ChE lecture

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THE PROSPECTS OF POPULATION BALANCES

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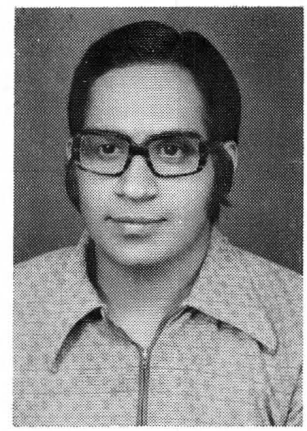
THE DISPERSION OF one phase into another has been the crux of the chemical engineer's craft for carrying out a host of transfer operations. Thus, numerous separation processes based on direct phase-contacting such as liquid-liquid extraction, distillation, absorption etc. are conducted in dispersed phase systems. There are others that are essentially particulate in nature such as crystallization, fluidization, communition, microbial growth, etc. The behavior of such systems is a complex combination of processes occurring at the single particle level. Thus, each individual particle may participate in rate processes (such as by its neighborhood in the continuous phase being under non-equilibrium conditions) and in processes such as *breakage* and *agglomeration* with other particles, that continually *destroy the identity* of existing particles.

The method of population balances falls somewhat naturally into the mathematical treatment of dispersed phase systems but for a variety of reasons, the methodology has not been adequately exploited. A notable exception is, perhaps the area of crystallization, mainly due to the efforts of Randolph and Larson [1]. Chiefly among the reasons for the unpopularity of population balances are (1) the complexity of the integro-differential equations, which result from them, and (2) the lack of suitable experimentation to evaluate the models. It is the objective of this communication to provide an overview of progress in the application of population balances and to point to their lucrative credentials for further work.

WHAT ARE POPULATION BALANCES?

THE CENTRAL IDEA of population balances is to formulate a *number balance* equation for particles of each "type". Particles are identified by "types" that are quantified as *discrete* variables or more discreetly, as *continuous* variables. Any given type may be destroyed into, or formed from, other types. In writing a number balance for each type one is concerned with the "source" and "sink" terms for that type.

Population balances are essential for the description of systems in which not only are particles present but where the *identity* of individual particles is modified or destroyed by processes



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such as breakage or agglomeration. The framework becomes somewhat redundant in situations where the identity is preserved permanently for all particles.

The description of rate processes of course proceeds through the formulation of the equations of transport phenomena. Thus, for example, to describe mass transfer in a single drop in a liquid-liquid extraction process, the required apparatus is furnished by the methodology of transport phenomena. However, this is true only insofar as the *identity* of the drop is preserved without disappearing into another type. Clearly, therefore in dispersed phase systems the population balance framework is essential. More detailed considerations have been presented elsewhere [2, 3].

MATHEMATICAL FRAMEWORK

THE PARTICLE "TYPE" is described by one or more *state* variables* generally regarded as continuous. If a single variable is used then we refer to it as a *scalar* state variable as against a vector state variable for types described by more than one variable. The number of particles in the system is assumed to be sufficiently large that a *continuous* variable may be used to denote the total number of particles in the system. The choice of the state variables depends much on the system of interest. Generally, one must select all particle properties which determine completely the behavior of single particles.

Let the particle state be denoted by a vector $\mathbf{x} \equiv (x_1, x_2, \ldots, x_s)$, which is a set of s physical quantities, whose numerical values will identify a given particle (Particles of identical states are assumed to be indistinguishable). The fundamental quantity describing the population is the *number density* function, $n(\mathbf{x},t)$, which is regarded as a smooth function of x and t. It is the number of particles per *unit volume* of the state space. The total number of particles, $N(t)$ in the system is given by

$$N(t) = \int n(\mathbf{x},t)\,dV$$

where dV is an infinitesimal volume in the state space of dimension, s. Limits on the volume integral have been excluded by design to indicate that the integration extends to the entire state space.

*Examples of state variables are particle size, age, temperature, concentration of some dissolved solute etc.; physical space variables may also be included.

The state of any given particle may change due to one reason or another. We are here referring to *continuous* changes in particle state in which the identity of the particle is preserved. Thus a change in particle size by "growth" such as in a growing crystal or a microorganism comes under the present context, whereas a size change due to, say particle breakage does not. Such changes in state can be frequently modeled on a physical basis, e.g. conservation principles. We denote the rate of change of a particle of state x by a vector function $\dot{\mathbf{X}}$, which may depend on x and variables assocated with the continuous phase.

There are other processes that are essentially particulate in nature such as crystallization, fluidization, communication microbial growth, etc. The behavior of such systems is a complex combination of processes occurring at the single particle level.

For the purpose of deriving the population balance equation in the number density function, it is useful to regard the particles as *embedded* in a continuum which deforms in accordance with the *kinematic field* represented by the vector $\dot{\mathbf{X}}(\mathbf{x})$. (For the present we exclude variables connected with the continuous phase). By embedding the particles on this deforming continuum we imply that a particle at a point x moves with the local velocity $\dot{\mathbf{X}}(\mathbf{x})$. Alternatively, no relative velocity can exist between the continuum and the particle. This viewpoint makes the derivation of equations particularly convenient. Besides in dealing with situations where particle state changes *randomly* about a mean rate, we may look upon the particles as *diffusing* in the continuum deforming with the *mean* velocity field.

Let $h^+(\mathbf{x},t)\,dV$ be the **rate** of increase in the number of particles in a volume dV about x in the state space. Similarly we may define a *sink* function $h^-(\mathbf{x},t)$ so that the *net generation* rate $h(\mathbf{x},t)$ is given by

$$h(\mathbf{x},t) \equiv h^+(\mathbf{x},t) - h^-(\mathbf{x},t) \qquad (1)$$

The population balance equation can now be readily written by invoking the continuity operator in the particle state space.

$$\frac{\partial}{\partial t} n(x,t) + \nabla \cdot \dot{X}\, n(x,t) = h(x,t) \qquad (2)$$

Equation (2) has been derived by Hulburt and Katz [4]. It must be coupled with mass balance equations for continuous phase variables (see for example [5]).

At this point, it must be pointed out that what we have accomplished is only the mathematical formulation of a rather obvious accounting principle for particle numbers. Equation (2) by itself is therefore not to be construed as a population balance *model.* The modeling lies in identifying the *nature* of the functions $\dot{X}$ and $h(x,t)$ for a given situation.

As observed earlier, $\dot{X}$ may often be modeled by physical conservation principles and transfer coefficients. The function $h(x,t)$ depends on the process by which particle-types appear and disappear. For example, communition operations involve particle splitting. For such processes, one identifies a *specific rate* of splitting of particles of state x' (a transition probability function), say $\Gamma(x')$, a function $\nu(x')$ representing the mean number of particles formed by splitting of a parent particle of size x', and a conditional probability distribution $p(x,x')$ for the sizes of particles formed from breakage. Thus for the present case we have

$$h^+(x,t) = \int \nu(x')\, \Gamma(x')\, p(x,x')\, n(x',t)\, dx' \qquad (3)$$

and

$$h^-(x,t) = \Gamma(x)\, n(x,t) \qquad (4)$$

When Equations (1), (3) and (4) are substituted into (2), the population balance model is completely identified. Of course boundary and initial conditions must also be appended. The important point to note is that the functions, $\Gamma(x')$, $\nu(x)$, $p(x,x')$ are actually unknown and must be obtained by more detailed modelling of the splitting process, or must be inferred from suitable experiments.

Similar problems arise also in the modelling of agglomerating populations. Thus, consider a population of particles distributed according to their volumes, in which any two particles of volumes v and v' agglomerate in the time interval t to t+dt with probability $q(v,v')\,dt$. Then it is readily shown that

$$h(v,t) = \frac{1}{2}\int_0^v q(v-v',v')\, n(v',t)\, n(v-v',t)\, dv' - n(v,t)\int_0^\infty q(v,v')\, n(v',t)\, dv' \qquad (5)$$

Again, the transition probability of agglomeration, $q(v,v')$ requires identification by more detailed modelling and experimentation.

As pointed out earlier, the significant difficulties in the application of population balances are in the solution of the integro-differential equations, and in the identification of the probability functions which describe particle behavior. Some past work is reviewed here in regard to either of these aspects.

SOLUTION OF EQUATIONS

SINCE, FREQUENTLY the leading moments of the number density function is a satisfactory description of the population, it has been suggested [4, 6, 7] that moment equations be directly obtained from the balance equation. Frequently, this leads to trouble either in the form of unclosed moment equations, equations with fractional moments, or those that simply do not directly yield moments. To overcome these difficulties, a Laguerre function expansion of the number density function, has been suggested [4]. These methods can be readily shown [8] to be a special (and therefore restricted) application of the method of weighted residuals. Thus, Subramanian and Ramkrishna [9] have solved population balance equations for a microbial population distributed according to their mass, in which individual cells grew by assimilating nutrient material from the environment and reproduced by binary division. Solutions for the population balance equation, which was coupled to the mass balance equation for the substrate concentration, were obtained using Laguerre functions as trial functions and orthogonalizing the residual with various choices of weighting functions.

The choice of the trial function is a vital aspect of success with weighted residual techniques. Thus, "standard" choices such as Laguerre polynomials can often be significantly improved upon. For example, one may generate "problem-specific polynomials" [10] from the set $\langle x^n \rangle$ by Gram-Schmidt orthogonalization using suitably weighted inner products. A desirable weight function for the inner product should essentially have a shape and trend similar to that of the solution. The advantage of generating such polynomials as trial functions for solving population balance equations

by the method of weighted residuals has been demonstrated by Singh and Ramkrishna [11, 12]. Thus transient solutions have been obtained in which specifically generated time-dependent trial functions assure rapid convergence of the solution at all times[12].

When the particle state variable is a vector, the resulting multivariate number density functions are likely to be much harder to solve for. This problem requires further investigation. An alternative route to obtaining solutions, however lies in simulation techniques [13-17]. Although simulation techniques often involve arbitrarily discretizing the time interval, a recent method due to Shah et al [17], handles the artificial evolution of the system in an elegant manner by generating random numbers representing "intervals of quiescence". Each interval of quiescence is a period, in which every member of population retains its identity, and has an exactly calculable probability distribution. Thus no tests for the adequacy of the fineness of discretization would be necessary in such a simulation procedure.

MODEL IDENTIFICATION

THE PROBABILITY FUNCTIONS characterizing random particle behavior must be identified before population balance equations can be quantitatively applied to real systems. As an example, consider the particle-splitting process referred to earlier, for which the model was defined by the functions, $\Gamma(x')$, $\nu(x')$, $p(x,x')$. A direct experimental determination of such probability functions is a very difficult task. With suitable additional modelling, however the problem may at times be tractable. In a liquid-liquid dispersion, with a low dispersed phase fraction coalescence between droplets is likely to be negligible during the temporal evolution of the dropsize distribution which primarily occurs by drop breakage. By proposing that the breakage probability function for a drop of volume v is given by $\Gamma(v) = kv^n$, it can be shown [18] that the cumulative-volume distribution of drop-volume denoted $F(v,t)$ has an explicit similarity solution in the variable $v^n t$, i.e., $F(v,t) = g(\xi)$, where $\xi = v^n t$. In order to test this hypothesis, if experimental data on dropsize distributions are available at various times in a batch vessel, then a plot of *l*nv versus *l*nt for any fixed value of F should produce a straight of slope — n. Besides, parallel straightlines should be obtained if the plots are made for different fixed values of F. From the experimental data of Madden and McCoy [19], such tests have in fact shown [18] that a power law breakage model may be a good representation of $\Gamma(v)$. The similarity plot using the calculated value of n, can then be used to determine the size distribution of the droplets formed from the broken drop [18]. The data of Madden and McCoy yield approximately a value of 2 for the power n. Based on modelling drop breakage as a result of relative velocity fluctuations across the droplet surface, arising from the continuous phase turbulence, the application of Kolmogorov's theory of local isotropy appears to vindicate the power law expression with n having a value of about 2.67 [20].

The central idea of population balances is to formulate a number balance for particles of each "type." Particles are identified by "types" that are discrete variables or more discreetly, as continuous variables. Any given type may be destroyed into, or formed from, other types.

As another example, one may consider denser liquid-liquid dispersions with high dispersed phase fraction. Since breakage and coalescence are both important in this situation the breakage and coalescence probabilities must be known. Following an earlier visualization by Curl [21] of the coalescence-redispersion process as a *single-step* process, Bajpai *et al* [22] proposed that droplets in a dispersion coalesce and immediately redisperse into two new droplets in a perfectly random manner. They solved the population balance analytically to obtain an *exponential drop-volume distribution* at equilibrium, which showed good agreement with experimental data from diverse sources.

The implication of the two preceding paragraphs is that there seems to be sufficient evidence pointing to the tractability of population balance models from an experimental viewpoint.

SMALL POPULATIONS

POPULATION balance equations are essentially sentially for describing the behavior of large particle populations in which random behavior of individual particles is averaged out. The number density function $n(x,t)$ is the *expected* population density. Although most systems of interest in

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ChE involve large populations, there are also situations in which small particle populations may be encountered. Thus bubble populations arising in a gas phase fluidized bed, continually agglomerate as they ascend through the bed, to form small populations. Such situations cannot always be described by population balance equations. Ramkrishna and Borwanker [23-25] have shown that the framework of population balances derives as a special case of the theory of point processes. Thus the population balance equation is shown to be the *first* of an infinite hierarchy of equations in what have been called as *product densities* all of which are required for the analysis of small populations in which random fluctuations may be important. Further, they have shown [25] that the model (5) normally used for agglomerating populations would be incorrect, when particle states are correlated. In such a case, additional members of the hierarchy of product density equations must be accounted for. Substantial particle size correlations have been predicted for some agglomeration probabilities, These have far-reaching practical implications. Thus in a fluidized bed reactor, one may raise the question as to whether or not randomly behaving bubble populations would give rise to fluctuations in reactor conversion.

Indeed, there are many engaging problems in the analysis of dispersed phase systems. Undoubtedly, considerably more detailed experimentation is required for further quantitative application of population balances. In view of the large variety of applications, the method of population balances deserves more vigorous pursuit. □

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