

STOCHASTIC MODELING OF CHEMICAL PROCESS SYSTEMS

Part I: Introduction

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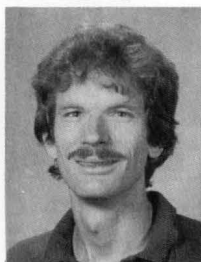
A STOCHASTIC SYSTEM is a system evolving according to probabilistic laws as opposed to deterministic laws. In practical terms this implies that given a system in a certain measurable state, the evolution of the system through other possible states can only be predicted in terms of a probability. We are thoroughly familiar with deterministic systems whereby, for example, knowledge of the initial position and momentum will allow us to exactly determine the future position.

Imagine a system for which knowledge of the initial conditions only allows us to predict the future position with a certain probability. Such a system would seem to go against the scientific belief of strict determinism. For our purposes, however, we can assume that although in principle it may be possible to make strict deterministic statements about the behavior of

any physical system, such statements would require exact and complete knowledge about the initial conditions and the external forces acting on the system. Since such exact knowledge is often beyond us, the reality as we perceive it may be represented best by stochastic models. This philosophy is in line with current theories involving deterministic chaos where a small error in the value of the initial conditions produces an enormous error in later predictions about the process (see, *e.g.*, reference 1).

Consider, for example, a bubbling fluidized bed. Theoretically, it is possible to exactly predict the sizes and positions of bubbles at each moment in time. However, the prediction would be dependent upon the initial conditions since the bubbles do not occur with exactly the same positions and sizes each time a fluidized bed is started up. Such a system appears to us to be stochastic, and thus we speak of the random coalescence and movement of the bubbles. This is equivalent to stating that although in principle we may be able to understand the mechanism of coalescence for two or three isolated bubbles in a deterministic manner, we are unable to extend the deterministic model to accurately predict the behavior of a large swarm of bubbles. Therefore, we resort to a model involving random movement and coalescence. Nevertheless, it is important to note that neither the deterministic nor the probabilistic mode of modeling excludes or negates the utility of the other. Indeed, while the deterministic model may be intractable for large complicated systems, the basic knowledge it provides about the dependence of the rate constants appearing in the probabilistic model on system parameters is invaluable. Both modes of modeling should be seen as working hand-in-hand, providing complementary understanding of complicated systems. An example of this aspect can be found in the recent work of Muralidhar and Ramkrishna [2] in modeling coalescence efficiencies.

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At this point we wish to carefully distinguish between the deterministic models mentioned above, which allow an exact determination of the behavior of the system, and macroscopic models, which are also deterministic but are volume-averaged over the exact deterministic equations. Macroscopic models, therefore, are deterministic models involving variables such as overall temperature and concentration. In contrast, the exact deterministic or so-called microscopic models deal with the position and momentum of individual molecules. The exact relationship between these two domains is the subject of study of statistical mechanics. Although the stochastic models considered in this paper are less detailed than microscopic models, they are more detailed than the macroscopic models describing only the average behavior of a system. Thus, our desire to arrive at an accurate formulation of the stochastic model necessitates a close scrutiny of the mechanisms underlying the kinetic behavior of the process. In fact, a multitude of stochastic models corresponds to any given macroscopic model. Hence, the *ad hoc* addition of fluctuating terms to a macroscopic model is of relatively limited value if we wish to predict the effect of changing operating conditions on the higher moments of the probability distribution of the random variables.

BRIEF HISTORY

Numerous chemical process systems lend themselves to a stochastic description due to their inherent complexity and fluctuating nature. Examples of such systems can be found in dispersed phase flow, turbulence, solids mixing, and in many other chemical engineering fields of study. Research efforts in these areas have been reported extensively. For example, by using probabilistic methods, coalescence and breakage in dispersed phase systems have been studied by Valentas and Amundson [3], Ramkrishna and Shah [4], Ramkrishna [5], and Bajpai, Ramkrishna and Prokop [6], among others. Stochastic modeling of mixing and chemical reactions has been reported by Krambeck, Katz, and Shinnar [7], King [8], Pell and Aris [9], Mann and O'Leary [10], and Nauman [11], as well as work done by Fan and co-workers [12-14], and others. A fluidized-bed reactor is a notable example of a stochastic system with the random generation and coalescence of bubbles leading to pressure and density fluctuations. Stochastic mod-

els for fluidized beds have been discussed by Bukur, *et al.* [15], Shah, *et al.*, [16], Ligon and Amundson [17, 18], and recently by Fox and Fan [19].

RATIONALE FOR STOCHASTIC ANALYSIS AND MODELING

The incorporation of stochastic analysis and modeling into the repertoire of our profession is a matter of great urgency. Indeed, the need for a monograph or textbook on this subject is noted in a list compiled by Bird [20] and published in this journal. Devising appropriate stochastic models for chemical process systems, however, can be difficult. Construction of valid models requires the proper determination of the source of fluctuations and the mechanisms by which they evolve. The fact that relatively little interest has been shown for stochastic analysis and modeling of chemically reacting systems rests most likely with the nature of the internal fluctuations; such systems contain roughly the Avogadro number of molecules. A well-known result of statistical mechanics states that the number of density fluctuations are of the order of \sqrt{N} where N equals the total number of molecules in the system. The implication is that, in terms of concentration, the fluctuations are negligible with respect to the mean value equations and thus will be of little concern in the macroscopic description of chemical reactions. This result may be satisfying to the physicist who wishes to build a unified theory of matter based on molecular dynamics, but it is usually of little practical value to the chemical engineer modeling an actual chemically reacting system.

Visible or detectable fluctuations do exist in countless process systems, but their roots are not to be sought at the molecular level. A fluidized bed, for example, often fluctuates violently. These fluctuations obviously do not stem from the transfer of individual molecules among different phases in the bed; they stem from the transfer of relatively large entities, *e.g.*, clusters of particles and bubbles. It is well known that the bubbles can be modeled as entities which randomly enter into the bed, coalesce in it, and leave from it. Thus, the importance of properly identifying the source of fluctuations for a successful description of their impact on the system is obvious. Stochastic models based on independent molecular processes will show that the fluctuations are negligible in large systems, while a stochastic model based on mechanisms

involving, for example, bubble interactions will yield significant fluctuations.

From the stochastic model of a chemically reacting system, the more familiar kinetic expressions found in the chemical reaction engineering literature can be derived by calculating the average numbers of molecules of each species and expressing these in terms of continuous variables. The latter is of course possible and quite accurate since the number of molecules in any system is usually very large—it is on the order of the Avogadro number. As noted earlier, the variance of the numbers of molecules of each species will be of the order of the mean number of molecules. Consequently, when working in terms of molar concentration, the standard deviation will be several orders of magnitude smaller than the mean concentration. The

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probability distribution of the random variables will then approach a delta function centered at the mean or average concentration for a system containing a large number of independent particles. In the statistical physics literature, this limit is often referred to as the thermodynamic limit. In this limit it is possible to describe the system in terms of the thermodynamic variables of chemical concentration and temperature instead of more fundamental quantities such as position and momentum.

From the discussion presented thus far it should be clear that the stochastic model is more fundamental in nature than the deterministic rate equations of chemical kinetics or, in general, macroscopic models. However, we are justified in using the deterministic rate equations when the number of molecules in the system is extremely large. In general, we can say that stochastic population balances for large numbers of independent entities almost always reduce to the deterministic mean value rate expressions. Nevertheless, in all cases, the stochastic model represents a fundamentally more basic description of the physical behavior of the system. It recognizes the existence of the individual members of the population and their ability to undergo change at random times.

For relatively small populations the random nature of the changes in the population numbers can be quite significant. For example, the change in the number of bubbles of each size in a fluidized bed takes place rather quickly, resulting in the widely fluctuating behavior of this system. A detailed stochastic model of

the fluidized bed might include a stochastic population balance for the bubble phase from which other physically important quantities, *e.g.*, the total surface area of the bubble phase, could be derived and their random nature quantified [19, 21]. These observations, of course, carry over to dispersed phase systems in general where deterministic population balances are widely used (see, *e.g.*, Ramkrishna [22]).

STOCHASTIC MODELS AND THE MASTER EQUATION

An appropriate stochastic model should depict the details of the internal mechanisms generating the fluctuations and can be solved by means of a rational approximation technique when the resultant equations are non-linear or be amenable to numerical simulation. A general formulation possessing both of these qualities is known in the modern literature as the master equation (see, *e.g.*, van Kampen [23] and Gardiner [24]). The master equation was first introduced into the statistical chemistry literature as a method of deriving statistical mechanics from molecular dynamics (see, *e.g.*, Cohen [25]). In the ensuing years much work has been done to understand the nature of the solutions to the master equation. Numerous approximation schemes have been devised to solve nonlinear master equations [24]. Perhaps the most successful of these has been the system size expansion [23].

A stochastic formulation based on the Janossy density function can be found elsewhere [26, 27]. However, we prefer to work with the master equation formulation for several important reasons: (1) the master equation uses as random variables the numbers of entities or particles that are the natural variables when considering a population balance; (2) although the Janossy density function and the joint probability distribution in the master equation are theoretically interchangeable through a correct change of variables, the master equation is easier to formulate once the fundamental events that change the values of the numbers of entities in each state are known; (3) in contrast to the Janossy density function, there is a vast body of literature pertaining to the master equation wherein numerous solutions are discussed, rational approximation techniques are introduced, and statistics such as the first passage time and the probability of large fluctuations are derived (see, *e.g.*, van Kampen [23] and Gardiner [24] for partial lists of references and basic derivations, solutions, and approximation techniques); (4) the rates of transition for each possible event appearing in the master equation are exactly the quantities needed when performing a

Monte-Carlo simulation of the system; (5) the procedure to go from the master equation to a multivariate Fokker-Planck equation or to a stochastic differential equation is straightforward, thus opening the possibility of applying the large body of literature in these fields to problems involving the master equation; and (6) except for the limited work carried out with the Janossy density function in the chemical engineering literature, the master equation formulation is perhaps the most commonly used stochastic formulation for population balance problems in the current scientific literature.

Numerous physico-chemical systems have been studied through formulation of their master equations. In particular, various chemically-reacting systems have been thoroughly studied and numerous examples are available in the literature [23, 24, 28, 29]. Nicolis and Prigogine [28] discuss stochastic methods for reaction-diffusion systems and non-equilibrium statistical mechanics with an emphasis on self-organization in nonequilibrium conditions. Oppenheim, *et al.* [29] present an interesting and useful compilation of basic papers on stochastic methods in chemical physics. Van Kampen [23] discusses in detail the effects of internal and external fluctuations in chemically reacting systems, while Gardiner [24] has collected many examples of nonlinear chemical reactions in both lumped and distributed systems. These authors and others have also dealt with the effects of fluctuations on the so-called "critical slowing down" in chemical systems and with other random effects and have presented methods for the stochastic treatment of mean passage time in bistable systems. While these systems are well documented in the statistical physics literature, the results have made little headway into chemical engineering.

Many chemical process systems are governed by nonlinear equations; this, in turn, implies that the stochastic model should also be nonlinear. This complication naturally leads to a coupling between the moment equations describing the population. It is then no longer possible to find the moments of the probability distribution of the random variables by solving an independent equation for each moment. To solve these equations, approximation techniques need to be introduced. Common *ad hoc* assumptions of independence between random variables or formulation of the higher-order moments as products of lower-order ones are of limited value. Instead, a rational expansion technique where the magnitude of higher-order terms can be controlled is clearly preferable. This technique will allow us to uncouple and solve the equations for lower order moments and then to use them in the

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coefficients of the equations for higher order moments while minimizing the error introduced through the approximation procedure. The System Size Expansion is such an approximation technique for the master equation [23].

Part II of this series will be concerned with the derivation and solution of the master equation. The System Size Expansion will also be outlined and used to find approximations for the moments and correlation functions of the random variables. For illustration the master equation will be applied to the modeling of a chemically-reacting system in the final part, Part III. It will be demonstrated that fluctuations in a large population are extremely small compared to the mean value and thus can often be ignored.

ACKNOWLEDGEMENTS

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REFERENCES

1. Crutchfield, J.P., J.D. Farmer, N.H. Packard, and R. Shaw, "Chaos," *Sci. Amer.*, **235** (6), p. 46-57 (1986)
2. Muralidhar, R., and D. Ramkrishna, "Analysis of Droplet Coalescence in Turbulent Liquid-Liquid Dispersions," *Ind. Eng. Chem. Fund.*, **25**, p.554-560 (1986)
3. Valentas, K.J., and N.R. Amundson, "Breakage and Coalescence in Dispersed Phase Systems," *Ind. Eng. Chem. Fund.*, **5**, p.533-542 (1966)
4. Ramkrishna, D., and B.H. Shah, "A Population Balance Model for Mass-Transfer in Lean Liquid-Liquid Dispersions," *Chem. Eng. Sci.*, **28**, p.389-399 (1973)
5. Ramkrishna, D., "Drop-Breakage in Agitated Liquid-Liquid Dispersions," *Chem. Eng. Sci.*, **29**, p.987-992 (1974)
6. Bajpai, R.K., D. Ramkrishna, and A. Prokop, "A Coalescence Redispersion Model for Drop-Size Distributions in an Agitated Vessel," *Chem. Eng. Sci.*, **31**, p.913-920 (1976)
7. Krambeck, F.J., S. Katz, and R. Shinnar, "Stochastic Mixing Models for Chemical Reactors," *Ind. Eng. Chem. Fund.*, **6**, p.276-288 (1967)
8. King, R.P., "Continuous Flow Systems With Stochastic Transfer Functions," *Chem. Eng. Sci.*, **23**, p.1035-1044 (1968)
9. Pell, T.M., and R. Aris, "Some Problems in Chemical Reactor Analysis With Stochastic Features," *Ind. Eng. Chem. Fund.*, **8**, p.339-345 (1969)
10. Mann, U., and M. O'Leary, "Modeling of Flow Sys-

- tems by Stochastic (Monte Carlo) Simulation," Proc. 2nd World Cong. of Chem. Eng., Montreal Canada (1981)
11. Nauman, E.B., "Residence Time Distribution in Systems Governed by the Dispersion Equation," *Chem. Eng. Sci.*, **36**, p.957-966 (1981)
 12. Nassar, R., J.R. Too, and L.T. Fan, "Stochastic Modeling of Polymerization in a Continuous Flow Reactor," *J. of App. Poly. Sci.*, **26**, p.3745-3759 (1981)
 13. Fan, L.T., J.R. Too, and R. Nassar, in *Residence Time Distribution Theory in Chemical Engineering*, Verlag Chemie, Weinheim (1982)
 14. Too, J.R., L.T. Fan, and R. Nassar, "Markov Chain Models of Complex Chemical Reactions in Continuous Flow Reactors," *Comp. Chem. Eng.*, **7**, p.1-12 (1983)
 15. Bukur, D., H.S. Caram, and N.R. Amundson, in *Chemical Reactor Theory, A Review*, Prentice Hall, Englewood, NJ (1977)
 16. Shah, B.H., D. Ramkrishna, and J.D. Borwanker, "Simulation of Bubble Populations in a Gas Fluidized Bed," *Chem. Eng. Sci.*, **32**, p.1419-1425 (1977)
 17. Ligon, J.R., and N.R. Amundson, "Modeling of Fluidized Bed Reactors - VI(a) An Isothermal Bed With Stochastic Bubbles," *Chem. Eng. Sci.*, **36**, p.653-660 (1981a)
 18. Ligon, J.R., and N.R. Amundson, "Modeling of Fluidized Bed Reactors - VI(b) The Nonisothermal Bed With Stochastic Bubbles," *Chem. Eng. Sci.*, **36**, p.661-671 (1981b)
 19. Fox, R.O., and L.T. Fan, "Application of the Master Equation to the Bubble Population in a Bubbling Fluidized Bed," *Chem. Eng. Sci.*, **42**, p.1345-1358 (1986)
 20. Bird, R.B., "Book Writing and Chemical Engineering Education," *Chem. Eng. Ed.*, **17**, p.184-193 (1983)
 21. Fox, R.O., PhD Dissertation, Kansas State University (1987)
 22. Ramkrishna, D., "The Status of Population Balances," *Rev. Chem. Engg.*, p.49-95 (1985)
 23. van Kampen, N.G., *Stochastic Processes in Physics and Chemistry*, North-Holland, New York (1981)
 24. Gardiner, C.W., *Handbook of Stochastic Methods*, Springer, New York (1983)
 25. Cohen, E.G.D., *Fundamental Problems in Statistical Mechanics*, North-Holland, Amsterdam (1962)
 26. Ramkrishna, D., and J.D. Borwanker, "A Puristic Analysis of Population Balance - I," *Chem. Eng. Sci.*, **28**, p.1423-1435 (1973)
 27. Ramkrishna, D., and J.D. Borwanker, "A Puristic Analysis of Population Balance - II," *Chem. Eng. Sci.*, **29**, p.1711-1721 (1974)
 28. Nicolis, G., and I. Prigogine, *Self Organization in Nonequilibrium Systems*, Wiley, New York (1977)
 29. Oppenheim, I., K.E. Shuler, and G.H. Weiss, *Stochastic Processes in Chemical Physics - The Master Equation*, M.I.T. Press, Cambridge, MA (1977) □

DEPARTMENT: Arizona

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with a tendency for high quality. Many of the early PhD graduates, for instance, went on to become professors and administrators at major universities.

Since the majority of graduate students in a developing program were in the MS degree program, they were very closely supervised and generally produced publication-quality work. Many have gone on to important positions: three are company vice presidents; one is a director of overseas development; and several are heads of company divisions of various types. Several others pursued PhDs at other universities and have entered academia or research and development.

As mentioned before, the PhD/MS student ratio has recently increased to a level that will ensure a high rate of PhD graduates in future years. It appears that the department is beginning to achieve its early objectives for the graduate program. In terms of doctoral students, the department has been long on quality but short on quantity. Now that graduate enrollment has reached the desired level, we are focusing our efforts on maintaining quality in both graduate and undergraduate programs. □

WORKING IN THE IC INDUSTRY

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phases: gas and solid. Because of problems with particulates, liquids have been all but eliminated from the clean room. The reactors are small, and a batch of product can be held in one hand. Reaction times are on the order of minutes rather than days, so the turnaround is fast. Process control is simply a matter of using *in situ* diagnostics to predict the endpoint of an etch or deposition step. Compared with the difficulties of death, mutation, complex organic chemistry, living membranes, and mass transfer limitation typical of bio-engineering, the challenges of the IC industry are controllable. The problems are straightforward, but they generally require experimental solutions. There is enough work to be done to keep surface scientists occupied for several decades. Not only do the problems require experimental solutions, but the chemical engineer who lacks knowledge of device physics is just as handicapped as the electrical engineer with his/her ignorance of continuum mechanics. The need for a cross-disciplinary education cannot be overemphasized.

In conclusion, if you have the people skills to run for congress, the patience to spend a day in a junior high school, the perseverance to climb Mt. McKinley, the hands-on skills to keep dual Weber carburetors perfectly tuned on a 1960 Porsche, and the desire to help an industry which is vital to our national security and economy, consider obtaining a graduate degree in IC processing and joining a US IC company. □