Simulation of Particulate Systems Using the Concept of the Interval of Quiescence

A simulation procedure is presented in this work which can analyze the behavior of any dispersed phase system consisting of particles whose random behavior is specified in terms of probability functions. The procedure distinguishes itself from its predecessors in being free from arbitrary discretization of time or any other parameter along which the system evolves, and its ability to predict the behavior of randomly behaving small populations. Where population balance equations, which describe the behavior of particulate systems, cannot be readily solved, the simulation technique presented herein represents an efficient alternative to the modeling of such systems. Tables and a flow chart are given which would enable the use of the method for any system with specified particle behavior.

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SCOPE

Particulate systems occur commonly in chemical engineering. Thus they cover the large variety of separation processes in which contacting between say, two immiscible phases is accomplished by dispersing one of them finely in the other. The description of rate processes in particulate systems requires the framework of population balances, which lead to complex integrodifferential equations that are frequently difficult to solve. An alternative to this approach is to resort to Monte Carlo simulations, which are artificial realizations of the process of interest on the computer using appropriate random number generating techniques.

In the past, simulation techniques have been discussed by various workers (Spielman and Levenspiel, 1965; Collins and Knudsen, 1970; Rao and Dunn, 1970; Zeitlin and Tavlarides, 1972). Although these techniques may be used satisfactorily on large population systems, they cannot be adapted for situations in which random behavior of individual particles may result in a randomly behaving population; this is characteristic of small populations which may be of significance in coalescing dispersions such as a bubbling fluidized bed. Besides, earlier simulation techniques have been based on discretizing the time interval, a frequently hazardous procedure.

A simulation procedure is presented in this work which has been used by the authors in various problems involving particulate systems (Ramkrishna et al., (1976); Shah et al., (1977). This technique is free from procedures of arbitrary discretization of the time interval and efficiently handles the stochastic behavior of small systems.

CONCLUSIONS AND SIGNIFICANCE

The simulation procedure presented herein can deal with models of particulate systems for small and large populations alike. No consistency checks are required on the size of discretization of the time interval to verify the results of the simulation.

The technique has been used on simulating chemical reactions in a liquid-liquid system in a CSTR using Curl's model. Drop populations as small as 50 were found to be sufficient as against 500 used by Spielman and Levenspiel in a corresponding effort. As a result, substantial saving in computer time could be achieved. Tables 1 and 2 and Figure 1 summarize the simulation procedure conveniently for use in any particulate system, where models are available for particle breakage and agglomeration.

The method is easily adapted to situations in which multivariate number density functions are involved. Thus, rate processes in dispersed phase systems can be handled with alterations that are readily incorporated. It is essential to use the technique presented here to analyze stochastic effects associated with small populations. Thus, for example, the conditions under which stochastic effects may be present in a bubbling fluidized bed may be ascertained by the current simulation procedure (Shah et al., 1977). A further problem of interest that could be investigated is whether random conversions result in fluidized-bed reactors because of randomly changing bubble populations.

The mathematical formulation of models of particulate systems frequently leads to integro partial differential equations which are difficult to solve except in a few simple cases. Since random phenomena constitute the evolution and performance of a particulate system, Monte Carlo simulation offers an interesting alternative to analyze these systems. In the recent past, a few papers have appeared dealing with the application of Monte Carlo simulation. Spielman and Levenspiel (1965) suggested a simulation scheme for the coalescence-redispersion model of Curl (1963) in a liquid-liquid system. They made a few simplifications for the purposes of simulation. The entry and exit

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were assumed to occur at the end of uniform intervals of time. The total number of droplets in the vessel remains fixed. Between two entry (or exit) events, a fixed number of coalescence-redispersion events (equal to the expected value of the actually random number) take place. These simplifications do not conform to the model of the random phenomena. Any of the droplets has the same chance of leaving. Since the average number of droplets entering is equal to the average number of droplets leaving and the coalescence-redispersion events do not change the number of droplets in the vessel, the total number is a random variable with constant expected value. Thus, the stochastic nature of the model cannot be brought out by the scheme of Spielman and Levenspiel (1965), although stochastic features were not important in the situations of interest to them. Rao and Dunn (1970) have used a similar scheme for simulation of a turbulent plug flow reactor. Collins and Knudsen (1970) simulated experimentally observed drop size distributions in a turbulent pipe flow. In their scheme, a certain number of discrete steps are deemed equivalent to a length of the pipe. However, how many such steps are necessary for a given length of pipe is not certain. The discretization of the length is somewhat arbitrary in their scheme. Zeitlin and Tavlarides (1972*a, b, c*) have also used similar techniques of simulation in their analysis of droplet phenomena in liquid-liquid dispersions.

We present here a simulation procedure for particulate systems which conforms exactly to the mathematical model. The procedure has been used by the authors to simulate a variety of systems (Shah, 1975; Shah et al., 1976, 1977). The evolution parameter (such as time or length) along which the process evolved is discretized in a natural way.

In the considerations that follow, we refer to as a particulate event or phenomenon any event that destroys the identity of any given particle in some region in space. Thus, coalescence and breakage of droplets are particulate events. Particle entry into a given space or exit from it may also be regarded as particulate events. We define an interval of quiescence (IQ) as the length of time that elapses after a particulate phenomenon takes place and before the next one. During an IQ, no particulate event takes place. The evolution of the system is thus represented in terms of a series of particulate events. Since the phenomena are stochastic, the IQ is a random variable. Here we give the probability distribution of the IQ for different types of phenomena. We provide no details of the derivation of such distributions, since they are based on rather simple use of the rules of probability. Growth of the property of particles is also incorporated. The formation of new particles from some particulate phenomena may be governed by other probability laws. These are also included in the sequence of random variables representing the evolution of a particulate system.

THE MATHEMATICAL MODEL

The mathematical model of a particulate system consists of assumptions about three basic aspects: the initial condition in terms of number and properties of the particles, the transition probabilities or frequencies of the particulate phenomenon, and the growth behavior of particles, if any. Any simplification introduced in the governing population balance equation or the simulation scheme are extraneous to the model and introduce approximations.

The behavior of a particulate system is a reflection of the experiences of the individual particles in the system. The evolution of the system will be determined by a series of stochastic particle events separated in time. Each event may influence one or more particles, thereby altering the property distribution and the system behavior as a whole.

The initial condition of a particulate system may be specified by fixing the properties of individual particles or may be generated in terms of the initial distribution (Shah, 1975). The particulate phenomena are described in terms of their transition probabilities usually referred to as frequencies. We consider only two categories of phenomena:

Table 1. Probability Distributions of the Interval of Quiescence and the Indicator Variable for Different Cases in the Absence of Growth

Class of particulate phenomena	Cumulative probability distribution of IQ $F_T(\tau\|A_t) = Pr[T \leq \tau\|A_t]$		Probability distribution of the indicator variables	
One monoparticle	$F_T(\tau\|A_t) = 1 - \exp[-\tau S_b]$	(3)	$Pr[u = j\|A_t, T] = \dfrac{b(x_j)}{S_b}$	(7)
m types of monoparticle	$F_T(\tau\|A_t) = 1 - \exp[-\tau S_{bm}]$	(4)	$Pr[u = (k,l)\, A_t, T] = \dfrac{b_k(x_l)}{S_{bm}}$ $k = 1, 2, \ldots, m$ $l = 1, 2, \ldots, N(t)$	(8)
One biparticle	$F_T(\tau\|A_t) = 1 - \exp[-S_q]$	(5)	$Pr[u = (k,l)\, A_t, T] = \dfrac{q(x_k, x_l)}{S_q}$ $k = 1, 2, \ldots, N(t) - 1$ $l = k + 1,\ k + 2, \ldots, N(t)$	(9)
m types of monoparticle and one biparticle	$F_T(\tau\|A_t) = 1 - \exp[-\tau\{S_{bm} + S_q\}]$	(6)	$I = 1$ monoparticle event $I = 2$ biparticle event	
			$Pr[I = 1\|A_t, T] = \dfrac{S_{bm}}{S_{bm} + S_q}$	(10)
			$Pr[I = 2\|A_t, T] = \dfrac{S_q}{S_{bm} + S_q}$	(11)
			$Pr[u = (k,l)\|A_t, T, I = 1] = \dfrac{b_k(x)}{S_{bm}}$ $k = 1, 2, \ldots, m$ $l = 1, 2, \ldots, N(t)$	(12)
			$Pr[u = (k,l)\|A_t, T, I = 2] = \dfrac{q(x_k, x_l)}{S_q}$ $k = 1,2, \ldots, N(t) - 1$ $l = k + 1,\ k + 2, \ldots, N(t)$	(13)

TABLE 2. PROBABILITY DISTRIBUTIONS OF THE INTERVAL OF QUIESCENCE AND THE INDICATOR VARIABLE FOR DIFFERENT CASES IN THE PRESENCE OF GROWTH

Class of particulate phenomena	Cumulative probability distribution of IQ $F_T(\tau\|A_t) = PR[T \leq \tau\|A_t]$	Probability distribution of the indicator variables
One monoparticle	$F_T(\tau\|A_t) = 1 - \exp\left[-\int_o^\tau S_{bg}(\tau')\,d\tau'\right]$ (14)	$Pr[u = j\|A_t, T] = \dfrac{b(x(t+T; x_j, t))}{S_{bg}(T)}$ (18)
m types of monoparticle	$F_T(\tau\|A_t) = 1 - \exp\left[-\int_o^\tau S_{bmg}(\tau')\,d\tau'\right]$ (15)	$Pr[u = (k, l)\,A_t\,T] = \dfrac{b_k(x(t+T; x_l, t))}{S_{bmg}(T)}$ (19) $k = 1, 2, \ldots, m$ $l = 1, 2, \ldots, N(t)$
One biparticle	$F_T(\tau\|A_t) = 1 - \exp\left[-\int_o^\tau S_{qg}(\tau')\,d\tau'\right]$ (16)	$Pr[u = (k, l)\|A_t, T] = \dfrac{q(x(t+T; x_k, t), x(t+T; x_l, t))}{S_{qg}(T)}$ (20) $k = 1, 2, \ldots, N(t) - 1$ $l = k + 1, k + 2, \ldots, N(t)$
m types of mono particle and one biparticle	$F_T(\tau\|A_t) = 1 - \exp\left[-\int_o^\tau \{S_{bmg}(\tau') + S_{qg}(\tau')\}d\tau'\right]$ (17)	$I = 1$ monoparticle event $I = 2$ biparticle event $Pr[I = 1\|A_t, T] = \dfrac{S_{bmg}(T)}{S_{bmg}(T) + S_{qg}(T)}$ (21) $Pr[I = 2\|A_t, T] = \dfrac{S_{qg}(T)}{S_{bmg}(T) + S_{qg}(T)}$ (22) $Pr[u = (k, l)\|A_t, T, I = 1] = \dfrac{b_k(x(t+T; x_l, t))}{S_{bmg}(T)}$ (23) $k = 1, 2, \ldots, m$ $l = 1, 2, \ldots, N(t)$ $Pr[u = (k, l)\,A_t, T, I = 2] = q(x(t+T; x_k, t), x(t+T; x_l, t))/S_{qg}(T)$ $k = 1, 2, \ldots, N(t) - 1$ $l = k + 1, k + 2, \ldots, N(t)$

Symbols used in Tables 1 and 2

$$S_b = \sum_{i=1}^{N(t)} b(x_i) \quad (25) \qquad S_{bg}(\tau') = \sum_{i=1}^{m} b(x(t+\tau'; x_i, t)) \quad (28)$$

$$S_{bm} = \sum_{i=1}^{m} \sum_{j=1}^{N(t)} b_i(x_j) \quad (26) \qquad S_{bmg}(\tau') = \sum_{i=1}^{m} \sum_{j=1}^{N(t)} b_i(x(t+\tau'; x_j, t)) \quad (29)$$

$$S_q = \sum_{i=1}^{N(t)-1} \sum_{j=i+1}^{N(t)} q(x_i, x_j) \quad (27) \qquad S_{qg}(\tau') = \sum_{i=1}^{N(t)-1} \sum_{j=i+1}^{N(t)} q(x(t+\tau'; x_i, t), x(t+\tau'; x_j, t)) \quad (30)$$

monoparticle and biparticle events.* The frequency is a function of the property of the particles involved in the event. The frequencies of the two types of events are defined as follows.

Pr [a given particle of property x undergoes a monoparticle event in time t to $t + dt$] $= b(x)dt + O(dt)$ (1)

$O(dt)$ represents terms which when divided by dt tend to zero as dt tends to zero.

Pr [a given particle of property x interacts with another given particle of property y in time between time t and $t + dt$] $= q(x, y)dt + O(dt)$ (2)

THE SIMULATION TECHNIQUE

Given the initial state of the system, the particles undergo events with associated transition probabilities postulated in the model. Two subsequent events will be separated by the interval of quiescence, denoted T. At the end of an IQ, one of the possible particulate events takes place. The one or two particles involved in an event are designated by a random indicator variable u whose probability distribution also depends on the frequency. The realization of the process consists of a series of random variables

$$T_1, u_1, \quad T_2, u_2, \quad \ldots \quad (3)$$

where T_i is the i^{th} IQ, and u_i is the indicator of the event at the end of it. The properties of new particles formed as a result of the phenomenon may be governed by some other specified probability laws. Their realizations are included by appropriate random variables. Once the probability distributions of these random variables are known, they can be generated on the computer by well-known methods (Moshman, 1967).

The probability distributions of T_i and u_i depend on the state of the system, the frequencies, and the growth behavior of the particles. The probability distributions are summarized in Tables 1 and 2.

* Independent breakage of a single particle is a monoparticle event. Agglomeration of two particles is a biparticle event.

The system may be simulated a sufficient number of times, keeping a record of the state at various values of time. Let S be the number of simulations carried out. The overall properties of the system or the property distribution of particles can be estimated from the results of the S simulations. Let $N(x, t)$ be the number of particles with property $\leq x$. Then

$$N(x,t) = \int_o^x n(x',t)\,dx' \tag{4}$$

where $n(x, t)$ is the random population density (Ramkrishna and Borwanker, 1973). The expected cumulative property distribution is

$$\beta_1(x,t) = EN(x,t) = \int_o^x f(x',t)dx' \tag{5}$$

where f is the population density. Also, let $W(t)$ be an overall property of the system like average property of the population, total transfer rate, and so on. $W(t)$ can be written in terms of the contribution of individual particles $w(x)$. Thus, if $W(t)$ is the total transfer rate, then $w(x)$ is the transfer rate from a particle of property x:

$$W(t) = \int_o^\infty w(x)\ n(x,t)\,dx = \sum_{i=1}^{N(t)} w(x_i) \tag{6}$$

Here x_i, $i = 1, 2, \ldots, N(t)$, are properties of the particles present at t. Let $N_j(x, t)$ and $W_j(t)$ be the values computed in the j^{th} simulation $j = 1, 2, \ldots, S$. The estimates of $\beta_1(x, t)$, $EW(t)$, and $VW(t)$ denoted $\hat{\beta}_1(x, t)$, $\hat{EW}(t)$, and $\hat{VW}(t)$, respectively, are given by

$$\hat{\beta}_1(x,t) = \frac{1}{S}\sum_{j=1}^{S} N_j(x,t) \tag{7}$$

$$\hat{EW}(t) = \frac{1}{S}\sum_{j=1}^{S} W_j(t) \tag{8}$$

$$\hat{VW}(t) = \frac{1}{S-1}\sum_{j=1}^{S} [W_j(t) - \hat{EW}(t)]^2 \tag{9}$$

The confidence intervals on estimates for a specified confidence level, say 95%, can also be found. Thus, confidence interval for EW is

$$\hat{EW} - k \leq EW \leq \hat{EW} + k \tag{10}$$

where

$$k = c\sqrt{\frac{\hat{VW}}{S}} \tag{11}$$

c is a constant which depends on the number of degrees of freedom $S - 1$ and is tabulated in standard references (for example, Owen, 1962).

SUMMARY OF THE SIMULATION PROCEDURE

A simulation technique has been designed incorporating the concept of the interval of quiescence (IQ), the period between successive particulate events. The technique simulates the representative sequence of random variables which is equivalent to the evolution of the particulate system in time. The procedure starts with the initial state of the system A_o, representing the properties of the particles at time $t = 0$:

$$A_o = [x_i;\quad i = 1, 2, \ldots, N_o] \tag{12}$$

The initial condition may be specified exactly when the information on the initial population is known with certainty. For random initial conditions, the probabilistic information about the initial population can be incorporated in the form of probability statements about the number of particles with property $\leq x$. The variables representing the state of the system are initialized, a term we use to replace the initial condition by the present condition:

$$N_o \rightarrow N(t),\quad A_o \rightarrow A_t \tag{13}$$

The procedure then goes ahead with generating the IQ in terms of the state of the system at time t. The probability distribution of the IQ depends on the type of the particulate phenomena, whether growth of the particles is present, and on the frequencies of the various particulate events. Now the discrete random variable represents the type of event and/or the one or the pair of the particles involved in the event. The probability distributions of the IQ and the indicator variables are summarized in the Tables 1 and 2. For example, in a population of particles distributed according to property x, with $b(x)$ representing the frequency of a monoparticle event, the probability that a particle of property x does not undergo the said event (that is, retains its identity) until time τ is easily seen to be $e^{-b(x)\tau}$. Given that initially there are N particles of states $x_1, x_2, \ldots, x_n$, etc., the probability that all of them retain their identity until time τ is

$$\exp\left[-\sum_{i=1}^{N} b(x_i)\tau\right].$$

The cumulative distribution function for IQ is then

$$1 - \exp\left[-\sum_{i=1}^{N} b(x_i)\tau\right].$$

More detailed considerations have been given by Shah et al. (1976).* The new particles are generated, and the changes in the state of the system are then determined. The value of time t, the state, and the number and properties of the particles are then updated, taking into account the growth rate of particles. In Tables 1 and 2, $x(t + \tau, x_i, t)$ represents the solution of the equation $dx/dt = \dot{x}(x)$ with the initial condition $x(t) = x_i$. The above procedure is continued up to the desired final value of time T_f.

The estimation computations for various quantities of interest are incorporated. The simulation up to time T_f is repeated a number of times, S and the summations required for estimations [Equations (7) to (11)] are performed. Finally, the estimates and the confidence limits are computed.

Results at different values of time T_{f1}, T_{f2}, ... can be obtained by making minor modifications of the procedure described. Thus, we have:

Input data

S; T_f: values of property x where $\beta_1(x, t)$, $\beta_2(x_1, x_2, t)$, ... are needed. [These values of x are denoted x_j^{es}, $j = 1, 2, \ldots, N_x$.]

Parameters of frequencies and growth rate. Initial condition.

Output results

Estimates and confidence intervals of the required quantities like $EN(t)$, $\beta_1(x, t)$, $\beta_2(x_1, x_2, t)$, average property, overall transfer rate, and so on.

A flow chart for the simulation procedure is shown in Figure 1, with a glossary of the symbols used.

* These details refer to the specific problem of microbial population growth. However, biparticle events were neither considered nor relevant to that work.

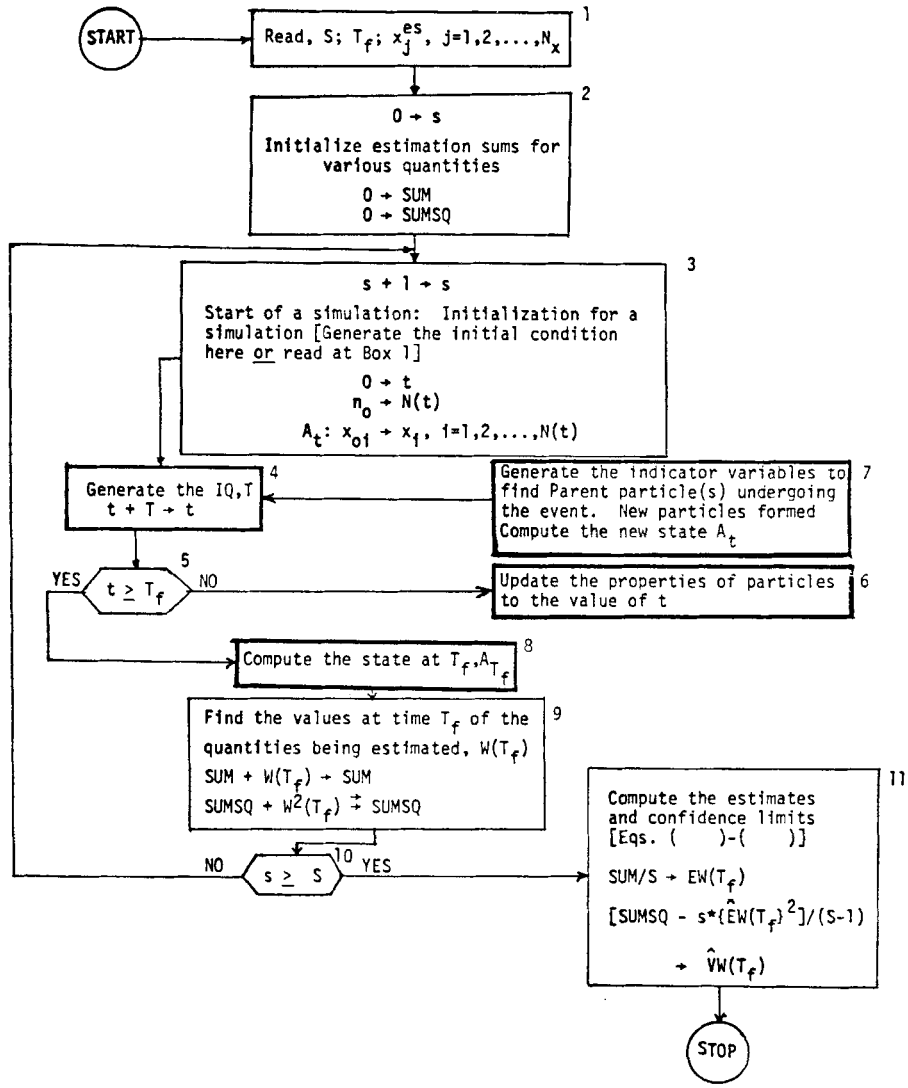

Fig. 1. The flowchart or Monte Carlo simulation of particulate systems

S	= total number of simulations to be performed	N_o	= initial total number of particles
T_f	= final value of time up to which each simulation carried on	$N(t)$	= total number of particles at time t
x_j^{es}	= values of property x at which $\beta_1(x,t)$, $\beta_2(x_1,x_2,t)$ are required, $j = 1, 2, \ldots, N_x$	A_t	= state of the system at time t
		x_{oi}	= properties of initial particles
s	= index variable keeping track of the number of simulations	x_i	= properties of particles at time t
SUM	= sum of the values of a quantity being estimated	T	= interval of quiescence
SUMSQ	= sum of the square of the values of a quantity being estimated	W	= quantity being estimated
		$\hat{EW}$	= estimate of W
t	= time	$\hat{VW}$	= estimate of variance of W

DESCRIPTION OF THE FLOW CHART

The symbols $a \rightarrow x$ means that the constant a or value of the variable a is assigned to the variable x.

Box 1: Read input data.

Box 2: Initialize the index s to count the number of simulations. *SUM* and *SUMSQ* are set to zero. The first sum is used to estimate the expected value and second to estimate the variance of any quantity of interest. *SUMSQ* represents the sum of squares.

Box 3: Index s is incremented by 1. To start a simulation, the value of time is set to zero. The total number of particles and the properties are set to their respective initial values.

Box 4: The IQ, T is generated using the appropriate probability distribution from Table 1 or 2 depending on the model of the system. Update the value of time t to $t + T$.

Box 5: If $t \geq T_f$, the simulation up to T_f is completed and the control is transferred to box 8, otherwise to box 6.

Box 6: Before the one or two particles involved in the particulate event at the end of the IQ can be determined, the properties of all the previous particles should be updated to the new value of time t by growth computations.

Box 7: Generation of indicator variables determines the particle(s) undergoing the event. New particles formed from the event are found according to the specified model. This might require further use of random number generation. New state of the system A_t is found by deleting the parent particles and including the newly formed ones.

Box 8: The control enters this box if the value of time t exceeds T_f. The state of system is updated to T_f from t by growth computations if growth is present.

Box 9: The value of the quantity $W(T_f)$ is obtained from the state A_{T_f}. The sums *SUM* and *SUMSQ* are updated by adding $W(T_f)$ and $W^2(T_f)$, respectively.

Box 10: If $s \geq S$, the required number of simulations have been completed, and the control is transferred to box 11. Otherwise, the control is transferred back to box 3 to start the next simulation.

Box 11: Estimates of expected value and variance of $W(T_f)$ are computed from *SUM* and *SUMSQ*. The confidence limits are found by Equations (10) and (11).

The boxes 4, 5, 7, and 8 are specific to the model of particulate system under consideration. The rest of the boxes are common to all models.

AN EXAMPLE

We present as an example for the demonstration of our technique the dispersed phase mixing model due to Curl (1963) for chemical reaction in a liquid-liquid dispersion produced in an agitated vessel. We do not include the treatment of small populations in this paper, since the results of such work without details of the simulation procedure used have already been published elsewhere (Ramkrishna et al., 1976).

In Curl's model, all droplets in the vessel, which is operated as a continuous flow reactor, are assumed to be of identical size. The coalescence-redispersion process is then viewed as a single-step process which results in mixing of the contents of the drops. The feed and exit streams flow at equal volumetric rates and have the same dispersed phase fraction. A reaction of the n^{th} order occurs in the droplets.

First, we identify monoparticle events, which are droplet entry into the vessel and droplet exit. The biparticle event is the coalescence-redispersion event. The feed droplets are assumed to enter at an average rate of N_f droplets, each of concentration C_o per unit time. During the interval t to $t + dt$, the exit transition probability of all drops is taken to be $1/\theta$, where θ is the residence time, which is because the vessel is assumed to be perfectly mixed. The overall frequency of the coalescence-redispersion events is denoted by Y. Thus, the probability that any of the droplet pairs interact in the time interval $(t, t + dt)$ is Ydt.

The interval of quiescence T in the present context is the time elapsed between two successive particulate events, where each may be any one of the three events referred to above. If there are $N(t)$ particles in the vessel at time t, then T has the cumulative distribution function

$$F_T(\tau|A_t) = 1 - \exp\left\{ -\tau \left[N_f + \frac{N(t)}{\theta} + Y \right] \right\}$$

The indicator random variable identifies which of the particulate events has occurred at the end of an IQ. Thus, we take

$$I = \begin{cases} -1 & \text{if a droplet leaves the vessel at the end of the IQ} \\ 1 & \text{if a feed droplet enters the vessel at the end of the IQ} \\ 2 & \text{if a coalescence-redispersion event occurs at the end of the IQ} \end{cases}$$

It is easily shown that

$$Pr\{I = -1|A_t, T\} = \frac{N_f}{\left[N_f + \frac{1}{\theta} N(t) + Y \right]}$$

$$Pr\{I = 1|A_t, T\} = \frac{\frac{1}{\theta} N(t)}{\left[N_f + \frac{1}{\theta} N(t) + Y \right]}$$

$$Pr\{I = 2|A_t, T\} = \frac{Y}{\left[N_f + \frac{1}{\theta} N(t) + Y \right]}$$

where the probabilities are conditional on knowledge of the IQ. We let u be the indicator random variable for identifying the exiting droplet, with $u = i$. If the i^{th} droplet leaves, then

$$Pr\{u = i|A_t, T, I = -1\} = \frac{1}{N(t)} \quad i = 1, 2, \ldots, N(t)$$

Let v be a two-dimensional random variable indicating the specific droplet pair undergoing the coalescence-redispersion event. Thus, $v = (i, j)$ if the i^{th} droplet interacts with the j^{th} droplet. Assuming equal probability for each droplet pair, we have

$$Pr\{v = (i, j)|A_t, T, I = 2\} = \frac{2}{N(t)[N(t) - 1]}$$

$$i = 1, 2, \ldots, N - 1$$

$$j = (i + 1), i + 2, \ldots N(t)$$

The simulation procedure is now easily understood as follows. At the end of an IQ, the concentrations in each droplet are updated using the solution of the equation

$$\frac{dC}{d\tau} = -kC^n$$

subject to the initial condition given by the concentration of the droplet at the end of the previous particulate event. When I is generated, the specific particulate event is identified. If a particle entry transpires, a droplet of feed concentration C_o is added to the population. A particle exit would require the generation of u to identify which particle is to be removed from the population. If a coalescence-redispersion event takes place, the generation of v would indicate the specific pair involved.

The results of our simulation are plotted in Figures 2 through 4. Figure 2 represents the approach to steady state for a zeroth-order reaction, taking $N_o = 50$. An identical plot is obtained with $N_o = 100$. The steady state values are the same as those obtained by Curl (1963) and by Spielman and Levenspiel (1965). Figure 3 shows the re-

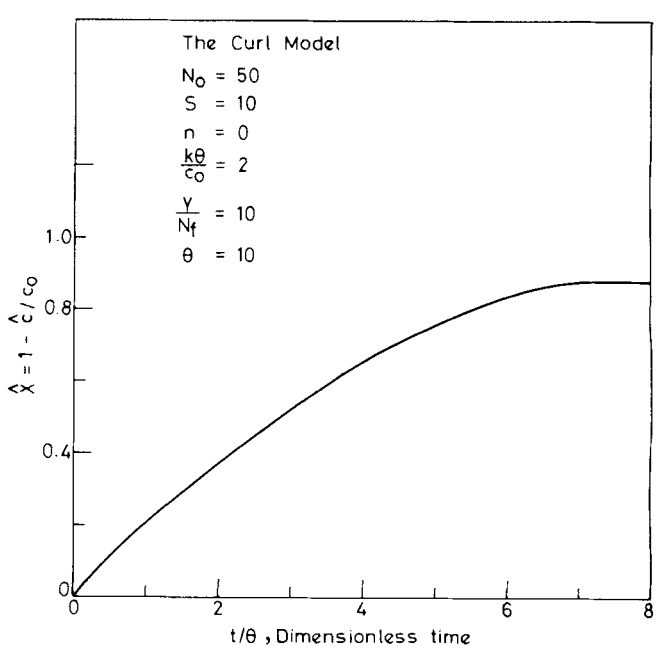

Fig. 2. Variation of conversion with time.

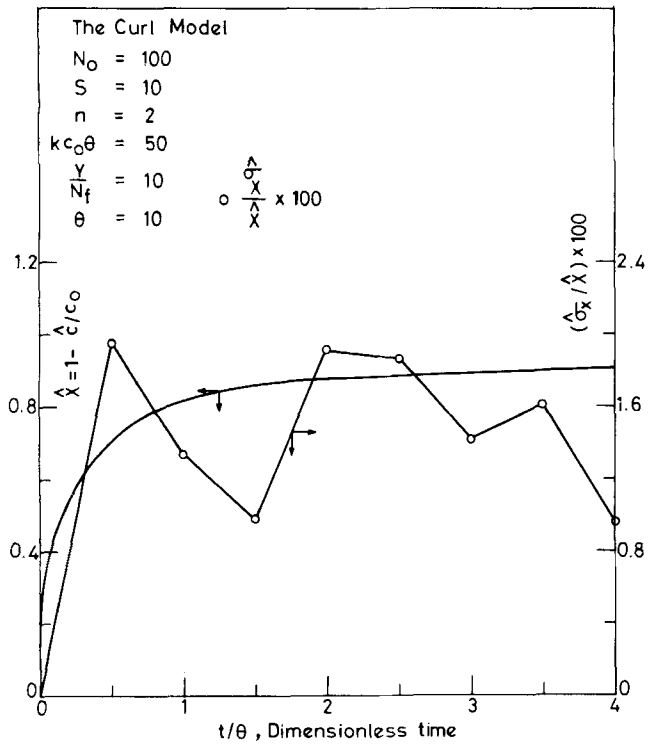

Fig. 3. Variation of conversion with time.

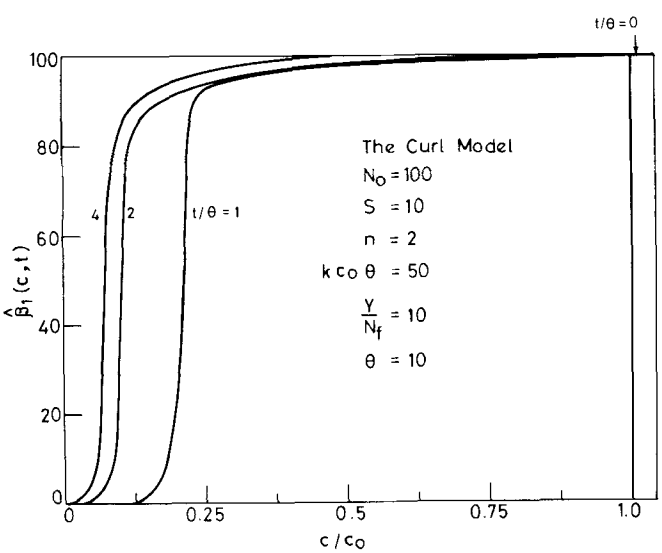

Fig. 4. Cumulative concentration distribution.

sults for a second-order reaction with $N_o = 100$. The approach of the reaction conversion to the steady state value is evident in this figure. The percent coefficient of variation about the mean value is also shown, which is indeed small. The confidence intervals for conversion were also computed but were too small to be shown in the figure. The cumulative, reactant concentration distributions among the drop population are also plotted at various times in Figure 4. The approach to a steady state distribution should be clear.

CONCLUSIONS

From the results of our simulation presented here and elsewhere (Ramkrishna et al., 1976), a relatively small number of particles may be used to predict the behavior of a large population system (provided the number is not so small that particle correlations and fluctuations about mean behavior become important). Thus, in obtaining the results for the Curl model, as few as fifty particles were sufficient (as against the 500 used by Spielman and Levenspiel), leading to substantial saving in computer time. Increasing the number of simulations gives more accurate results with narrower confidence limits. The reduced computation time follows from the fact that statistical averaging has been performed on multiple simulations, each simulation being conducted over a fixed period of time sufficiently but not redundantly long. Also, the statistical purity of the mixing process has been preserved by the simulation procedure through the use of quiescence interval. Thus, a more efficient averaging process emerges. Previous simulation techniques presume that during the discretized time interval particles undergoing any event (such as breakage, coalescence, etc.) can experience it only once. The present technique does not contain such presumptions because the quiescence interval automatically adjusts to a changing population.

NOTATION

b = frequency of a monoparticle event
C = concentration of reactant
C_o = concentration in feed
E = expected value
$f(x, t)$ = expected population density
F_T = cumulative probability distribution function of IQ, given the state of the system at time t
I = indicator random variable
n = order of reaction
$n(x, t)$ = random population density
$N(t)$ = total number of particles at time t
N_f = number feed rate of particles or feed frequency
N_o = initial number
q = frequency of biparticle event
S = number of simulations
t = time
T_f = final time
u, v = indicator random variables for one or more particles undergoing a random event
V = variance
w = contribution of a particle of property x to the property W of the population
W = overall property of a population of particles
x = property of particle which is distributed among the population
β_1, β_2 = cumulative property distributions
θ = average residence time in continuous flow vessel
σ = standard deviation
τ = value of IQ (interval of quiescence)

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Manuscript received March 17, 1977; revision received July 13, and accepted July 25, 1977.

Generalized Vapor Pressure Behavior of Substances Between Their Triple Points and Critical Points

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Several approaches are utilized for the estimation of the parameters associated with the normalized vapor pressure equation

$$\ln P_R = \alpha + \frac{\beta}{T_R{}^m} + \gamma T_R{}^7$$

to develop a capability for the prediction of vapor pressures consistent with the theorem of corresponding states. In this development, conditions and restrictions associated with the critical point and the normal boiling point were used to establish the vapor pressure parameters α, β, γ, and m. For the evaluation of these parameters, five different approaches were applied, and vapor pressures calculated with each of them were compared with corresponding experimental values presented in the literature. These comparisons were further examined using the results of four other well-known vapor pressure equations available in the literature.

This evaluation included 138 substances of all types and involved a total of 7,633 literature reported vapor pressure values to show that improved results are possible through the involvement of the generalized vapor pressure equation of this investigation.

SCOPE

The perennial involvement of the vapor pressure behavior of substances makes it mandatory that simple and exacting relationships be established that are capable of predicting vapor pressures over the complete liquid region included between the triple point and the critical point of a substance. In this context, a generalized vapor pressure equation, consistent with the theorem of corresponding states, has been examined and tested to show that improved results are possible with it. The capability of this generalized relationship permits the calculation of vapor pressures that find use in vapor-liquid equilibria of both simple and complex mixtures, the estimation of latent heats of vaporization over the complete liquid range, and thermodynamic properties associated with the saturated vapor-liquid state. In addition, the analysis associated with this study constitutes a basis for evaluating parameters that find use in the application of the theorem of corresponding states for both gases and liquids.

CONCLUSIONS AND SIGNIFICANCE

Average percent deviations resulting from the use of this generalized vapor pressure equation are smaller than those obtained from corresponding relationships available in the literature. The capability of the vapor pressure equation examined in this study has been extensively tested using 138 substances and involving a total 7 633 vapor pressure values reported in the literature. One of the proposed schemes for estimating the vapor pressure

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