Analysis of Dispersed-Phase Systems: Fresh Perspective

Doraiswami Ramkrishna and Arun Sathyagal
School of Chemical Engineering

G. Narsimhan
Dept. of Agricultural Engineering
Purdue University, West Lafayette, IN 47907

Dispersed-phase systems are analyzed with a fresh perspective where the volume fraction of the dispersed phase is emphasized, not particle numbers as in population balance. Such volume fraction balances are more pertinent to engineering because they deal with the amount of the dispersed phase relative to that of the continuous phase. Although it is easy to make detailed volume fraction balances directly or from population balance, many interesting features are identified here with balance equations in terms of volume fraction, which simply characterize the dispersion process and structure the resulting equation. They lead to equivalent "single-particle" (comprising the entire dispersed phase) processes which can be simulated with great simplicity allowing rapid calculation of quantities associated with the dispersed phase and dispersion. The techniques can solve an inverse problem for mass-transfer coefficients of individual droplets from (simulated) measurements of the bivariate distribution of drop size and concentration of a transferring solute. Such inverse problem method is important in developing experimental techniques to measure multivariate population distributions such as those of Bae and Tavlarides (1989) and of flow cytometry.

Introduction

Dispersed-phase systems form a significant part of the chemical process industry. The high interfacial area characteristic of the dispersed phase is generally an attractive feature for many separation and reaction processes. Liquid-liquid extraction, distillation, crystallization, nitration and sulfonation of many organic chemicals, alkylation reactions, and phase transfer catalytic reactions are some of the well-known examples of such processes. Possible use of dispersed-phase systems for carrying out multicomponent precipitation reactions in the manufacture of ceramic mixtures (Kumar, 1990) represents promising areas of future application.

The design and control of process equipment in which the dispersed phase is present hinge crucially on methods of analysis of both the dispersion process and physico-chemical processes in the system which occur concurrently. The population balance framework has been an indispensable tool in this regard (Hulburt and Katz, 1964; Randolph and Larson, 1964; Ramkrishna and Borwanker, 1973). The status of population balance was assessed recently by Ramkrishna (1985). Population balance is concerned with the *number* of particles of the dispersed phase expressed in terms of a *density* in physical space, as well as in an abstract property space. The abstract property space may consist of several variables characterizing the particle state including primarily a measure of particle size such as the volume or mass of the particle.

This article shows that the analysis of dispersed-phase systems is better accomplished by a *cumulative* volume (or mass) distribution (rather than a number density function) of the dispersed phase for several reasons. This viewpoint, although conceptually simple, deserves special expression in the literature because the cumulative volume fraction has many attributes too compelling to be ignored.

Correspondence concerning this article should be addressed to D. Ramkrishna.

First, chemical process systems are more influenced by the *amount* of dispersed-phase material, not the number of particles. For example, when one views the breakup of a drop into two nearly equal-sized droplets and several "satellite" microdroplets in terms of numbers, the satellite droplets which may be of negligible volume fraction assume an exaggerated degree of importance in relation to their effect on physicochemical processes occurring in the system. The cumulative volume fraction will naturally weight different-sized particles of the dispersed phase in accord with their contribution to the overall process.

The characterization of the breakup process is accomplished here by a *single* bivariate function as against *three* functions in the number-oriented description. Thus, the second attribute of the cumulative volume fraction of the dispersed phase is its simplicity in characterizing the dispersion process.

The third attribute is the simplicity with which "self-similar" distributions are characterized, that is, by the direct invariance of the cumulative fraction along curves or surfaces in particle state space on which the similarity variable remains fixed. Such self-similar behavior has been observed in systems in which either breakup or aggregation occurs alone (Ramkrishna, 1974; Narsimhan et al., 1980, 1984; Tobin et al., 1990; Wright et al., 1990; Wright and Ramkrishna, 1992). This self-similar representation is very convenient to obtain particle-specific information regarding breakup or aggregation from dynamic distribution measurements.

In addition, the integrodifferential equations satisfied by the cumulative volume fraction are much simpler in constitution than the population balance equation. For example, in a pure breakage system, the population balance on particles of a particular size will feature a "source" term representing formation by breakup of larger particles and a "sink" term representing loss to smaller sizes. The cumulative volume fraction equation (Ramkrishna, 1974), however, will contain only a single (source) term for a particular size because breakup can only reduce particle size. Similarly, the cumulative volume fraction equation for aggregating systems (Muralidhar and Ramkrishna, 1989) will feature a single "sink" term because aggregation can only increase particle size.

Finally, the equation in the cumulative volume fraction can also represent abstract *single particle* processes that can be simulated efficiently on a computer. Such procedures are conceptually very simple and do not require the usual cataloguing procedures for tracking particles of the population of different states.

These attributes characterize the dispersed-phase system better than the number density function. Some of these may not be entirely clear, and the following sections will establish them more rigorously. We also show an interesting application of the cumulative volume fraction equation, in which statistical experimental data on particle populations can be used to learn about individual particle behavior, such as the relationship between the cumulative volume fraction and the number density. Restricting our concern only to particle volume, for a dispersed-phase system in which the dispersed-phase volume fraction is given by ϕ, we have

$$F(v, t)=\frac{1}{\phi}\int_0^v v' n(v', t)dv'; \quad n(v, t)=\frac{\phi \partial F(v, t)}{v \partial v} \tag{1}$$

To identify the equations to be satisfied by $F(v, t)$ for the processes of interest to this article, we relied on the better known population balance equations (Ramkrishna, 1985) as their source. Thus, the population balance equations are readily modified by using Eqs. 1 to obtain the corresponding equations in the cumulative volume fraction $F(v, t)$.

Breakup Systems

For a fresh characterization of the breakage process, we assume breakup of any given particle to occur independent of all other particles. Define the probability that a particle of volume v' at time t breaks during the time interval t to $t+dt$ to produce a daughter particle population with a cumulative volume fraction of sizes between 0 and v to be given by $B(v|v')dt$. We will refer to this as the breakage function which alone is sufficient to characterize the breakage process envisaged here. This function has several properties. First, for $v'=v$, it represents the *breakage frequency* of a drop of volume v' (Valentas and Amundson, 1966). Thus, we set $\Gamma(v)\equiv B(v|v)$ to represent the breakage frequency of drops of volume v. The function

$$G(v, v')\equiv\frac{B(v|v')}{B(v'|v')} \tag{2}$$

is a cumulative volume distribution function which represents the conditional probability that daughter droplets arising from the breakup of a droplet of volume v' have volume less than or equal to v. Valentas and Amundson (1966) defined two other functions to characterize breakup in the number-oriented description. One is the mean number of droplets $\nu(v')$ formed by the breakup of a drop of volume v', and the other is the *density* of daughter drop size distribution $p(v, v')$. Both of these functions are related to the breakage function $B(v|v')$.

$$G(v, v')=\frac{\nu(v')}{v'}\int_0^v v'' p(v'', v')dv'' \tag{3}$$

If G is sufficiently smooth, the above equation may be inverted to obtain

$$\nu(v')p(v, v')=\frac{v'}{v}\frac{\partial G(v, v')}{\partial v} \tag{4}$$

Thus, the function $\nu(v')p(v, v')$ can be obtained from $B(v|v')$ using Eqs. 2 and 4 subject to the smoothness of B with respect to its arguments. This function [without the need for further resolution into $\nu(v')$ and $p(v, v')$ individually] was used in the source term appearing in the population balance equation (Valentas and Amundson, 1966). It is also possible to calculate $\nu(v')$ [and hence $p(v, v')$] individually from

$$\nu(v')=\int_0^{v'}\frac{v'}{v}\frac{\partial G(v, v')}{\partial v}dv \tag{5}$$

which clearly arises from integration of Eq. 4.

The above characterization of the breakage process is sufficient to derive the dynamic equation for the process. Thus, particles in the size range $(0, v)$ are never lost by breakup,

while particles larger than volume v can clearly contribute to this range: the volume fraction of droplets of differential range about volume $v'(>v)$ at time t, given by $\partial F(v', t)$, contributes to the volume fraction of particles in the range $(0, v)$ during the time interval t to $t+dt$ equal to $B(v|v')\partial F(v', t)dt$. Thus, the increment in the volume fraction of particles in the range $(0, v)$ during time t to $t+dt$ is given by

$$\partial F(v, t) = \int_v^\infty B(v|v')\partial F(v', t)dt$$

which reduces to the integrodifferential equation

$$\frac{\partial F(v, t)}{\partial t} = \int_v^\infty B(v|v')\partial F(v', t) \qquad (6)$$

strikingly simpler than the corresponding population balance equation. This equation can also be derived directly from the population balance equation, using Eqs. 1-5. We next show that Eq. 6 also represents an abstract single particle process which can be simulated with remarkable simplicity.

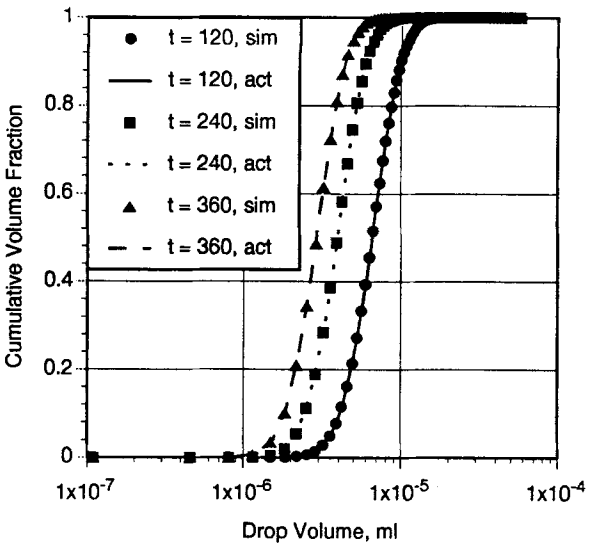

Figure 1. Single-particle simulation vs. direct numerical solution for pure breakage.

Abstract single-particle process

Consider a single particle of volume $V(t)$ at time t which undergoes random, discontinuous "erosion" to smaller sizes in accord with the probabilistic law:

$$Pr\{V(t+dt) \le v | V(t) = v'\} = B(v|v')dt$$

We let $F(v, t)$ be the cumulative distribution function for the size of the single particle undergoing random erosion. Suppose that the cumulative probability distribution of the particle volume at time $t+dt$ is desired from consideration of its size at time t. If the particle has to have at time $t+dt$ volume less than or equal to v, it can arise from either of two mutually exclusive possibilities. One is that the particle had volume $\le v$ at time t, and the other is that it had volume $\ge v$ at time t and underwent random erosion during the time interval t to $t+dt$ to a size $\le v$. Mathematically, this becomes

$$F(v, t+dt) = F(v, t) + \int_v^\infty B(v|v')\partial F(v', t)dt$$

which, on transposing and letting dt tend to 0, clearly leads to Eq. 6.

Simulation of a breakup process

The above single-particle process can be simulated in a very simple manner. In view of the equivalence of the single-particle erosion process to a population of particles undergoing breakage alone, the simulation procedure is applicable to the latter with a minimum of the bookkeeping that is characteristic of simulation strategies. Suppose that the size of the particle is known at any instant t. Following Shah et al. (1977), we may define a quiescence interval T as the period in which the particle does *not* undergo random erosion (but that it certainly does during the instant following T). Using the methods of the cited reference, it is easy to derive the cumulative distribution function for this quiescence time interval as

$$Pr\{T \le \tau | V(t) = v'\} = 1 - \exp[-B(v'|v')\tau] \qquad (7)$$

which can be used to generate the quiescence time. The size of the particle can be updated by generating a random number whose distribution is given by $G(v, v') \equiv B(v|v')/B(v'/v')$. The sample path of the process, starting from some time $t=0$, is now completely defined. Sample paths of this single particle erosion process can be averaged to give the behavior of a population of particles very accurately. (For 10,000 sample paths, it takes approximately 2 min on a Gould NP1 machine and about 55 s on an Ardent Titan/P3 machine.) The simulation results are presented in Figure 1, as well as the direct numerical solution of a discrete version of Eq. 6 (this is straightforward for any arbitrary breakage function $B(v|v')$; because of the upper triangular nature of the matrix, an analytical solution can be readily identified). The breakage function determined by Narsimhan et al. (1984) is used in the simulation. The simulation procedure is effective because it can accommodate chemical reaction or transport processes occurring in the drop population as a process occurring in the single particle.

Application to a mass-transfer system

We consider application of the simulation procedure above to a liquid-liquid mass-transfer system. Consider a well-stirred mixer to which continuous and dispersed phases are fed continuously at the same rate at which the dispersion is withdrawn. The feed drops may be assumed to be of a given size distribution (for example, monodispersed), containing a solute to be transferred into the continuous phase across individual droplet surfaces at a rate determined by individual mass-transfer coefficients. The dispersed-phase fraction is assumed to be very small so that coalescence plays a negligible role in the evolution of the drop size distribution. Thus, breakup is the only important droplet process to be considered which is viewed as

being independent of either the solute concentration or the mass-transfer rate. Breakup must depend on the interfacial tension, an average value of which over the prevailing solute concentration range, may serve as a reasonable value. Also the presence of surfactant impurities may overwhelm the effect of the transferring solute on the breakup process. Das et al. (1988) provide some evidence in support of the foregoing assumptions.

Transfer of the solute to the continuous phase containing a uniform concentration c_c of the solute is described by

$$\frac{\partial F(v, c, t)}{\partial t}+\frac{\partial}{\partial c}\left[\int_0^v \dot{C}(v', c; c_c)\partial F(v', c, t)\right] = \int_v^\infty B(v|v')\partial F(v', c, t)+\frac{1}{\theta}[F_o(v, c, t) - F(v', c, t)] \quad (8)$$

$$\frac{dc_c}{dt}=\frac{1}{\theta}[c_{co}-c_c]-\phi\int_{c_o}^{c^*(c_c)} dc \int_0^\infty \dot{C}(v, c; c_c)\partial F(v, c, t) \quad (9)$$

where the function $F(v, c, t)$ is cumulative with respect to drop volume, but a *density* with respect to concentration, and represents the dispersed-phase droplets in the vessel, while $F_o(v, c, t)$ is a similar function which refers to the droplet in the feed. The function $\dot{C}(v', c; c_c)$ is the rate of change in concentration due to mass transfer *to* a drop of volume v' and solute concentration c to the continuous phase with (local) solute concentration c_c; θ is the average residence time in the well-mixed vessel, and c_{co} is the concentration of the solute in the continuous-phase feed. The function $c^*(c_c)$ represents the solute concentration in the drop in equilibrium with the concentration c_c in the continuous phase. Equations 8 and 9 are easily derived from the corresponding population balance equation in the number density equation and using Eq. 1. The form of the population balance equation for the mass-transfer process of this section is readily inferred from the general discussion by Ramkrishna (1985).

For a feed that does not vary with time, we may envisage a steady-state distribution determined by steady-state versions of Eqs. 8 and 9 obtained by setting the time derivatives equal to zero. This steady-state situation can be envisaged as a single particle process with the particle entering the vessel environment with the feed solute concentration (either a known fixed value or generated according to a feed concentration distribution). Subsequent to entry, we may view, as a period of quiescence, the time interval during which the particle retains its presence in the vessel without undergoing a discontinuous change in size. During the quiescent period, mass transfer of the solute occurs at the rate determined by the concentration in the drop, the steady-state concentration in the continuous phase (unknown), and the size of the drop that determines the transfer coefficient. The distribution of this quiescence interval is readily calculated to be:

$$Pr\{T\le\tau|V(t)=v'\}=1-\exp\left[-\left(B(v'|v')+\frac{1}{\theta}\right)\tau\right]$$

The foregoing quiescence interval distribution is again obtained by the methods of Shah et al. (1977). At the end of the quiescence period, there occurs either a departure of the drop from the vessel or a discontinuous size reduction, the probability distribution for which, using simple arguments from probability theory, is given by

$$Pr\{\text{exit}\,|\,\text{either exit or size reduction has occurred}\} = \frac{\frac{1}{\theta}}{\left[B(v'|v')+\frac{1}{\theta}\right]}$$

$$Pr\{\text{size reduction}\,|\,\text{either exit or size reduction has occurred}\} = \frac{B(v'|v')}{\left[B(v'|v')+\frac{1}{\theta}\right]}$$

The generation of random variables satisfying the above distribution will either reduce the drop to a size determined by generating the random variable satisfying the distribution function $G(v, v')$ or exit the drop at size v' and concentration determined by solving the differential equation

$$\frac{dc}{d\tau}=\dot{C}(v', c, c_c),\ \tau>\tau_i;\quad c(\tau_i)=c_i \quad (10)$$

where c_i is the solute concentration either at its "birth" (signified by the entry of the drop into the vessel $\tau_i=0$) or at the instant τ_i when the drop suffered its latest size reduction. Indeed, the exit of the drop from the vessel may then be viewed as the "death" of the drop. The solution of Eq. 10 yields the concentration of the exiting drop with volume v'. Each exiting drop will yield a sample point for the bivariate size, concentration distribution so that by repeating the simulation a sufficient number of times the distribution can be estimated.

The significant hindrance to this procedure of estimating the steady-state bivariate distribution at this stage lies in the fact that c_c is unknown. A trial-and-error remedy would seem imminent, but we will presently see that it is not necessary. We first recognize that the exit probability of the drop from the vessel is independent of the concentration of the transferring solute. Next, we note that the steady-state version of Eq. 9 is

$$c_c=c_{co}-\theta\phi\int_{c_o}^{c^*(c_c)} dc \int_0^\infty \dot{C}(v, c; c_c)\partial F(v, c) \quad (11)$$

Now we switch from concentration at exit to the variable representing the exit age or "life span," τ_S of the drop setting $d\tau_s=\dot{C}(v, c; c_c)dc$. Denoting the cumulative volume fraction distributed according to the life span by $F_T(v, \tau_S)$, Eq. 11 may be rewritten as

$$c_c=c_{co}-\theta\phi\int_0^\infty d\tau_s \int_0^\infty \partial F_T(v, \tau_s) \quad (12)$$

By following the size and life span of the drop in the vessel, the averaging of sample paths from the simulation procedure outlined above directly computes the integral on the righthand

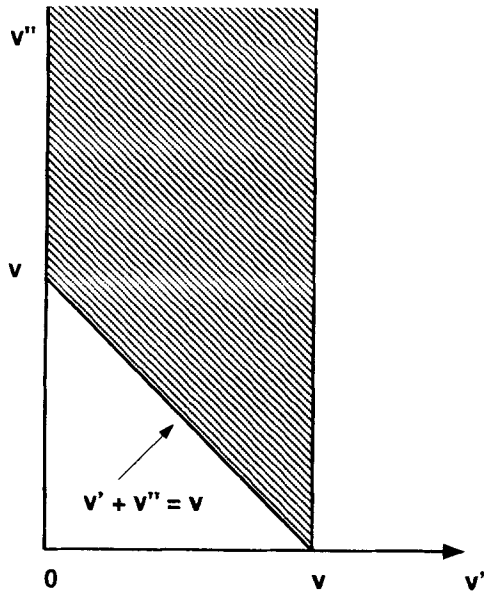

Figure 2. Region of integration for an agglomerating system.

side of Eq. 12. Thus, the steady-state concentration of the solute in the continuous phase is readily obtained by the foregoing simulation procedure.

Agglomerating Systems

We are concerned here with a population of particles which cannot break up but can only agglomerate to form larger particles. Agglomeration between particles of volumes v and v' occurs with a frequency $q(v, v')$ assuming that ternary and higher agglomerations do not occur within the time scale of observation. To derive the proper equation for a purely agglomerating system in terms of the cumulative volume fraction $F(v, t)$, one only need recognize the following. The agglomeration process can only remove particles from the interval [0, v] (since any source can only be from within itself). The loss of particles from this volume interval must necessarily occur by agglomeration between particles in the interval and other particles (which may or may not be in the interval) such that the resulting particles have volume larger than v. If both particles in the pair (agglomerating to a size larger than v), say (v', v''), arise from the interval [0, v], clearly the volume contributed by that particle is included. These considerations are readily incorporated (see Figure 2) to obtain

$$\frac{\partial F(v, t)}{\partial t} = -\int_0^v v' dv' \int_{v-v'}^{\infty} n(v', t) n(v'', t) q(v', v'') dv''$$

which, on substitution for the number density in terms of the cumulative volume fraction $[n(v, t)dv = \partial F(v, t)/v]$, becomes

$$\frac{\partial F(v, t)}{\partial t} = -\int_0^v \partial F(v', t) \int_{v-v'}^{\infty} \frac{\partial F(v'', t)}{v''} q(v', v'') dv'' \tag{13}$$

a balance equation notably more compact than the corresponding number balance equation. Equation 13 can also be obtained by multiplying the number balance equation by v and integrating over particle volume. As in the breakup system, we demonstrate that Eq. 13 also holds for the following abstract single-particle growth process.

Abstract single-particle growth process

Consider a single particle of size $V(t)$ at any time which is distributed according to the cumulative distribution function $F(v, t)$: it is the probability that $V(t) < v$. At any stage we can consider a "discontinuous" growth process which causes a sudden *increment* in the size of the particle. This increment is made as follows. Create another particle of the *same* distribution as the existing particle and coalesce it with the particle present. This occurs with some transition probability to be specified. At each instant of time we have only the single particle in question. Assume that the discontinuous growth process satisfies the conservation of mass. We want to derive an equation for $F(v, t)$. The transition probability that, given the particle is of volume v at time t, it will undergo a shift to size $v + v'$ during time t to $t + dt$ is *defined* by

$$\partial F(v', t) q(v, v') dt / v'$$

Observe that the particle at time $t + dt$ will have size between 0 and v if it had so at time t, and it did not undergo any discontinuous increase in size between t and $t + dt$ in such a way that its size increased above volume v. The probability that the particle of volume v' at time t undergoes an increase in size to volume greater than v at time $t + dt$ is given by

$$\int_{v-v'}^{\infty} \partial F(v'', t) q(v', v'') dt / v''$$

The probability that a particle of volume v' does not undergo an increase in size to a volume greater than v at time $t + dt$ is

$$1 - \int_{v-v'}^{\infty} \partial F(v'', t) q(v', v'') dt / v''$$

Clearly then we have

$$F(v, t + dt) = \int_0^v \partial F(v', t) \left[1 - \int_{v-v'}^{\infty} \partial F(v'', t) q(v', v'') dt / v'' \right]$$

Transposing appropriate terms, dividing by dt, and letting dt tend to zero, we have the same evolution equation as Eq. 13. An abstract single-particle growth process is thus identified which grows by independent discrete increments with the increment and the particle satisfying the same distribution function at each instant of time. This process obeys the same equation as that satisfied by an agglomerating population for its cumulative volume fraction.

Although we have identified a single-particle process for an agglomerating population of particles, an important distinction here from the situation encountered in the breakup system

lies in the nonlinearity of the process which does not allow a direct simulation procedure. Thus, a sample path of the single-particle growth process cannot be produced without the averaged dynamic distribution function. Disregarding this aspect for the present let us compute the quiescence interval (following the instant t) for the particle assumed to have volume v at time t. As in the breakup process, the quiescence interval represents the time during which the particle retains its size at the outset. Its distribution function, following Shah et al. (1977), is readily found to be

$$Pr\{T \le \tau \mid V(t) = v\} \equiv F_T(\tau \mid v, t)$$
$$= 1 - \exp\left[-\int_0^{\tau} du \int_{v'=0}^{\infty} \partial F(v', t+u) q(v, v')/v' \right]$$

which displays the distribution function $F(v, t)$ to be calculated from the simulation. Updating of the particle volume is to be accomplished by generating a random increment calculated according to the cumulative distribution function (readily obtained by applying the basic laws of probability):

$$\frac{\partial F(v', t+T) q(v, v')/v'}{\int_0^{\infty} \partial F(v', t+T) q(v, v')/v'}$$

Because the distribution function $F(v, t)$ to be calculated also appears in the quiescence interval distribution function and in the above distribution function, a successively iterative approach is therefore required in which *a priori* approximation for F is improved by simulation of the single-particle process. Assume that $F^{(n)}(v, t)$ is the nth averaged distribution function and then a sample path for the calculation of $F^{(n+1)}(v, t)$ will be based on using $F^{(n)}(v, t)$ for the increment. The quiescence interval distribution function, presented above, may then be taken to be

$$F_T^{(n)}(\tau \mid v, t) = 1 - \exp\left[-\int_0^{\tau} du \right.$$
$$\left. \times \int_{v'=0}^{\infty} \partial F^{(n)}(v', t+u) q(v, v')/v' \right] \quad (14)$$

and the distribution function for updating the particle size is

$$\frac{\partial F^{(n)}(v', t+T) q(v, v')/v'}{\int_0^{\infty} \partial F^{(n)}(v', t+T) q(v, v')/v'}$$

so that sample paths from which $F^{(n+1)}(v, t)$ is computed are well defined. From a practical standpoint, however, an efficient simulation procedure will depend on accelerating the procedure for updating the distribution function appearing in the righthand side of Eq. 14. For example, as sample paths accumulate, their progressively calculated averages can be substituted into Eq. 14 for subsequent sample paths.

Since the record of each sample path can be stored computationally, $F^{(n)}(v, t)$ can be evaluated for the $(n+1)$th sample path at each time t from the previous n sample paths. This $F^{(n)}(v, t)$ is used to calculate the quiescence time interval and the size addition for the $(n+1)$th sample path. However, as this procedure becomes computationally intensive, we can carry out this procedure for a limited number of sample paths until the distribution approaches somewhat close to the actual. This approximate distribution is then used as $F^{(n)}(v, t)$ for all the remaining sample paths. The results of this single-particle simulation are presented in Figure 3, along with the analytical result for the sum coalescence frequency: $q(v, v') = v + v'$ and a monodisperse initial condition. The number of sample paths used in the simulation was 5,000, with the $F^{(n)}(v, t)$ calculation updated up to the 1,000th sample path. The computation time for this result was approximately 15 min on an Ardent Titan/P3 machine. We envisage further reduction in simulation times with more efficient strategies. For example, the generation of quiescence times consumes the bulk of computation time during simulations. Until the convergence of the successive iteration process, one may perform simulations over a suitably fixed set of times after which a quiescence interval strategy may be employed for a more accurate computation.

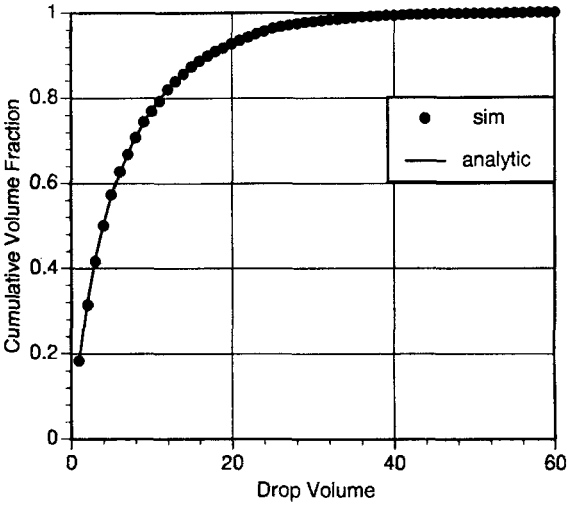

Figure 3. Single-particle simulation vs. analytical solution for pure coalescence.

Indeed, a single-particle process is easily envisaged from the foregoing treatment for simulating a dispersion in which both breakup and coalescence occur. Thus, the single particle in question may undergo random decreases (by breakup) or increase (by coalescence) in size. The resulting problem is an example of a classic "jump" process on stochastic processes (Gardiner, 1985). The pure breakup and pure coalescence processes are also jump processes with the jumps of fixed signs.

The advantage of the single-particle simulation process lies in its ability to accommodate transport or reaction processes in the dispersion. In the following example, an application is provided of the simulation technique for a continuous flow extractor in which mass transfer of a solute occurs between a population of droplets (evolving by breakage alone) and the continuous phase.

Application to an Inverse Problem in Mass Transfer

We consider here an application to a mass-transfer process in a continuous well stirred mixer fed with both the continuous-

and dispersed-phase droplets. The dispersed-phase fraction is assumed to be very small so that the drop size distribution evolves by breakup processes alone. We further assume that the drop breakup rates are known such as from the experiments of Narsimhan et al. (1984). In this regard, Sathyagal (1994) has investigated the problem of determining drop breakup rates from transient measurements of drop size distributions and established the breakage functions for droplets in a stirred dispersion.

Transport of a solute in the dispersed phase occurs from the droplets to the continuous phase. Since the dispersed-phase fraction is small, the influence of the transport process on the solute concentration in the continuous phase may be neglected. We shall describe the transport rate by an *overall* mass-transport coefficient which will produce the solute flux when multiplied by the difference between the average concentration in the droplet and the uniform concentration in the well-mixed continuous phase. (The more rational description of mass transport in the drop through the continuity equation is a difficult problem in view of the poor specification of the flow field in the drop.) This transport coefficient (which will vary with drop size) is generally inaccessible either theoretically (because the flow field specification is extremely difficult for a drop describing random relative motion in the turbulent continuous phase) or experimentally (because it would require the almost impossible task of making a Lagrangian observation of the drop). Of more significance is posing a suitable *inverse problem* which seeks to extract the size-dependent transport coefficients (the transport coefficients will also depend on other variables affecting the convective diffusion process) from knowledge of the size-specific drop breakup rates and other appropriate experimental data. A particularly interesting possibility lies in the work of Bae and Tavlarides (1989) which obtains the bivariate distribution of solute concentration and drop size in such a mass-transport process by examining individual droplets in the dispersion allowed to flow through a small capillary. Flow cytometry offers prospects of similar measurements in the future. We thus pose the following inverse problem. From measurements of the steady-state bivariate drop-size-solute concentration distribution in the continuous stirred tank described above for a particular feed distribution in terms of drop size and solute concentration the mass-transfer coefficients are determined in the droplets as a function of drop size and solute concentration.

Inverse problem

We retain the setting of the continuous mixer above and assume that all the inlet drops have the same concentration of solute. We neglect the change in drop size as a result of mass transfer. The steady-state equation for the bivariate volume density $f(v, x)$ may be obtained by multiplying the population balance equation by v, redefining the partitioning function $p(v, v')$ as in Eq. 4, and denoting by $g(v, v')$ the density function obtained by partially differentiating with respect to v the cumulative distribution function $G(v, v')$. The result is

$$\alpha\kappa(v)\frac{\partial f(v,x)}{\partial x}=\frac{1}{\theta}[\tilde{f}(v)\delta(x)-f(v,x)]+\int_v^\infty \Gamma(v')g(v,v')f(v',x)dv'-\Gamma(v)f(v,x) \quad (15)$$

where x is the dimensionless solute concentration, α is the equilibrium distribution coefficient, $\kappa(v)$ is the mass-transfer coefficient times the mass-transfer area per unit volume of the single drop of volume v, and $\tilde{f}(v)$ is the size distribution of all the incoming droplets with dimensionless concentration $x=0$. It is convenient to discretize the size interval and rewrite the above equation in transformed coordinates as

$$\frac{df}{dx}=\boldsymbol{A}\boldsymbol{f}+\boldsymbol{b}\delta(x) \quad (16)$$

where the matrix $\boldsymbol{A}$ is an upper triangular matrix. The details of the $\boldsymbol{A}$ and $\boldsymbol{b}$ matrices are given in the Appendix.

The inverse problem consists of the determination of $\kappa(v)$ given measurements of $f(v, x)$; the discrete version calls for determining $\kappa_1, \kappa_2, \ldots, \kappa_N$, given measurements of $\boldsymbol{f}$. Toward this end, we note that Eq. 16 can be solved to obtain

$$\boldsymbol{f}=\sum_{j=1}^{N}\beta_j e^{\lambda_j x}\boldsymbol{u}_j, \quad x>0 \quad (17)$$

where $$\lambda_j\equiv-\frac{1}{\alpha\kappa_j}\left[\Gamma_j+\frac{1}{\theta}\right],$$

β_j a constant, and $\boldsymbol{u}_j$ the jth eigenvector of $\boldsymbol{A}$ corresponding to eigenvalue λ_j. The details of the modal matrix $\boldsymbol{U}$ and the constants β_j are given in the Appendix. Since v_1 is the smallest droplet $\Gamma_1\equiv\Gamma(v_1)=0$. The dimensionless concentration x is so defined that it increases with mass transfer. For large enough x, Eq. 17 yields

$$\boldsymbol{f}\approx\beta_1 e^{\lambda_1 x}\boldsymbol{u}_1\equiv\boldsymbol{f}_1^\infty \quad (18)$$

From Eq. 18, plots of $\ln f_i(x)$ vs. x, will produce a family of parallel straightlines for large enough x with

$$\text{slope } \lambda_1 \text{ or } \lambda_1\equiv-\frac{1}{\alpha\kappa_1}\left[\Gamma_1+\frac{1}{\theta}\right]$$

from which κ_1 becomes available since Γ_1 and θ are both known. The intercept obtained by extrapolating the $\ln f_i$ vs. x curve backward to $x=0$ yields the value of $\beta_1 u_{i1}$ where u_{i1} is the ith element of $\boldsymbol{u}_1$. The eigenvector $\boldsymbol{u}_1$ may be estimated from the intercepts. The asymptotic function $\boldsymbol{f}_1^\infty$ may be subtracted from $\boldsymbol{f}$ in Eq. 17 and a plot of $\ln(\boldsymbol{f}-\boldsymbol{f}_1^\infty)$ vs. x, in principle, yields a new asymptotic distribution given by

$$\boldsymbol{f}-\boldsymbol{f}_1^\infty\approx\beta_2 e^{\lambda_2 x}\boldsymbol{u}_2\equiv\boldsymbol{f}_2^\infty \quad (19)$$

Repeating the steps (taken earlier with $\boldsymbol{f}$) for $\boldsymbol{f}-\boldsymbol{f}_1^\infty$ we obtain λ_2 and $\boldsymbol{u}_2$. The strategy may be conceived to yield progressively the eigenvalues $\lambda_1, \lambda_2, \ldots$, from which the transfer coefficients $\kappa_1, \kappa_2, \ldots$ can be estimated. There are many other interesting attributes to this estimation procedure because β_j, $\boldsymbol{u}_j$, $\boldsymbol{v}_j$ are explicitly known in terms of the coefficients of $\boldsymbol{A}$ and represent useful complementary equations for estimating the transfer coefficients, the detailed discussion of which is omitted here.

In practice (with either simulated or experimental data), significant number of drops cannot be identified with a specific

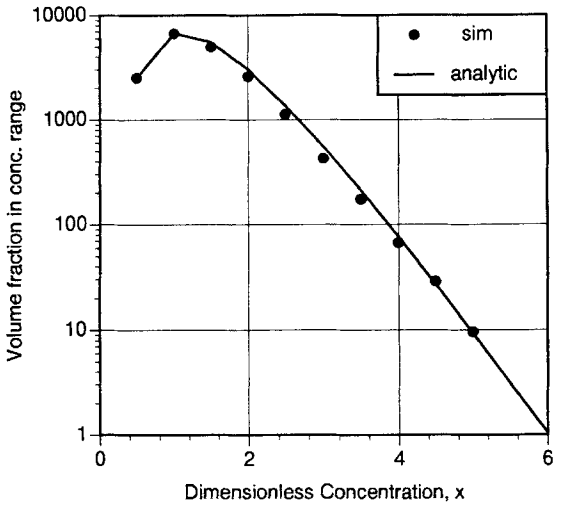

Figure 4. Analytical vs. simulation results for a 362-μm-dia. drop with 30-s residence time in the vessel and 400-rpm agitator speed.

concentration so that it is more advantageous to work with the volume fraction of droplets in suitably selected concentration *ranges*. An initial estimate of the eigenvalues (and hence mass-transfer coefficients) is obtained by plotting the volume fraction of drops in such concentration ranges vs. the average concentration for each range. For the largest drop v_N, the upper triangular nature of the matrix A leads to a single exponential factor featuring the eigenvalue λ_N (which has the largest absolute value) alone, so that a plot of $\ln f_N$ vs. x gives a straight line for *all* concentrations (not necessarily large concentrations). The slope of this straight line will give a good estimate of λ_N and hence of the mass-transfer coefficient κ_N. For v_{N-1}, we can subtract out the component of the distribution due to λ_N. The resulting distribution will give a straight line for all dimensionless concentrations when plotted on semilogarithmic

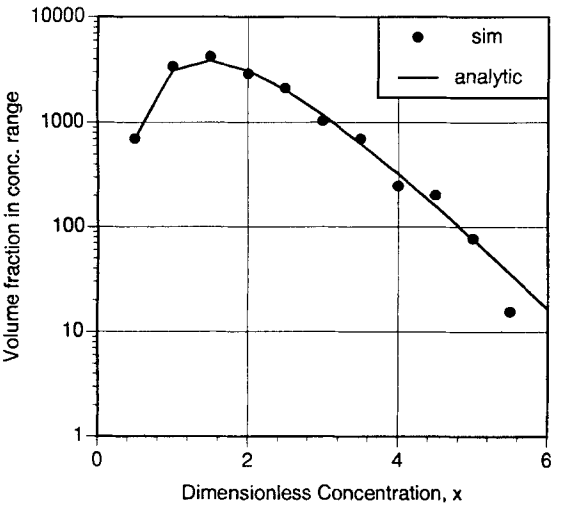

Figure 5. Analytical vs. simulation results for a 347-μm-dia. drop with 60-s residence time in the vessel and 400-rpm agitator speed.

Table 1. Inverse Problem for Mass-Transfer Coefficients

Drop Dia. μm	Actual Mass-Transfer Coeff., s^{-1}	Calc. Mass-Transfer Coeff., s^{-1}
250.8	4.925453	4.379753
295.0	3.985284	3.855735
325.4	3.509690	3.43632
351.6	3.176742	3.151689
362.5	3.054547	3.141484
390.8	2.773876	2.635103
399.7	2.695334	2.67322
407.8	2.627474	2.714452
437.7	2.401647	2.392542
445.2	2.350396	2.415536
452.5	2.302693	2.523643
477.5	2.151093	2.151093

coordinates. The slope of this straight line will give an improved estimate of the mass-transfer coefficient. However, since the coefficients in the biorthogonal expansion depend on the mass-transfer coefficient κ_{N-1}, this procedure has to be repeated until the value of the slope converges. This converged value gives a much better estimate of the mass-transfer coefficient than the initial estimate. The procedure is progressively applied from size v_N down to v_1. For size v_i, the components of the volume fraction corresponding to λ_{i+1} to λ_N are subtracted so that the volume fraction in the ith range alone is plotted vs. the average concentration. The ith eigenvalue λ_i is obtained from such a plot (or equivalently a linear regression procedure).

To test the effectiveness of this inverse problem approach, data were simulated using the procedure presented earlier, as shown in Figures 4 and 5 and in Table 1. The foregoing procedure used above to calculate the mass-transfer coefficients of individual droplets illustrates the value of inverse problems in extracting particle-specific information, otherwise inaccessible, from population measurements. Clearly, they add considerably to the strength and utility of experimental techniques such as those of Bae and Tavlarides (1989) and others such as those of flow cytometry (more commonly used in biological systems) in obtaining multivariate population data.

Conclusions

We have presented a perspective of the analysis of dispersed-phase systems based on the volume fraction of the dispersed phase. Although the relevant equations for the volume fraction distribution are readily obtained from the better known population balance equation, we have identified several interesting features of the equations in terms of the cumulative volume fraction. Besides the obvious aspect of providing the more relevant description of dispersed-phase systems from an engineering standpoint, equations in the cumulative volume fraction have been shown to possess: (i) simplicity of structure and characterization; (ii) equivalence to *single*-particle processes leading to efficient methods of simulation. The latter is important particularly for the numerical solution of discrete versions of population balance equations such as those of Bleck (1970), Sastry and Gaschignard (1981), and Hounslow et al. (1988). These methods are effective because *any discrete* choice of the particle size can be calculated. Furthermore, growth processes omitted in prior solutions pose no special problems in the simulation strategy presented here.

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Notation

A = matrix in Eq. 16
b = vector in Eq. 16
B = breakage function
c = solute concentration in drop
f = volume fraction density of drops
F = cumulative volume fraction of drops
g = volume fraction density of daughter drops
G = cumulative daughter drop distribution function
n = number density of drops
p = probability density of daughter drop distribution
q = coalescence frequency
t = time
v, v', v'' = drop volume
x = dimensionless solute concentration $= \ln (\alpha c_f - c_c)/(\alpha c - c_c)$

Greek letters

α = equilibrium distribution coefficient, c_c^*/c_d^*
Γ = breakage rate
δ = Dirac delta function
θ = residence time in vessel
κ = mass-transfer coefficient times the mass-transfer area per unit volume of a drop
ν = mean number of daughter drops
ϕ = dispersed-phase volume fraction

Subscripts and superscripts

c = continuous phase
co = continuous-phase feed
d = dispersed phase
o = feed
* = equilibrium

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Appendix

Equation 15 for the steady-state volume fraction density $f(v, x)$ can be discretized and rewritten as Eq. 16:

$$\frac{df}{dx} = \boldsymbol{A}\boldsymbol{f} + \boldsymbol{b}\delta(x)$$

A is an $n \times n$ upper triangular matrix whose elements are

$$a_{ij} = -\frac{\left(\frac{1}{\theta} + \Gamma_i\right)}{\alpha\kappa_i} \quad \text{if } i = j$$

$$a_{ij} = \frac{\Gamma_i g_{ij}}{\alpha\kappa_i} \quad \text{if } i < j$$

$$a_{ij} = 0 \quad \text{if } i > j$$

$\boldsymbol{f}$ is an n-dimensional vector with $f_i = f(v_i, x)$ and $\boldsymbol{b}$ is also an n-dimensional vector with

$$b_i = \frac{\tilde{f}_i}{\theta\alpha\kappa_i}$$

The solution of the set of linear differential equations given by Eq. 16 can be written as

$$f = \sum_{j=1}^{N} \beta_j e^{\lambda_j x} \boldsymbol{u}_j, \quad x > 0$$

where $\lambda_j = a_{jj}$ is the jth eigenvalue of $\boldsymbol{A}$, $\boldsymbol{u}_j$ is the jth eigenvector of $\boldsymbol{A}$ corresponding to the eigenvalue λ_j, and β_j is a constant

which can be calculated from the jth eigenvector and eigenrow as:

$$\beta_j = \frac{\langle \boldsymbol{v}_j, (\boldsymbol{b} + \hat{\boldsymbol{f}}) \rangle}{\langle \boldsymbol{u}_j, \boldsymbol{v}_j \rangle}$$

$\boldsymbol{v}_j$ is the jth eigenrow and $\langle ., . \rangle$ denotes the inner product.

The eigenvectors, $\boldsymbol{u}_j$, and the eigenrows, $\boldsymbol{v}_j$, can be written in matrices $\boldsymbol{U}$ and $\boldsymbol{V}$, where each column of the corresponding matrix is an eigenvector (for $\boldsymbol{U}$) or an eigenrow (for $\boldsymbol{V}$).

The elements, U_{ij}, of the matrix $\boldsymbol{U}$ can be written as:

$$U_{ij} = 0 \qquad i > j$$

$$U_{ij} = 1 \qquad i = j$$

$$U_{ij} = \frac{1}{\lambda_j - \lambda_i} \sum_{k=j}^{i+1} \frac{\Gamma_k g_{ik}}{\alpha \kappa_i} U_{kj} \qquad i < j$$

The elements, V_{ij}, of the matrix $\boldsymbol{V}$ can be written as:

$$V_{ij} = 0 \qquad i < j$$

$$V_{ij} = 1 \qquad i = j$$

$$V_{ij} = \frac{1}{\lambda_j - \lambda_i} \sum_{k=j}^{i-1} \frac{\Gamma_i g_{ki}}{\alpha \kappa_k} V_{kj} \qquad i > j$$

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