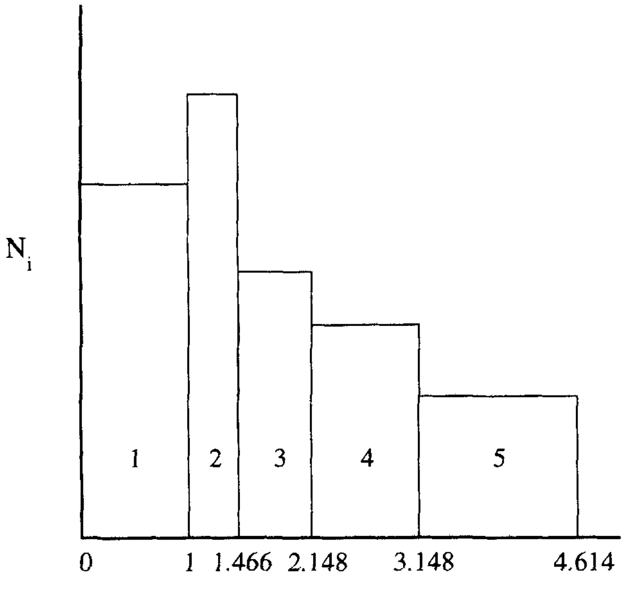


Figure 4. Geometric-size intervals with a ratio of 1.466.

geometric ratio approaches 1.618, the number of particles formed in interval 4 approaches zero.

Due to observations 11 and 16, there are special equations for intervals 1, 2, 3, and 4. Intervals larger than four may be modeled by a general equation. The new set of discretized equations is given in Table 1.

Geometric-size intervals: 1.414 ≤ r < 1.4656

Previous observations still valid are 1, 3, 6, 11, 12, and 16. For this range of geometric ratios, the following additional rules apply:

17. For all intervals other than the first two intervals, agglomeration between particles in intervals i and $i-1$ or between intervals i and $i-2$ does not produce any particles in interval i. However, interval i may combine with any interval smaller than $i-2$ to form a particle in interval i.
18. Particles in interval $i-2$ cannot form particles in interval i if combined with particles from intervals smaller than $i-4$. It may have an intrainterval interaction to produce particles in interval i. As the geometric ratio approaches 1.4656, the number of particles formed in interval i from intervals $i-2$ and $i-4$ approaches zero.
19. As the geometric ratio approaches 1.414, the number of particles formed in interval i from intraintervals interactions within interval $i-1$ approaches zero. When particles agglomerate within interval i for $i > 2$, they may produce particles only in interval $i+2$ when $r = 1.414$.
20. When particles agglomerate between intervals 1 and 3, they may produce particles in intervals 3, 4 and 5. As the geometric ratio approaches 1.4656, the number of particles formed in interval 5 approaches zero.

Due to observations 11, 16, and 20, there are special equations for intervals 1 through 5. Intervals larger than 5 may be modeled by a general equation. The new set of discretized equations is given in Table 2.

Agglomeration equations for 1 < r < 1.414

We now describe how to extend the derivations just given to smaller geometric ratios. We first determine the range of r over which a set of observations is valid. To do this, it is necessary to determine the endpoints of the size ranges. One place to look for these endpoint values is the intrainterval

Table 1. Agglomeration Equations for 1.4656 ≤ *r* < 1.618

For $i = 1$, Eq. 33 can be used as given. For $i = 2$:

$$\frac{dN_2}{dt} = a_{1,2}N_2N_1\frac{\bar{v}_3-\bar{v}_2}{\bar{v}_4-\bar{v}_2} + \frac{1}{2}a_{1,1}N_1^2\frac{0.5\bar{v}_3-1.5\bar{v}_1}{\bar{v}_3-\bar{v}_2} - N_2\sum_{j=1}^{\infty}a_{2,j}N_j. \tag{37}$$

For $i = 3$:

$$\frac{dN_3}{dt} = a_{1,2}N_2N_1\frac{\bar{v}_4-\bar{v}_3-\bar{v}_1}{\bar{v}_4-\bar{v}_3} + a_{1,3}N_3N_1\frac{\bar{v}_4-\bar{v}_3-\bar{v}_1}{\bar{v}_4-\bar{v}_3} + \frac{1}{2}a_{1,1}N_1^2\frac{1.5\bar{v}_1-0.5\bar{v}_2}{\bar{v}_3-\bar{v}_2} + \frac{1}{2}a_{2,2}N_2^2\frac{\bar{v}_4-2\bar{v}_2}{\bar{v}_4-\bar{v}_3} - N_3\sum_{j=1}^{\infty}a_{3,j}N_j. \tag{38}$$

For $i = 4$:

$$\frac{dN_4}{dt} = a_{1,2}N_2N_1\left(\frac{\bar{v}_2-\bar{v}_3}{\bar{v}_4-\bar{v}_2} + \frac{\bar{v}_1}{\bar{v}_4-\bar{v}_3}\right) + a_{1,3}N_3N_1\frac{\bar{v}_1}{\bar{v}_4-\bar{v}_3} + a_{2,3}N_3N_2\frac{\bar{v}_5-\bar{v}_3-\bar{v}_2}{\bar{v}_5-\bar{v}_4} + N_4\sum_{j=1}^{2}a_{4,j}N_j\frac{\bar{v}_5-\bar{v}_4-\bar{v}_j}{\bar{v}_5-\bar{v}_4} + \frac{1}{2}a_{2,2}N_2^2\frac{2\bar{v}_2-\bar{v}_3}{\bar{v}_4-\bar{v}_3} + \frac{1}{2}a_{3,3}N_3^2\frac{\bar{v}_5-2\bar{v}_3}{\bar{v}_5-\bar{v}_4} - N_4\sum_{j=1}^{\infty}a_{4,j}N_j. \tag{39}$$

For $i > 4$:

$$\frac{dN_i}{dt} = a_{i-2,i-3}N_{i-2}N_{i-3}\frac{\bar{v}_{i-2}+\bar{v}_{i-3}-\bar{v}_{i-1}}{\bar{v}_i-\bar{v}_{i-1}} + a_{i-1,i-2}N_{i-1}N_{i-2}\frac{\bar{v}_{i+1}-\bar{v}_{i-1}-\bar{v}_{i-2}}{\bar{v}_{i+1}-\bar{v}_i} + N_{i-1}\sum_{j=1}^{i-3}a_{i-1,j}N_j\frac{\bar{v}_j}{\bar{v}_i-\bar{v}_{i-1}} + N_i\sum_{j=1}^{i-2}a_{i,j}N_j\frac{\bar{v}_{i+1}-\bar{v}_i-\bar{v}_j}{\bar{v}_{i+1}-\bar{v}_i} + \frac{1}{2}a_{i-2,i-2}N_{i-2}^2\frac{2\bar{v}_{i-2}-\bar{v}_{i-1}}{\bar{v}_i-\bar{v}_{i-1}} + \frac{1}{2}a_{i-1,i-1}N_{i-1}^2\frac{\bar{v}_{i+1}-2\bar{v}_{i-1}}{\bar{v}_{i+1}-\bar{v}_i} - N_i\sum_{j=1}^{\infty}a_{i,j}N_j. \tag{40}$$

Table 2. Agglomeration Equations for $1.414 \le r < 1.4656$

For $i = 1$, Eq. 33 can be used as given. For $i = 2$, Eq. 37 can be used as given.

For $i = 3$:

$$\frac{dN_3}{dt} = a_{1,2}N_2N_1\frac{\bar{v}_4 - \bar{v}_3 - \bar{v}_1}{\bar{v}_4 - \bar{v}_3} + a_{1,3}N_3N_1\frac{\bar{v}_4 - \bar{v}_3}{\bar{v}_5 - \bar{v}_3} + \frac{1}{2}a_{1,1}N_1^2\frac{1.5\bar{v}_1 - 0.5\bar{v}_2}{\bar{v}_3 - \bar{v}_2} + \frac{1}{2}a_{2,2}N_2^2\frac{\bar{v}_4 - 2\bar{v}_2}{\bar{v}_4 - \bar{v}_3} - N_3\sum_{j=1}^{\infty} a_{3,j}N_j. \tag{41}$$

For $i = 4$:

$$\frac{dN_4}{dt} = a_{1,2}N_2N_1\left(\frac{\bar{v}_2 - \bar{v}_3}{\bar{v}_4 - \bar{v}_2} + \frac{\bar{v}_1}{\bar{v}_4 - \bar{v}_3}\right) + a_{1,3}N_3N_1\left(1 - \frac{\bar{v}_1}{\bar{v}_5 - \bar{v}_4}\right) + a_{2,3}N_3N_2\frac{\bar{v}_5 - \bar{v}_3 - \bar{v}_2}{\bar{v}_5 - \bar{v}_4}$$
$$+ a_{1,4}N_1N_4\frac{\bar{v}_5 - \bar{v}_4 - \bar{v}_1}{\bar{v}_5 - \bar{v}_4} + \frac{1}{2}a_{2,2}N_2^2\frac{2\bar{v}_2 - \bar{v}_3}{\bar{v}_4 - \bar{v}_3} + \frac{1}{2}a_{3,3}N_3^2\frac{\bar{v}_5 - 2\bar{v}_3}{\bar{v}_5 - \bar{v}_4} - N_4\sum_{j=1}^{\infty} a_{4,j}N_j. \tag{42}$$

For $i = 5$:

$$\frac{dN_5}{dt} = a_{13}N_1N_3\left(\frac{\bar{v}_1}{\bar{v}_5 - \bar{v}_4} + \frac{\bar{v}_3 - \bar{v}_4}{\bar{v}_5 - \bar{v}_3}\right) + a_{1,4}N_4N_1\frac{\bar{v}_1}{\bar{v}_5 - \bar{v}_4} + a_{2,3}N_2N_3\frac{\bar{v}_2 + \bar{v}_3 - \bar{v}_4}{\bar{v}_5 - \bar{v}_4} + N_4\sum_{j=2}^{3} a_{4,j}N_j\frac{\bar{v}_6 - \bar{v}_4 - \bar{v}_j}{\bar{v}_6 - \bar{v}_5}$$
$$+ N_5\sum_{j=1}^{2} a_{5,j}N_j\frac{\bar{v}_6 - \bar{v}_5 - \bar{v}_j}{\bar{v}_6 - \bar{v}_5} + \frac{1}{2}a_{3,3}N_3^2\frac{2\bar{v}_3 - \bar{v}_4}{\bar{v}_5 - \bar{v}_4} + \frac{1}{2}a_{4,4}N_4^2\frac{\bar{v}_6 - 2\bar{v}_4}{\bar{v}_6 - \bar{v}_5} - N_5\sum_{j=1}^{\infty} a_{5,j}N_j. \tag{43}$$

For $i > 5$:

$$\frac{dN_i}{dt} = N_{i-2}\sum_{j=i-4}^{i-3} a_{i-2,j}N_j\frac{\bar{v}_{i-2} + \bar{v}_j - \bar{v}_{i-1}}{\bar{v}_i - \bar{v}_{i-1}} + N_{i-1}\sum_{j=1}^{i-4} a_{i-1,j}N_j\frac{\bar{v}_j}{\bar{v}_i - \bar{v}_{i-1}}$$
$$+ N_{i-1}\sum_{j=i-3}^{i-2} a_{i-1,j}N_j\frac{\bar{v}_{i+1} - \bar{v}_{i-1} - \bar{v}_j}{\bar{v}_{i+1} - \bar{v}_i} + N_i\sum_{j=1}^{i-3} a_{i,j}N_j\frac{\bar{v}_{i+1} - \bar{v}_i - \bar{v}_j}{\bar{v}_{i+1} - \bar{v}_i}$$
$$+ \frac{1}{2}a_{i-2,i-2}N_{i-2}^2\frac{2\bar{v}_{i-2} - \bar{v}_{i-1}}{\bar{v}_i - \bar{v}_{i-1}} + \frac{1}{2}a_{i-1,i-1}N_{i-1}^2\frac{\bar{v}_{i+1} - 2\bar{v}_{i-1}}{\bar{v}_{i+1} - \bar{v}_i} - N_i\sum_{j=1}^{\infty} a_{i,j}N_j. \tag{44}$$

interaction in interval 1, where the maximum size of the particle formed is $2v_1$. Since v_2 is rv_1, the particles fall into two intervals when $rv_1 \ge 2v_1$ or $r \ge 2$. Since v_3 is r^2v_1, the particles fall into three intervals when $\sqrt{2} \le r < 2$. Similarly, since v_4 is r^3v_1, the particles fall into four intervals when $\sqrt[3]{2} \le r < \sqrt{2}$. In general, the particles fall into h' intervals when $2^{1/(h'-1)} \le r < 2^{1/(h'-2)}$, where h' is an integer greater than 2. Therefore, endpoints of ranges include any nonnegative integral root of 2, that is, 1.414, 1.260, 1.189, and so on.

A similar approach can be taken for the interaction between intervals i and $i+1$, where $i > 1$. When particles from intervals i and $i+1$ interact, the maximum particle size can be the maximum particle size in interval $i+2$. In this case $v_i + v_{i+1} = v_{i+2}$, which is equivalent to $1 + r = r^2$ or $r = 1.618$. When $r > 1.618$, the resulting particles fall into intervals $i+1$ and $i+2$. When an interaction of particles in intervals i and $i+1$ produces a maximum particle size of v_{i+3}, we have $v_i + v_{i+1} = v_{i+3}$, which is equivalent to $1 + r = r^3$ or $r = 1.325$. For $1.325 \le r < 1.618$, the resulting particles fall into intervals $i+2$ and $i+3$. In the case of $1 + r = r^4$ or $r = 1.221$, there is another endpoint to a size range. For $1.221 \le r < 1.325$, the resulting particles fall into intervals $i+3$ and $i+4$. In general, the resulting particles fall into intervals $i+h$ and $i+h+1$ when $f \le r < g$ and $i > 1$. Here, f is defined by $1 + f = f^{h+1}$, g is defined by $1 + g = g^h$, and $h \ge 1$.

Similarly, there is the case where an interaction between intervals i and $i+2$ form a particle of size $i+2+h$ when $i > 1$. Here, we have $v_i + v_{i+2} = v_{i+2+h}$, which is equivalent to $1 + r^2 = r^{2+h}$. To find the endpoints of the ranges, we must solve for r for several values of h. For values of h of 1, 2, and 3, the corresponding values of r are 1.4656, 1.272, and 1.194, respectively. When $r > 1.4656$, an interaction between intervals i and $i+2$ produces particles in intervals $i+2$ and $i+3$. When $1.272 \le r < 1.4656$, an interaction between intervals i and $i+2$ produces particles in intervals $i+3$ and $i+4$. When $1.194 \le r < 1.272$, an interaction between intervals i and $i+2$ produces particles in intervals $i+4$ and $i+5$. In general, the resulting particles fall into intervals $i+h+1$ and $i+h+2$ when $f \le r < g$. Here, f is defined by $1 + f^2 = f^{h+2}$ and g is defined by $1 + g^2 = g^{h+1}$.

The two examples just given are for $v_i + v_{i+1} = v_{i+1+h}$ and $v_i + v_{i+2} = v_{i+2+h}$, where $i > 1$. This can be extended to a general case for $v_i + v_{i+j} = v_{i+j+h}$, where $i > 1$ and j and h can be any integers ≥ 1. As before, we need to solve for r when $1 + r^j = r^{j+h}$. In general, when there is an interaction between intervals i and $i+j$, the resulting particles fall into intervals $i+h+j-1$ and $i+h+j$ when $f < r < g$, and $i > 1$. Here, f is defined by $1 + f^j = f^{h+j}$ and g is defined by $1 + g^j = g^{h+j-1}$. Consider the case where $j = 1$, $h = 2$, and therefore $f = 1.325$ and $g = 1.618$; as demonstrated for $r = 1.466$ in Figure 4, an interaction between intervals 2 and 3 produces particles in intervals 4 and 5. For the case where $r = f$, all of the particles fall into interval $i+h+j$. Consider the case where $j = 1$ and $h = 1$, and therefore $f = 1.618$; where an interaction between intervals 2 and 3 produces particles only in interval 4 (Figure 3).

When $i = 1$, the general results given earlier are not valid. Instead, the particles may fall into more than two intervals when interval 1 combines with interval $1+j$. The general case is $v_1 + v_{1+j} = v_{1+j+h}$, where j and h can be any integer ≥ 1. As before, we need to solve for r when $1 + r^j = r^{h+j}$. In general, when there is an interaction between intervals 1 and $1+j$, the resulting particles fall into intervals $1+j$ through $1+h+j$ when $f \le r < g$. Here, f is defined by $1 + f^j = f^{h+j}$ and g is defined by $1 + g^j = g^{h+j-1}$. An example of this is shown in Figure 4 for $r = 1.466$; an interaction between intervals 1 and 2 ($j=1$, $h=2$, $f=1.325$, and $g=1.618$) may form particles in intervals 2, 3, and 4.

After defining the size ranges where a set of observations hold, equations that represent these observations can be developed. When an interaction between two intervals i and j produces particles in two intervals k and $k-1$, we can account for the particle birth in intervals $k-1$ and k by using $C_{i,j,k}$ and $D_{i,j,k-1}$ as defined by Eqs. 20 and 21. In the equation for interval $k-1$, a birth term must be included for $a_{i,j}N_iN_jD_{i,j,k-1}$. In the equation for interval k, a birth term must be included for $a_{i,j}N_iN_jC_{i,j,k}$. In intervals other than k or $k-1$, no birth term is needed. Again, given i and j, k and $k-1$ are determined by using the observations given earlier.

When an interaction between interval 1 and interval j produces particles in more than two intervals, a special set of equations must be used. In the case where particles fall into h intervals, interval $k-h+1$ through interval k, the fraction of particles that falls into interval p is $E_{1,j,p,k}$. Since the probability functions must sum to one,

$$\sum_{p=k-h+1}^{k} E_{1,j,p,k}=1. \tag{45}$$

To conserve volume, the volume of the particles removed from intervals 1 and j must be equal to volume of the child particles formed. Therefore,

$$\bar{v}_1+\bar{v}_j=\sum_{p=k-h+1}^{k}\bar{v}_pE_{1,j,p,k}. \tag{46}$$

Since there are two equations and h unknowns, $h-2$ variables can be set arbitrarily. As a first approximation, one can assume that if the resulting particles fall between v_{k-h} and v_k, the fraction of particles that falls into interval p is

$$E_{1,j,p,k}=\frac{v_p-v_{p-1}}{v_k-v_{k-h}}, \tag{47}$$

when $p<k-1$. Once these fractions are set, $E_{1,j,k-1,k}$ and $E_{1,j,k,k}$ can be determined from the number and volume balances.

Simulation Results

The simulation results of the new discretized equations are compared with the analytical solutions of the continuous equation and with the predictions of the conventional discretized agglomeration equation. For pure agglomeration, there are existing analytical solutions (Gelbard and Seinfeld, 1978; Scott, 1968) for the constant and linear coalescence kernels. Given the initial distribution of

$$n_0=\frac{N_0}{\nu_0}\exp\left(-\frac{v}{\nu_0}\right), \tag{48}$$

where N_0 is the total number of particles and ν_0 is the initial mean volume of the PSD, the solution for the constant kernel is

$$n(v,t)=\frac{4N_0}{\nu_0(\tau+2)^2}\exp\left(-\frac{2\tilde{v}}{\tau+2}\right) \tag{49}$$

where $\tau=N_0a_0t$ and $\tilde{v}=v/\nu_0$.

For the linear kernel, the analytical solution is

$$n(v,t)=\frac{N_0(1-T)}{vT^{1/2}}\exp[-(1+T)\tilde{v}]I_1(2\tilde{v}T^{1/2}), \tag{50}$$

where $T=1-e^{-\tau_1}$, $\tau_1=N_0\nu_0a_0t$, and I_1 is the modified Bessel function of the first kind of order one.

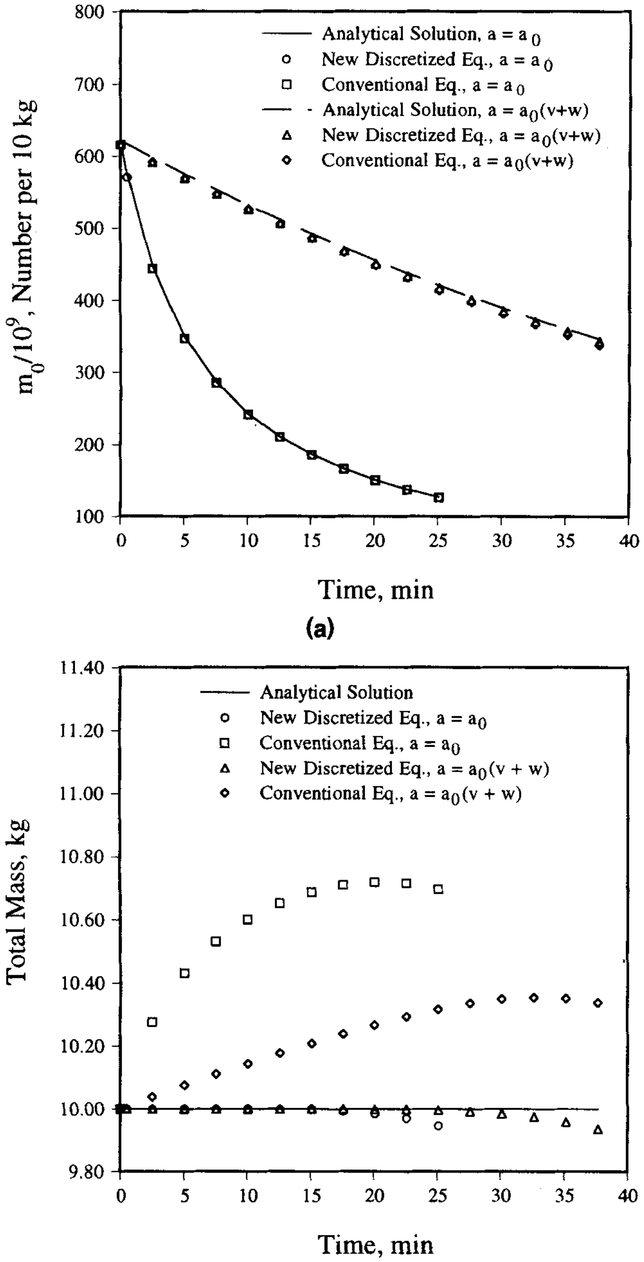
In the first set of simulations, 180 equal volume size intervals of 1000 μm^3 are used. Thus, the maximum size is 1.8×10^5 μm^3. The 10 kg of material has an initial mean volume of 5000 μm^3 and a density of 3.2 g/cm^3. This mass of material is distributed among the 180 size intervals according to Eq. 48; that is, the mass in each interval is determined by integrating $\rho n_0 v$ across a given size interval. The amount of material above the maximum size is negligible. Once the mass in each interval is determined, the initial number of particles in each interval is calculated by dividing the mass by the density and the mean particle volume. Using the arithmetic mean particle volume yields a different number of particles than what is given by the analytical solution. Therefore, in the following figures, the discretized equations and the analytical solution begin with a slightly different total number of particles at time zero. When using the constant kernel, a_0 is 5×10^{-13}/min; when using the linear kernel, a_0 is 5×10^{-18}/min.

Figure 5a shows the total number of particles as a function of time for the constant and linear coalescence kernels. The total number of particles predicted is almost identical to the analytical solution. This indicates that, despite the intrinsic discretization problems, the conventional equation provides sufficiently accurate predictions for this case.

In Figures 5b, it is shown that mass is not conserved by the conventional equation. Both curves based on the conventional discretized equation overshoot the initial 10 kg mass and drop back somewhat at a later time. The cause for the overshoot is that, as pointed out earlier, the conventional discretized equation tends to misplace child particles in an interval higher than the correct one. The gradual decline is caused by the well-known finite-domain problem. Child particles of size larger than the maximum size for the particle-size range are not counted. Clearly, Figures 5a and 5b combined indicate that the finite domain problem has little effect on number, but has a significant impact on volume, because the largest particles are not counted. For both the constant and linear coalescence kernels, the new discretized equation conserves mass but suffers the same finite-domain problem. This problem can be conveniently handled with geometric-size intervals.

This can be seen in the second set of simulations that are based on the same initial PSD and rate of coalescence. Three geometric ratios of 1.414, 1.5 and 2 are used for the new discretized equation. The maximum particle size is fixed at 3.115×10^8 μm^3, which for a spherical particle corresponds to a diameter of 841 μm. The number of intervals and the size of the first interval are listed in Table 3 for each case.

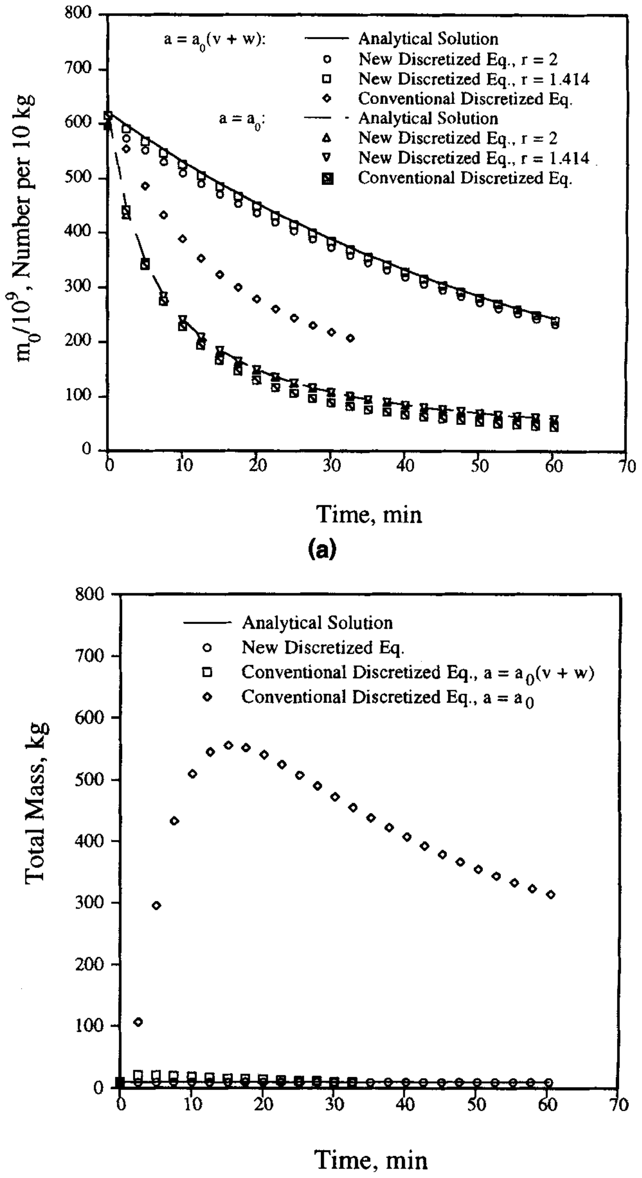
Figure 6a shows the total number of particles for constant and linear coalescence kernels. The new discretized equation



(a)

(b)

Figure 5. (a) Zeroth moment vs. time for constant and linear coalescence kernels with 180 equal-size intervals; (b) total mass vs. time for constant and linear coalescence kernels with 180 equal-size intervals.



(a)

(b)

Figure 6. (a) Zeroth moment vs. time for constant and linear coalescence kernels with geometric-size interval ratios 1.414 and 2; (b) total mass vs. time for constant and linear coalescence kernels with geometric-size interval ratios 1.414 and 2.

closely predicts the analytical solution results, but the conventional equation predicts too much agglomeration and its error increases with increasing time. The source of error for the case with the constant kernel is rather subtle and is explained below. Consider two PSDs each with two intervals. Specifically, N_1 and N_2 are 4 and 4, respectively, for the first PSD and 5 and 3, respectively, for the second PSD. In each case, we use the conventional discretized equation, Eq. 6, to predict the number of particles lost from the first interval. The first term predicts that none of the particles return to the first interval. For the first PSD, the second term predicts the loss of $32a_0$ particles from interval 1, while for the second PSD, the number of particles lost is $40a_0$. Although both distributions have a total of eight particles distributed over two intervals, the number of particles lost from interval 1 differs significantly. This exercise may be repeated for interval

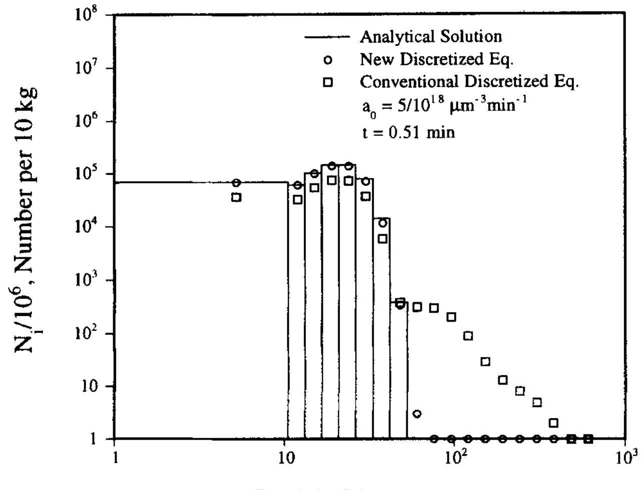
Table 3. Parameters Used in a Set of Simulations with the New Discretized Equation

Geometric Ratio	1.414	1.5	2
No. of Intervals	40	35	20
v_1, μm^3	420	321	594

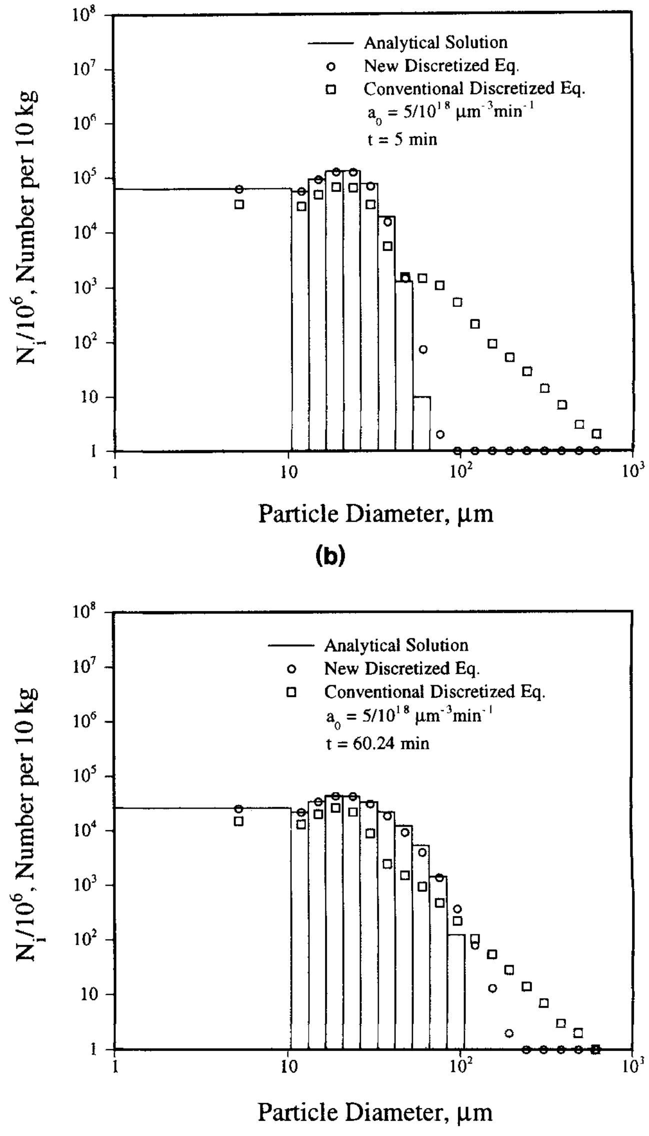
2. For the first PSD, $32a_0$ particles are lost and $8a_0$ are added, which yields a net loss of $24a_0$ particles. For the second PSD, $24a_0$ particles are lost and $12.5a_0$ are added, which yields a net loss of $11.5a_0$ particles. Similarly for interval 3, the first PSD adds $16a_0$ particles, while the second PSD adds $15a_0$ particles. Combining the results for all three intervals, we see that the first PSD lost a total of $40a_0$ particles, while the second PSD lost a total of 36.5 particles. This is what happens with the constant kernel in the conventional equation. Initially the PSD for the conventional equation is the same as for the continuous equation. However, recall that the conventional equation places child particles in a higher interval than they should be. The subsequent effect of this PSD change is that too many particles are removed. As expected, the error is more pronounced for the linear kernel than for the constant kernel because agglomeration is faster with larger particles.

In Figure 6b, the analytical solution for total mass is a horizontal line since mass is conserved for any coalescence kernel. For both the constant and linear kernels, the new equations for $r = 1.414$ and $r = 2$ yield almost identical results; therefore only the data for $r = 1.414$ with a constant kernel are presented in Figure 6b. Although the conventional equation with the constant kernel shows minor error in predicting the total number of particles in Figure 6a, it errs greatly in predicting the total mass of particles, Figure 6b. In fact, a review of the data shows that, at the end of 2.5 minutes, the conventional discretized equation is already producing particles larger than the maximum size of 3.115×10^8 μm^3 used in the simulation. This is why the total mass decreases with time after 15 minutes of simulation. In contrast, at the end of 2.5 minutes of simulation, the new discretized equation and the analytical solution predict maximum particle sizes of 152,075 and 107,533 μm^3, respectively. Here, we define maximum particle size as the size where 99.95% of the total particle mass consists of particles smaller than the maximum particle size. Since the linear kernel in Figure 6a shows much greater error than the constant kernel, we would expect the same feature in Figure 6b. However, in Figure 6b, the linear kernel shows better agreement with the analytical solution. This is misleading and can be explained by the large number of particles that exceed the maximum particle size used in the simulation. Once the particles exceed the maximum particle size, they no longer contribute to the total particle mass.

Although the new equation conserves mass and correctly predicts the total number of particles, there is no guarantee that it correctly predicts the PSD. In Figure 7a, 7b and 7c, PSDs are shown at 0.51, 5, and 60.24 minutes for the linear coalescence kernel and a geometric ratio of two. In all three cases, the new discretized PSD is much closer to the analytical solution than is the conventional equation PSD. This is particularly noticeable when comparing the largest particle size predicted by each equation. The conventional equation errs by an order of magnitude in predicting the largest particle size. It may appear unusual that interval 2 has fewer particles than intervals 1 and 3. Given the initial exponential



(a)



(c)

Figure 7. (a) PSD for linear coalescence kernel at 0.51 minute with a ratio of 2; (b) PSD for linear coalescence kernel at 5 minutes with a ratio of 2; (c) PSD for linear coalescence kernel at 60.24 minutes with a ratio of 2.

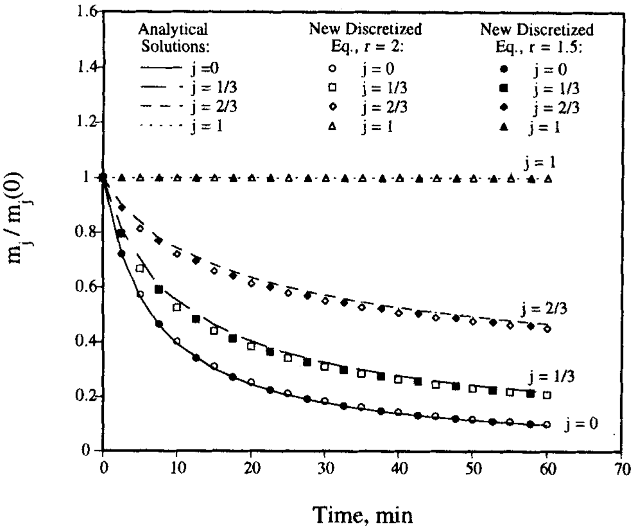
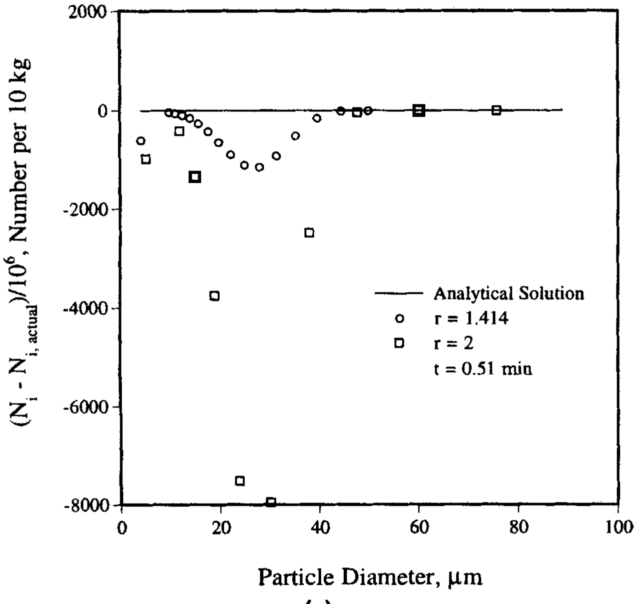
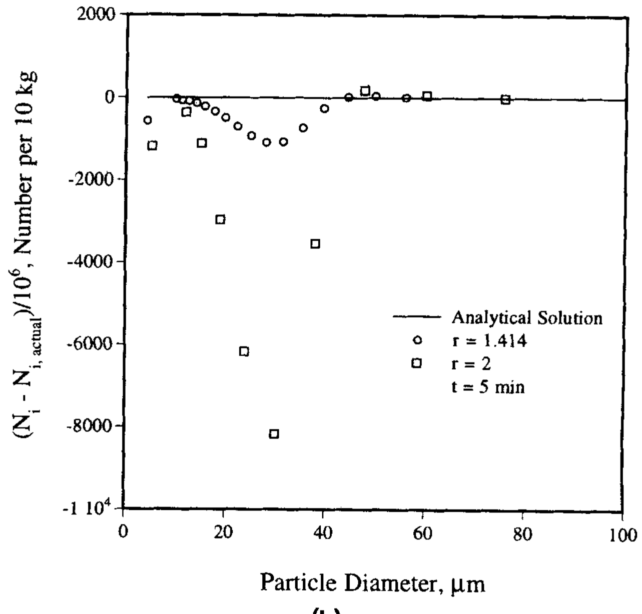


Figure 8. Moments vs. time for a constant coalescence kernel for both the continuous equation and the new discretized equation with ratios of 1.5 and 2.

distribution, the number of particles decreases with particle volume. Therefore, there are fewer particles in interval 2 than in interval 1. If equal-size intervals are used, interval 3 would have fewer particles than interval 2. However, for a geometric ratio of two, the first two intervals have the same width, while interval 3 has the same range as the first two intervals combined. Since it covers a wider range of particle volumes, interval 3 has more particles than interval 2.



(a)



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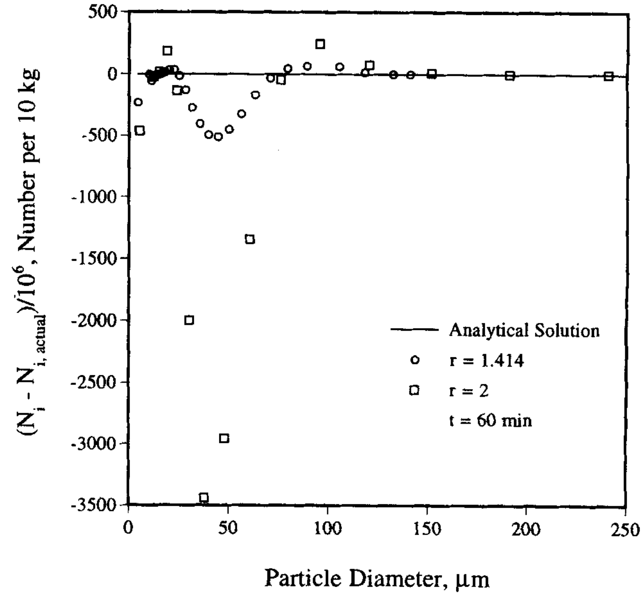

(c)

Figure 9. (a) Error in PSD for linear coalescence kernel at 0.51 minute with ratios of 1.414 and 2; (b) error in PSD for linear coalescence kernel at 5 minutes with ratios of 1.414 and 2; (c) error in PSD for linear coalescence kernel at 60 minutes with ratios of 1.414 and 2.

The ability of the new discretized equations to predict PSD can also be evaluated by examining the one third and two thirds moments, which represent length and area, respectively. For the constant kernel, the analytical solution given in Eq. 49 is substituted into the moment definition, Eq. 2. By using Laplace transforms to solve for m_j, one can show for the constant coalescence kernel that

$$\frac{m_j}{m_j(0)} = \left(\frac{2}{\tau + 2}\right)^{1-j} \tag{51}$$

In the case where the geometric ratio is two, there is a good match between the discretized equation and the continuous equation (Figure 8). The discretized equation errs little in predicting the length and the particle area. However, when using a smaller geometric ratio of 1.5, this error is further decreased. Clearly, for the same particle-size range, a smaller geometric ratio provides better predictions of the PSD.

To compare the effect of using different geometric ratios, it is helpful to observe the maximum particle size predicted by each ratio. Again, we define maximum particle size as the size where 99.95% of the total particle mass consists of particles smaller than the maximum particle size. All conditions are as previously described for the linear kernel and geometric ratios. After 60.24 min of agglomeration, the maximum particle diameter is 93.7 μm based on the analytical solution. For the new equation, the maximum particle diameters are 149, 166 and 210 μm at geometric ratios of 1.414, 1.5, and 2, respectively. At a ratio of two, the new discretized equation errs by a factor of 2 in predicting the maximum particle size. This error decreases as the geometric ratio is decreased.

Since mass is conserved and the total number of particles is correctly predicted for various geometric ratios, it can be difficult to see the advantage of having the various ratios. However, this advantage is clear when comparing the PSDs. To show the significant improvement in reducing the ratio, the difference between the new discretized equation and the analytical solution is plotted for each size interval. In Figure 9 a, b, and c, the results are for a linear coalescence kernel at geometric ratios of 1.414 and 2 at 0.51, 5, and 60 minutes, respectively. In all three cases, the error decreases significantly as the geometric ratio is decreased. Therefore, for users who desire a more accurate PSD, the flexibility of using smaller geometric ratios can be beneficial.

Concluding Remarks

A general procedure is presented for developing discretized equations to simulate agglomeration. For these new agglomeration equations, mass is always conserved, the number of particles is closely predicted, and the prediction of the PSD is significantly improved over the prediction from conventional discretized equations.

This method is flexible in that it allows the user the convenience of choosing equal-size intervals or geometric-size intervals with any geometric ratio. This feature can be used to deal effectively with the finite-domain error with minimum effort. Consider a situation where the PSD to an agglomeration problem at a given time is desired. Initially, one can use geometric-size intervals with a geometric ratio of, for example, two. It covers a particle-size range of seven orders of magnitude with merely 25 size intervals. Since mass is lost if particles larger than the given size range are generated and since conservation of mass is guaranteed with the new agglomeration equation, we know that the finite-domain error is insignificant as long as the total mass stays the same. Once the actual particle-size range is known, either equal-size intervals or geometric-size intervals with a smaller geometric ratio can be used to improve the PSD predictions.

As mentioned, there is a similar procedure that guarantees conservation of mass and number of particles for the breakage equation (Hill and Ng, 1995). Although the goal is the same for both the breakage and agglomeration discretization methods, the manner in which it is achieved is very different. For breakage, the distribution function for breakage and the specific rate of breakage are substituted into the continuous and the new discretized equation. Then, the zeroth and first moments of the new equation are matched to those of the continuous equation so as to determine two probability factors in the new discretized equation. In other words, the probability factors depend on the exact form of the parameters in the breakage equation, and the match is achieved in an overall sense for all the particles.

In constrast, the agglomeration equations are developed without assuming a form for the coalesence kernel. Therefore, these equations are applicable to other coalescence kernels; a comprehensive list of the typical forms is given by Smit et al. (1994) and the underlying physics is discussed in Ennis and Adetayo (1994). Here, instead of using the moments to determine the probabilities as in the breakage equation, we concentrate on conserving mass and correctly predicting the number for each interval interaction. If each interaction prediction is correct, then the sum of these predictions should also conserve mass and correctly predict the total particle number.

Although the equations are developed for a batch system, they also apply to a continuous system with inflow and outflow of particles. For a steady-state continuous system, we have

$$QN_i = V_t\left(\frac{dN_i}{dt}\right)_{\text{Agglomeration}} + QN_{i,\text{in}}, \tag{52}$$

where Q is the volumetric flow rate, V_t is the total volume of the equipment unit under consideration, and $N_{i,\text{in}}$ is the PSD of the inflow. The probability functions are identical to those developed for the batch system.

In the development of the equations in this article, the representative particle volume for a size interval is represented by the arithmetic mean. Actually, other definitions for $\bar{v}_i$ can be used. In the derviation of the geometric interval equations, no assumption is made about the form of $\bar{v}_i$. Therefore, these equations are valid for any reasonable form of the average particle volume. In contrast, the equal interval equation, Eq. 13, is based on the arithmetic average. By using a development similar to the one used for geometric-size intervals, the following general equal interval equation can be developed, which is applicable for any reasonable functional form of the representative particle volume:

$$\begin{aligned}\frac{dN_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1}\frac{\bar{v}_j + \bar{v}_{i-j} - \bar{v}_{i-1}}{\bar{v}_i - \bar{v}_{i-1}} a_{i-j,j}N_{i-j}N_j \\ + \frac{1}{2}\sum_{j=1}^{i}\frac{\bar{v}_{i+1} + \bar{v}_{i-j+1} - \bar{v}_j}{\bar{v}_{i+1} - \bar{v}_i} a_{i-j+1,j}N_{i-j+1}N_j \\ - N_i\sum_{j=1}^{\infty} a_{i,j}N_j.\end{aligned} \tag{53}$$

For example, a possible form is

$$\bar{v}_i = \frac{av_i + bv_{i-1}}{a+b}. \tag{54}$$

When Eq. 53 is used with the arithmetic mean definition for $\bar{v}_i$, it simplifies to Eq. 13.

Although we have matched the zeroth and first moments in this article, the method is flexible in that any two moments can be matched. For example, instead of Eqs. 18 and 19, the following two equations can be used for any ath and bth moments:

$$(\bar{v}_i + \bar{v}_j)^a = \bar{v}_k^a C_{i,j,k} + \bar{v}_{k-1}^a D_{i,j,k-1} \tag{55}$$

$$(\bar{v}_i + \bar{v}_j)^b = \bar{v}_k^b C_{i,j,k} + \bar{v}_{k-1}^b D_{i,j,k-1}. \tag{56}$$

When using this method, the properties represented by the ath and bth moments are correctly predicted.

Acknowledgment

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Notation

a, b = nonnegative constants
f, g = geometric ratios
n_0 = initial population density on volume basis, no/μm^3/μm^3
$n(v)$ = volume-based population density, no/μm^3/μm^3
r = size interval ratio for volume basis, μm^3/μm^3
t = time, min
T = dimensionless function of time
$v(t)$ = particle volume at a given time, μm^3
$\bar{v}$ = dimensionless volume used in Eq. 49, μm^3/μm^3
ρ = density, g/cm^3
τ, τ_1 = dimensionless time in analytical solutions to agglomeration equation

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