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Mathematics in Chemical Engineering: A 50 Year Introspection

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A review is made of the role of mathematics in the field of chemical engineering in the latter half of the twentieth century. The beginning of this era was marked by the concerted effort of a few to raise the mathematical consciousness of the profession to think fundamentally about processes. We have accomplished this review by providing a rough structure of the areas of mathematics, deliberating on how each area has matured through growing applications, to conclude that mathematics is the main medium to meditate not only about processes, but even about materials and products. As we are clearly entering another era where the domain of chemical engineering is expanding into new areas with a focus on discovery oriented high throughput technology, modeling and rapid computation must provide the guidelines for rational interpretation of multitudes of observations. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 7–23, 2004

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Introduction

We wish to trace the growth of the application of mathematics over the last fifty odd years in the field of chemical engineering. The beginning of this period was marked by a shift in paradigm, in which the discipline of chemical engineering was being transformed from one that relied on a coarse taxonomic view of the field into one that drew on the rationality of mathematical thinking. This transformation represented a preparation to view chemical processes on a finer scale, in which systemic differences contributed no more than to variations in the details of synthesis using essentially unifying more fundamental information. Chemical engineering had matured to a field that dealt with the application of scientific laws to systems, in which matter underwent physical and/or chemical changes, with a view to analyze, design, and control them. The effect of this fundamental viewpoint has been to greatly expand the scope of chemical engineering to contribute to areas far beyond its original domain of chemical processes. Consequently, chemical engineering is at present an ineluctable component of the quantitative treatment of biological and biomedical systems, and of the synthesis of a diverse variety of materials with an impressive spectrum of applications. In fact, yet another emerging feature of novelty to the profession of chemical engineering, noted in the past for its focus on processes, is that connected with the design of products for specific applications. While there are technological developments that have facilitated the enhanced activities of the profession, it would seem that this turn of events is also attributable to the mathematical legacy that has followed the paradigm shift in the middle of the last century. This legacy is contained in the mathematical maturity of chemical engineering that is featured both in breadth and depth, and it is our objective in this article to reflect from the literature, the representation of various areas of mathematics that have been applied to chemical engineering. (This legacy of mathematical maturity of chemical engineering did not come about without having to endure the resistance of some of the leading members of the profession at that time. Perhaps, such resistance may be viewed to have helped

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strengthen the foundation of the change that was occurring, but it would be well to acknowledge several activists in support such as Richard Wilhelm, Olaf Hougen, Charles Wilke, Bob Bird, Kenneth Watson, Robert Pigford, Robert Marshall, John Davidson, and Kenneth Denbigh!)

In discussing the effect of advanced mathematics on chemical engineering, it is necessary to discuss the position that it occupied at some earlier period. We flash back to pre-World War II days, as they had a pronounced influence on the education of students in science and engineering, more in the latter than in the former. For example, electrical engineering departments in Universities prewar were primarily active in power, radio, antenna theory, and control. Very early in the post war era, they became active in electronics of various kinds, and computer design and use thus displacing much of what they had before. Prewar chemical engineering was mainly taught including excellent courses in chemistry, a few good courses in the unit operations, stoichiometry and a survey of fluid mechanics comprising mainly hydraulics. The remainder of the time was spent on courses which the faculty thought would serve the students well in the chemical industry, but, which in fact were not productive for the time and effort spent. There must have prevailed a feeling that engineers were somehow different from other people!

The mathematics offered to undergraduate students stopped with less than a full year of the calculus and with no course in ordinary differential equations. At the graduate level, the students in chemical engineering departments, where a minor was required, generally chose physical chemistry. The course load was essentially one-half that of the major, and students almost never chose mathematics or physics for their minor. Physical chemistry was generally the best choice for a minor, so that they were exposed to advanced thermodynamics, statistical mechanics, and chemical kinetics, which, for those students, filled an enormous void. Graduate courses offered in the chemical engineering departments were in general mimics of the undergraduate courses and were heavy with long computational problems, which were not particularly challenging, thought provoking, or interesting. These courses were nonmathematical in the sense that they contained nothing beyond simple calculus.

The rumblings of some change could be heard beginning in the Fall of 1946 when the large number of military veterans returned to the university. The number was large since the federal government offered large well deserved subsidies to these veterans who wished to return or start anew at a university. This required the universities to hire a very large number of people who could teach and were trained in science and engineering. Many of these, who had worked in various corporate and government operations during the war, decided they would like to teach, and their entrance produced a favorable input. The new students were now more mature, anxious to get their degrees, enter the industry and earn a respectable living. Their opinions, which they were not bashful about expressing, had a strongly disrupting effect on the status-quo.

The changes were not immediate since the main problem at hand was the effective handling of the large number of students. From an examination of the literature, the reader will find that a wave of change appeared about 1947. To illustrate the prewar situation, there were only two journals for chemical engineering research—*Industrial and Engineering Chemistry* and *Chemical Engineering Progress.* As for a view of the state of academic affairs, the three volume set of Hougen and Watson started to appear, Volume I, a little earlier on Material and Energy Balances in 1943 (Hougen et al., 1943), Volume II on Thermodynamics in 1947 (Hougen et al., 1947), and Volume III on Kinetics and Catalysis in 1947 (Hougen and Watson, 1947). These three books spawned a plethora of others, but these three volumes initiated a great change in core chemical engineering for which we owe a debt of gratitude to the University of Wisconsin. Although there were many that talked about transport theory, it was up to Wisconsin, again by Bird, Stewart and Lightfoot, to publish their magnificent volume Transport Phenomena in 1960. This book had a remarkable impact on chemical engineering and was written at a level that was necessary if chemical engineering was to develop into a well-defined engineering science. It spurred the teaching of transport theory, essentially the guts of chemical engineering, and made the introduction of more mathematics, especially vector analysis and differential equations, much easier than it otherwise might have been. A sense of the value of that book can be had when one recognizes that it remained in print for 42 years before being replaced by the magnificent Volume II.

Early research in chemical engineering, not surprisingly, was primarily concerned with problems related to one of the unit operations. Some were more amenable to research than others, but almost all were cited with some attention. The introduction of massive computers was felt by some researchers to be essential. The scene had been set for the introduction of mathematics in a serious way and the profession was ready for the paradigm shift to which we had alluded at the outset.

In deliberating the effect of mathematics, the vastness of the field makes it impossible for one to be comprehensive in such coverage, and we hope that our blanket apologies in advance to those that are denied deserved mention would nevertheless be viewed as genuine. Our focus on the area of application (rather than on its authorship) is reflected in frequently relegating mention of the authors' names to the Literature Cited rather than in the text.

Broadly, our aim in this article is to ruminate on the effect of mathematics on the profession of chemical engineering. An objective measure of what is meant by "effect" is, of course, notably evasive, for what comes at once to mind is the multiplicity of perspectives from various corners of the profession. While the issue of assessing effectiveness is not one to be ignored, it is of some consequence to rely on the relative growth of professional activity in an area, as a measure not altogether irrelevant. We shall, therefore, launch our deliberation on the effect of mathematics on chemical engineering solely from this perspective. Furthermore, we will rely on several past discourses as complementary information on both the historical and evolutionary background of chemical engineering mathematics (Amundson, 1946b; Varma, 1982; Kevrekidis, 1995; Churchill, 1983). In particular, Varma (1982) mentions the early books on applied mathematics in chemical engineering and provides an interesting commentary.

To structure our discussion, it seemed desirable to begin with a view of chemical engineering, as well as that of mathematics captured as in Figure 1. In so doing, we have been content with some general features, for the diversities of the two fields would throw a truly accurate and detailed representation of their interpenetration into an indecipherable thicket.

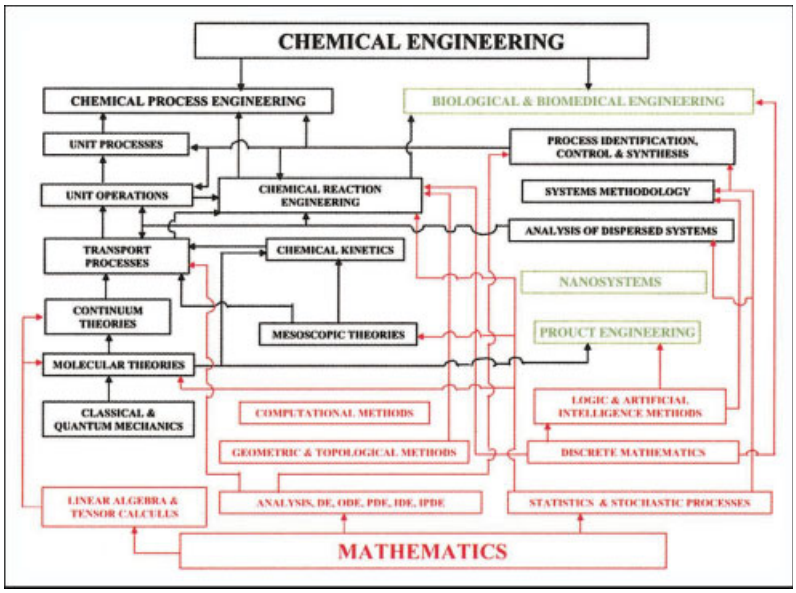

Figure 1. Chemical engineering and mathematics.

The black color is used to represent traditional areas of chemical engineering and the green for the newer areas. Mathematics is shown in red and the arrows used to designate the areas of chemical engineering influenced by various domains of mathematics.

Chemical engineering is concerned with the study of systems in which matter undergoes changes in composition, energy, and morphological structure brought about by physico-chemical processes spanning a wide spectrum of spatio-temporal scales. Figure 1 shows both chemical process systems, the original domain of chemical engineering, as well as the newer areas of acquisition, shown, respectively, in black and green, while the mathematical areas are shown in red.

We have viewed mathematics broadly as comprising a deterministic component and a statistical-stochastic component. The deterministic component has been depicted with considerably more structure, including: (i) linear algebra and tensor calculus; (ii) analysis and its implication to the solution of a diverse variety of linear and nonlinear equations; (iii) geometric and topological methods; (iv) logic and artificial intelligence methods; and (v) discrete mathematics. While our dissection of the area of statistical and stochastic methods in Figure 1 has been less detailed, this neglect is redressed to some extent by a subsequent, more focused discussion on the area. Computational methods have a diffused prevalence over most areas of mathematics (both deterministic and stochastic) and are consequently separated into a collective block. The red arrows display how different areas of mathematics have influenced chemical engineering in very diverse ways. This article will focus on each of the red blocks (representing different mathematical areas), inquire into the arrows reaching out to the different domains of chemical engineering from a historical perspective, and throw some light, wherever possible, into their prospects for the future. Finally, we wish to address trends in mathematics education of chemical engineers in the undergraduate and graduate spheres.

Linear Algebra and Tensor Calculus

Linear algebra is a natural fit for the treatment of stagewise processes and the application of vectors and matrices in chemical engineering. Thus, macroscopic mass balances on isothermal, multicomponent systems in contacting operations naturally lead to linear equations (except when invaded by nonlinear equilibrium relationships) that can be expressed in terms of matrices and vectors. Stoichiometry of chemical reactions allows for their elegant treatment using the mathematical theory of (finite dimensional) linear vector spaces.

Matrix theory

Although linear equations had been recognized early, curiously, a systematic application of matrix theory as, for example, presented by Amundson (1966), did not occur until later. Some noteworthy instances of the initial use of matrix theory is by Acrivos and Amundson (1955b), who were able to calculate from the tops (or bottoms) composition of a distillation column the liquid and vapor compositions in any plate without involving intermediate plate calculations through Sylvester's expansion for the n^{th} power of a matrix. (Apparently the first attention to distillation was that of Sorel (1893), and is described along with its many later modifications in Robinson and Gilliland (1950). Every third year, a chemical engineering student is exposed to the graphical method for binary mixtures, and with such mixtures, analytical methods became available by reference (Amundson, 1946a) for the equilibrium Raoult's law. This article is a very early introduction into the chemical engineering literature of matrices and of finite difference equations. A formal introduction of finite differences and matrices was made in Acrivos and Amundson (1955a). In this article, a compact short course in how a matrix can be used in multicomponent problems is spelled out in some detail. For example, the plate-by-plate method of Sorel is developed in an analytic way, and it shows that the numerical result is the same as the nonmatrix procedure. There are other applications presented. The matrizant, which will occur later, is presented as well as the solution for the transient problem of N continuously agitated tank

reactors with two consecutive reactions and three components. Finally, we also mention the articles of Amundson and Pontinen (1958) and Amundson et al. (1959), in the computerization of distillation calculations, which were programmed in machine language where almost every number had to be scaled, and were performed on the Remington Rand Univac Scientific Computer 1103 in St. Paul; this machine had 1,000 words of rapid access memory stored in tubes and 32,000 words on a drum, and the whole was programmed on paper tape by Arlene Pontinen, a new math BS graduate from Hamlin University.) Toor (1964b) and Stewart and Prober (1964) independently made effective use of Sylvester's expansion in solving transient multicomponent diffusion problems. (In fact the first article of Toor (1964a) was based on diagonalizing matrices and did not take advantage of Sylvester's theorem!) Ramkrishna and Amundson (1985, Chapter 8) present even more general applications of such spectral expansion for "finite dimensional problems." A profoundly interesting application of the spectral expansion of a matrix was demonstrated by Wei and Prater (1962), who showed how understanding of a spectral behavior can lead to designing experiments for extracting spectral data (that is, the eigenvalues and eigenvectors of a matrix) in the identification (that is, the determination of rate constants) of first-order reaction systems. Gavalas (1973) shows an interestingly different perspective of the same problem, which is less tortuous with respect to the determination of spectral data than the method of Wei and Prater.

The method of Wei and Prater (1962), however, is part of the more general subject of inverse scattering theory, which we shall address elsewhere. The treatment of chemical reactions satisfying mass action kinetics, using algebraic concepts, is discussed in two very stimulating articles by Feinberg (1977, 1980). (Aris (1965b, 1968) provides a rational treatment of systems of chemical reactions that thoroughly exploits their algebraic basis. The exceptional algebraic cleanliness with which chemical reactions were treated in the textbook by Aris (1965a), however, proved to be overly challenging to its undergraduate audience!) These articles build on algebraic characterizations of reaction mechanisms that have implications not only to the determination of rate constants, but also to the multiplicity and stability of equilibria. In this connection, an article of Krambeck (1970), which provides a treatment of the mathematical structure of chemical kinetics, and another of Horn and Jackson (1972), also deserve special mention. The work contained in these articles is of considerable depth.

Tensor calculus and continuum mechanics

Tensor calculus is essential to the mathematical formulation of continuum mechanics. An article by Serrin (1959) on the fundamental issues of continuum mechanics inspired a penetrating and very popular monograph by Aris (1962) that has come to be a standard reference on the basic attributes of fluid mechanics. Truesdell established the field of "rational" continuum mechanics (Truesdell and Toupin, 1960; Ericksen and Truesdell, 1958; Truesdell and Noll, 1965) and the journal for Rational Mechanics and Analysis, which has been the chief medium of expression for rigorous mathematical work on mechanics and thermodynamics. It is not reasonable in an article of this kind to undertake anything other than a superficial coverage of mathematical effort by chemical engineers in the area of continuum mechanics. In view of their pioneering nature, we shall first mention some of the early developments, although they have been covered in prior articles on applied mathematics in chemical engineering.

Following a doctoral dissertation in the area of distillation, Acrivos devoted his attention to fluid mechanics and vigorously championed the application of mathematics to this subject. Besides his own contributions, he has an impressive academic genealogy of strong contributors to fluid mechanics. As we have already observed, the book *Transport Phenomena* (Bird et al., 1960) can perhaps be described as the most influential in chemical engineering during this period. In celebration of its 35th anniversary, Astarita and Ottino (1995) discuss the influence of this book in the chemical engineering profession.

Thanks to the ubiquity of interfacial processes in chemical engineering, the general formulation of the surface equations of fluid mechanics by Scriven (1960) has had special significance as a very fundamental contribution. The analysis of Marangoni flows induced from fluid interfaces is widely regarded as a unique contribution to hydrodynamic stability (Sternling and Scriven, 1959). Dahler and Scriven (1963) developed a theory of structured continua that accounted for "point" structure derived from consideration of fine structure either at a molecular scale or higher, but microscopic, level. This development is related to the growth of continuum mechanics, in which fluid structure is complicated for one reason or another. In subsequent times, there have been a steady growth of contributions to the mathematics of rheology from chemical engineering. The book by Bird et al. (1987) represents an outstanding contribution of chemical engineers to the subject of rheology. Books by Happel and Brenner (1965) and Kim and Karilla (1991) are well known for their fundamental applications to particulate suspensions.

In regard to the rheology of viscoelastic fluids, an article of significant interest is that of Denn (1990). Caruthers and coworkers present a formulation of very general constitutive equations for visocoelastic solids and fluids based on the guidelines of rational continuum mechanics (Lustig et al., 1996). In a joint effort, Peppas and Caruthers have applied the principles of continuum mechanics to describe diffusive transport in polymeric mixtures (Lustig et al., 1992). Olbricht et al. (1982) discuss the relationship between flow and microstructure, while Feng and Leal (1997) provide an example of simulating flow of liquid crystalline polymers using the Doi theory. A recent review by Rey and Denn (2002) covers the status of available mathematical theories of liquid crystalline polymers with respect to their scope and limitations. The theories concerned are based on continuum approaches, but mesoscopic in nature in that their scale of description is intermediate between the molecular and macroscopic limits.

Developments beyond that of the rheology of fluids with microstructure are discussed by Beris and Edwards (1994). Of interest to the theory is the mutual interaction between microstructure and flow. Even thermodynamic phase transitions are within the purview of such mathematical treatment.

There are numerous other branches of continuum mechanics that have been of interest to chemical engineers. Thus, the interplay of transport equations with those of electromagnetic field theory occurs in the area of magneto-, ferrohydrodynamics, and so on. Particularly noteworthy is the book by Rosen-

zweig (1985) on the subject of ferrohydrodynamics and its applications to chemical engineering processes. For example, an issue that arose in this subject is the effect of applied magnetic fields on bubbling phenomena in fluidized beds.

Other areas in which continuum mechanics has flourished with contributions from chemical engineers is the flow of fluids in heterogeneous media. Fundamental to this field is the concept of volume-averaging in regard to which, a theorem due to Slattery (1972) that is concerned with interchanging differentiation and volume-averages, has played an invaluable role in the formulation of volume-averaged transport equations. Whitaker (1966, 1967, 1969) has an outstanding record of contributions to the mathematical formulation and analysis of flow in porous media, using averaged equations. There, of course, have been several other approaches to the treatment of porous media that take more detailed views of the morphology of the porous medium that are alluded to elsewhere in the article.

Another area of considerable interest to chemical engineers, associated with continuum mechanics in heterogeneous systems is that of multiphase flows. In particulate suspensions sedimentation phenomena have attracted the attention of Acrivos and coworkers (Davis and Acrivos, 1985). Enhanced settling of suspensions on an inclined wall has been addressed in an intriguing article by Acrivos and Herbolzheimer (1979). Acrivos (1995) describes how shear-induced diffusion of particles can create nonuniform spatial distributions of particles in a suspension. There are several other notable publications in this area that deserve mention, which are regretfully omitted from this discussion.

Multiphase flows feature flow transitions that can be predicted, for example, Dukler and coworkers (Taitel et al., 1978, 1980) for gas-liquid systems, and Gidaspow, Arastoopour and coworkers (Arastoopour and Gidaspow, 1979; Shih et al., 1982; Arastoopour et al., 1982) for gas-solid flows. A very notable article in this area that has aroused considerable interest is that of Sinclair and Jackson (1989). Models of fluidized beds have been the focus of attention in this regard. Of particular interest is an article by Anderson et al. (1995), which provides a theoretical explanation of how bubbles form in gas-phase fluidized beds while they do not in liquid phase fluidized beds. Models for fluidization including bubbling phenomena have also been accomplished by Gidaspow et al. (1983). The literature associated with this area is undergoing rapid growth. In many practical applications, however, the operation of fluidized beds is complicated by the appearance of more than two phases. For example, one encounters in Fischer-Tropsch synthesis two liquid phases (an aqueous phase and a hydrocarbon phase), a gas phase (for lower hydrocarbons), and a solid catalyst phase. Such systems have complicated flow regimes. We cite Fan et al. (1987) for an approach to more complex problems in multiphase flows.

Finally, in granular flows, in which particle-particle interactions must clearly play a significant role, a view of the nature of analysis can be had from Nott and Jackson (1992), Goddard and Alam (1999), Kaza and Jackson (1982).

We conclude this section with an interesting fundamental issue with fluid mechanics, recently raised by Brenner (2003a,b). He has expressed concern that the Eulerian definition of velocity does not enjoy an unambiguous identity with its Lagrangian origin as has been commonly assumed in more than two centuries of the past! This discrepancy is represented to be sufficiently serious under some circumstances to initiate a fresh approach to fluid mechanics.

Analysis, Linear and Nonlinear: Properties of Solutions

A striking feature of mathematics in its application to chemical engineering in the last century is its emergence from its somewhat peripheral status to one of serious engagement. New formulations have often led to engineering problems whose solutions cannot be acquired "off the shelf" as, for example, from tabulated inverse Laplace or Fourier transforms, or by regurgitating from standard texts in applied mathematics. Commerce with mathematicians is facilitated with learning their language and to enunciate problems with clarity. Engineers ventured into mathematical domains with a spirit of enquiry that had no precedence, establishing a new legacy of engineering science rooted in rational quantitative thinking.

For an appreciation of what mathematical analysis implies, the reader is referred to the stipulations of SIAM (Society for Industrial and Applied Mathematics) Journal on Mathematical Analysis. Broadly, analysis may be regarded as the process of extracting logical sequences of mathematical propositions from some starting point. Such a starting point, in our context, is usually a mathematical model of a system of interest, the purpose of analysis being to determine a sequence leading to meaningful conclusions about the system. The conclusions are, of course, contingent on the starting hypotheses, whose veracity is evaluated by comparison with experiment towards an iterative process of model refinement. Most importantly, the goal of mathematical analysis is often to extract properties of the solution without necessarily having to determine it completely. The discussion that follows is in the light of comments made here.

A fundamental aspect of mathematical analysis pertaining to the solution of mathematical equations is functional analysis. The authors' interest in the area was spurred by a course in the Mathematics department at the University of Minnesota during the mid-1960s, whose contents were published later into a book by Naylor and Sell (1972). (In fact the influence wielded by the Mathematics Department at the University of Minnesota on chemical engineering even in the 1950s and 1960s was extraordinary. In particular, Hans Weinberger's text (Weinberger, 1965) and course on partial differential equations were both very popular among chemical engineering students.) An article by Ramkrishna (1979) extolled the virtues of chemical engineers learning functional analysis. The book by Ramkrishna and Amundson (1985) demonstrates methods for symmetrizing apparently nonself-adjoint operators in a variety of applications to systems in which transport and/or reaction processes take place. (It is worth noting that Davis and Thomson (2000) have recently published a book on linear algebra and linear operators that makes liberal use of Mathematica. Two other books on applied mathematics for chemical engineers, but less "operator" based in their approaches, are by Varma and Morbidelli (1997) and by Rice and Do (1994).) While several of their applications have found favor in books on transport phenomena (Deen, 1998), examples of resolving elliptical partial differential equations into self-adjoint first-order pairs have remained less noticed. The technique, originally developed by the authors for solving boundary value problems with *oblique deriv-*

ative boundary conditions (Ramkrishna and Amundson, 1979) was shown to solve analytically the Graetz problem with axial diffusion and a general class of conjugated transport problems (Papoutsakis et al., 1980; Papoutsakis and Ramkrishna, 1981). (It is interesting to note that Acrivos (1980) recovered the leading terms in the expansion of Papoutsakis et al. (1980) by singular perturbation.)

The spectral theory of singular operators is of considerable interest to chemical engineers in view of the fact that many boundary value problems are defined on semi-infinite or infinite domains. In such cases, instead of discrete eigenvalues, one encounters a *continuous spectrum* such as that associated with the infinite Fourier transform. (The mathematically inclined will find it most interesting that operators of this kind can also possess a "smattering" of discrete eigenvalues that in fact contain information about the physical behavior of the system!) Parulekar and Ramkrishna (1984) have shown how the spectral theory of singular operators can be used to solve problems in infinite media. In other words, *ad hoc* continuous transforms are constructed from the theory that obtain analytical solutions to boundary value problems in infinite domains. An interesting further application of singular spectral theory to the fluid mechanics of drop oscillation is contained in the work of Parulekar et al. (1987). Continuous spectra have also arisen in the work of Gavalas and Aris (1966), who extended the work of Wei and Prater for continuous reaction mixtures.

The work of Wei and Prater (1962) is an example of how spectral information of an unknown self-adjoint operator can be gleaned from dynamic data in order to determine the operator. With this interpretation, the work of Wei and Prater falls in the domain of what is known in the mathematics literature as *Inverse Scattering Theory* (see, for example, Agranovich and Marchenko (1963)). Although it is not evident to us that such work exists in the chemical engineering literature, it is of interest to cite here the work of Kravaris and Seinfeld (1985) who have solved "inverse" Sturm-Liouville problems that have a number of important applications. Here, the solution to a Sturm-Liouville problem is specified as known (usually from "noisy" measurement) and the problem is to determine the Sturm-Liouville operator by which is meant functions appearing in the Sturm-Liouville expression such as, for example, a spatially varying diffusion coefficient. Seinfeld and Kravaris (1982) present applications to flow distributions in petroleum reservoirs. Inverse problems occur in several applications in chemical engineering, and considerable scope exists for further work in this area.

Model simplifications

Within the scope of what we have termed "analysis" is a set of ways to negotiate a model so that its evaluation is simplified in some way. The complexity of chemical process systems is such that simplification of one form or another is frequently forced on the modeler. Besides, the level of modeling must match that of observation. There have been numerous books on modeling, some specific to chemical engineering, that make interesting reading. From the academics' perspective, we recommend Aris (1999) and Denn (1986) as excellent references on the subject. The book of Franks (1972) is of interest as the author's perspective also bears the stamp of industrial experience that should reflect the extent of influence that mathematical modeling has had on chemical engineering practice.

For the purposes of our discussion, it is convenient to regard the behavior of a system as the evolution of its state along spatial and/or temporal coordinates. The simplifications to which we referred may either apply to the description of its state or the organization of its evolutionary coordinates. Both types have been of interest to chemical engineers and practiced vigorously in the past. An example of the first type is in the use of *continuous* mixtures when the number of components in the system is very large. Similarly the numerous stages in a large multistage process, may be "imbedded" into a continuously evolving spatial coordinate. The implication here is that the continuous formulation can condense a large number of discrete model equations into a small number of distributed model equations, which can sometimes be solved more easily than the original set. This idea has emerged from the work of Zeman and Amundson (1963) and exploited in a series of succeeding articles for polymerization reactions. More recently, McCoy and Madras (2001) have used continuous formulations for polymerization systems, using the method of population balances. Continuous formulations have also been used in modeling distillation processes. There are other examples of continuous distribution of components in the literature (Aris, 1989).

An alternative mode of model simplification consists in "lumping" of chemical species, usually of homologous sets thus forsaking the distinction between elements in the lump. The lumping of monomolecular systems can be discussed with some degree of exactness and has been done by Wei and Kuo (1969). Lumping is tacitly assumed in bioreactor kinetics even in the case of nonlinear reactions. However, in dealing with chemical reaction systems, Astarita and coworkers have addressed the problem of lumping nonlinear kinetic systems in several articles of which we cite two (Astarita and Ocone, 1988; Aris and Astarita, 1989).

We shall briefly deal with model simplifications connected with temporal and spatial (evolutionary) coordinates. Simplifications of temporal behavior based on pseudo-steady-state approximations are a common occurrence in modeling, although concerns have occasionally been expressed on conditions for their validity (Heineken et al., 1967). There have been other simplifications too based on disparate time scales of system variables (Palsson and Lightfoot, 1984).

Model simplifications associated with spatial coordinates have been based on some sort of spatial averaging. We have already referred to the use of local volume-averaging in flow through porous media and in dealing with multiphase flows. (It is interesting to note that Whitaker (1969) derives Darcy's law by volume-averaging the Navier-Stokes equations, thus providing a genesis of the permeability tensor specific to this route.)

Other kinds of local averaging have also been of interest to chemical engineers. For example, transport of chemical species in conduits of constant cross-section in fully developed flows are of diverse interest to applications. In the foregoing situation, the two-dimensional (2-D) axisymmetric transport of a solute along the radial and axial (flow) directions was shown, in a noted publication, by Taylor (1953) to be closely approximated by 1-D transport along the axial direction using a solute concentration variable suitably averaged along the cross-sec-

tion. This "dispersion" theory provides an *effective dispersion* coefficient for the axial direction, which depends on the dimension of the tube cross-section, the solute's molecular diffusivity in the medium and a coefficient determined by the fully developed velocity profile. The theory attracted considerable attention among researchers in chemical engineering because of its applicability to chemical reaction engineering and to a large class of dispersion processes in engineering and biological systems. (The name of Danckwerts is inextricably connected with the boundary conditions associated with axial dispersion models. Peculiarly, the boundary conditions were found to date back to an early publication by Langmuir (1908). Not withstanding this fact, these boundary conditions, continued to be named after Danckwerts, are among the most discussed and most used in the analysis of axially dispersed systems (Danckwerts, 1953). This famous article of Danckwerts introduced the concept of *residence time,* a statistical concept, that significantly contributed to predicting the performance of imperfectly mixed systems. While it was undoubtedly true that Danckwerts possessed an adeptness in mathematics far above that which was characteristic of his times, he had increasingly felt in subsequent years an overabundance of mathematics in chemical engineering (Danckwerts, 1982). Aris, however, makes the percipient observation in his Danckwerts memorial lecture in 1990 that Danckwerts' position on mathematics was that of an "intelligent mistrust" rather than of an "ignorant aversion," an observation with which we must wholly concur.) Aris (1980) provides an interesting perspective of such model simplifications along with a healthy coverage of the literature in this area. Of particular interest are the numerous contributions of Gill and coworkers of which we cite Gill and Sankarasubramanian (1970), those of DeGance and Johns (1978a,b), and of Brenner (1980) the last of which is in periodic porous media. Simplifications, which yield "lower" dimensional models, abound in fluid mechanics; the slender body approximation (Leal, 1992) is one such example.

More recently, Balakotaiah and coworkers have initiated what appears to be a novel approach to model reduction (Chakraborty and Balakotaiah, 2002) by employing the Liapunov-Schmidt reduction technique (see, for example, Golubitsky and Schaefer (1984)) to perform spatial averaging. They report that the procedure leads to two coupled differential equations containing two different averages of the concentration and show a number of interesting applications.

While the subject matter of this subsection is not particularly homogeneous and can be vastly diverse, its coverage has been motivated by its being a legitimate component of analysis. We now consider another aspect of analysis that has had a profound effect on fluid mechanics, transport phenomena, and chemical reaction engineering, viz., the method of asymptotic expansions. This method, which subsumes both regular and singular perturbations, produces analytical expressions as approximate solutions, generally by linear methodology, to nonlinear problems for asymptotic limits of suitably chosen parameters. The monumental text by Leal (1992) provides an excellent account of asymptotic analysis in transport processes.

Analysis of nonlinear systems

Nonlinear problems occur more commonly than linear problems in chemical engineering. In chemical reaction engineering, the nonlinearity is inherited from kinetics, the temperature dependence of rate constants, thermodynamic relationships, the dependence of transport coefficients on thermodynamic state, and so on. In fluid mechanics, nonlinearity is contained in the inertial terms, interfacial boundary conditions, and, frequently, in constitutive relationships for Non-Newtonian fluids.

We focus on evolutionary equations along the time axis that are concerned with the dynamics of the state of a system. If the state of the system is in a finite dimensional space and the rate of change of that state is governed only by the local state, the model equations are a set of ordinary differential equations. This is the case with many models in chemical processes where spatial uniformity is promoted by some mechanical device. If, however, the system state is described by functions defined on some domain of other coordinates, spatial or otherwise, then the model equations are partial differential in nature. Integral and integro-differential equations are also encountered in chemical engineering in dealing with processes where a *local* change of a system variable can be effected by what is associated with a larger domain of the state space. Such is the situation in transport processes involving radiation, and in dealing with particulate systems via the method of population balances.

Of particular interest in the behavior of dynamical systems is the existence of equilibrium (or steady-state) solutions, free of temporal dependence. They are frequently the desired operating states of a process and are obtained from the model by equating the time derivatives to zero. When the dynamics is governed by ordinary differential equations, the steady states are characterized by algebraic equations. With dynamics described by partial differential equations, the steady states would be described by ordinary or partial differential equations. It is then no surprise that the nonlinear analysis of dynamic models with ordinary differential equations took precedence in the literature. Naturally, the field of chemical reaction engineering, which features the proverbial continuous, stirred tank reactor, is the first to enter the discussion.

In dealing with steady states of a continuous, stirred tank reactor, the issue of primary interest is that of multiplicity of solutions of the algebraic equations. (While there had been discussions about periodic phenomena in chemical reaction equations and some other unusual happenings, there had been little discussion about whether a given system could exist in more than one steady state and whether there was a rational procedure to predict such a thing. This, along with stability, apparently had never been considered. Although it seems almost miraculous that it wasn't the clue to being able to discuss, this was the earlier study of nonlinear mechanics as developed and used by Poincare, Liapunov, Minorsky, and some others. In principle, this only involved the idea of considering what happens to a steady-state system when perturbed only infinitesimally from that state. This idea was exploited in some chemical systems with a continuous stirred-tank reactor.) Looking at the various kinds of steady states, van Heerden (1953) produced the familiar sigmoidal shaped diagram, which suggests the existence of multiple steady states for even a very simple first-order exothermic chemical reaction. What had remained was to apply the idea of perturbing the steady state by a small amount and following the transient path or rather to carry out the computation from a variety of initial states and determine where the steady states were. This was accomplished

by Bilous and Amundson (1955) with computations on an analogue computer. (A second article by Bilous and Amundson (1956) investigated the empty tubular reactor for parametric sensitivity and stability using the Laplace transform, recycle, and perturbation methods.) It was no surprise that the profiles led to the steady states predicted from van Heerden's sigmoidal curve and that there was, in general, for one simple reaction, one stable steady state which corresponds to a single state in van Heerden's diagram. (More generally, for more complex systems, transient profiles would produce an odd number of states and, in a rare case, no stable steady states, but rather a limit cycle implying perpetual oscillation about one of the steady states. With a more detailed and precise analysis by considering the algebra of the linearized system and plotting in the phase plane the full equation, there can be a great array of transients showing there is convergence to stable steady states and transient avoidance of unstable steady states. This analysis was carried out in many very complicated cases with multiple reactions, multiphase systems, polymerization systems, and more. In one interesting case with a polymerization system, where there might be many possible states in the same system, it was found that the difficulty of control was the attempt to operate about an unstable state.) The three part article by Aris and Amundson (1958a) considers control of the stirred tank reactor and the manipulation of steady states and their stability through variation of the tuning constant for proportional control. It may be regarded as the first article on bifurcation analysis with respect to the tuning constant as the parameter although the results were not presented in the usual bifurcation plot in bifurcation theory.

Fredrickson and Tsuchiya (1977) provide some of the early developments in the field of bioreaction engineering not only with respect to the nonlinear issues under discussion, but also from several other fundamental viewpoints.

There was considerable interest in predicting via analysis the conditions under which a system has a unique steady state or multiple steady states. A mathematical monograph by Gavalas (1968) provides an outstanding initiation into nonlinear analysis of chemically reacting systems, in which the nature of steady states and their stability is presented in considerable depth. This monograph represents a milestone in the use of higher mathematics by chemical engineers. We note two other significant and early contributors to the issue of uniqueness and stability of steady states, Luss and Varma, the former with special focus on catalyst particles (Luss, 1977) and the latter more concerned with reactors (Varma and Amundson, 1972). A most comprehensive treatment of reaction and diffusion in porous catalysts is available in Aris (1975). A detailed nonlinear study of diffusion and reaction in carbon burning is made in Amundson and Mon (1980). A review by Varma and Aris (1977) provides a comprehensive account of the nonlinear behavior of stirred and tubular reactors. Following contributions in the area of linearized stability analysis, there were also early attempts to apply Liapunov's "direct" method to determine the region of stability via the construction of Liapunov functions. Warden et al. (1964) construct Liapunov functions for control of simple reactions, second-order reversible reactions, and for polymerization systems in a stirred-tank reactor. Limit cycles are studied in detail and extensive numerical work is presented. We also call attention to an extensive review article on periodic phenomena in chemical reaction systems by Bailey (1977).

The literature in the application of nonlinear analysis to chemical reaction engineering has undergone prolific growth ever since the publication of Bilous and Amundson (1955). We shall, therefore, cite only certain articles that we hold to be landmark contributions in this area, indeed regretfully mindful of likely omissions in the process.

Although nonlinear analysis with regard to multiple equilibria and complex transient behavior had taken root among chemical engineers, the systematic application of bifurcation theory did not occur until after the notable publications of Uppal et al. (1974, 1976). Ray (1977) provides a detailed perspective of bifurcation theory in chemically reacting systems. The bifurcation analysis of stirred-tank reactors was followed by that of tubular reactors by Jensen and Ray (1982). Ray and coworkers are noted for their outstanding contributions to the nonlinear analysis of polymerization reaction systems together with an impressive experimental demonstration of many of the phenomena (Ray and Villa, 2000). The application of bifurcation theory to biological reactors first appeared in the publication of Agrawal et al. (1982).

Hlavacek and coworkers have a sustained record of contributions to the nonlinear analysis of chemical reactors and associated computational methods (Hlavacek and Vanrompay, 1981; Seydel and Hlavacek, 1987). From a computational point of view, Gilles and coworkers have also contributed significantly to nonlinear dynamics of chemical processes (Holl et al., 1988; Kroner et al., 1990). We also cite the book of Finlayson (1980) in this regard. Schmitz and coworkers provide a very comprehensive account of oscillatory phenomena in catalytic reactions (Schmitz et al., 1980; Sheintuch and Schmitz, 1977).

While the focus in the foregoing discussion on nonlinear analysis has been primarily on chemical reactors, there also has been an abundance of contributions in other areas of chemical engineering. An example in fluid mechanics is to be found in the work of Kevrekidis et al. (1994) who made a thorough investigation of the classical Benard convection instability. Shaqfeh (1996) provides a review of fluid instability from purely elastic sources. We also cite the work of Kumaran (1995), among several other publications of his, on the stability of flow in a tube surrounded by a flexible viscoelastic medium. Joshi et al. (2001) have most recently reviewed work on the hydrodynamic stability of multiphase reactors. Steady-state uniqueness and multiplicity have been of interest to several workers in distillation processes (Lucia, 1986; Kienle and Marquardt, 1991; Jacobs and Krishna, 1993; Kienle et al., 1995). Morari and coworkers have contributed significantly to the nonlinear analysis of both homogeneous and heterogeneous distillation processes with numerous publications of which we cite but two (Bekiaris et al., 1993, 1995).

Another landmark event in the application of nonlinear methods in chemical engineering is in the use of singularity theory developed by Golubitsky and Schaefer (1984). Balakotaiah, Luss and coworkers stand out in the global investigation of multiplicity using singularity theory with numerous publications of which we quote only the early ones (Balakotaiah and Luss, 1983, 1984). Polizopoulos and Takoudis (1986) applied singularity theory to reactions on catalytic surfaces. Guttinger and Morari (1997) have recently used singularity theory for predicting multiple steady states in distillation processes.

The issue of progression of periodic behavior of deterministic systems to chaos appeared first in the chemical engineering literature towards the latter half of the 1970s (Schmitz et al., 1977). This subject of transition to chaos and its applications have been discussed in a comprehensive review article by Doherty and Ottino (1988). Khakhar et al. (1986) provide an application of the theory to mixing. The contributions of Ottino and coworkers in the area of chaotic mixing are indeed unique and are best represented in the book by Ottino (1989).

A most interesting issue associated with nonlinear systems is their capacity to form spatial or spatio-temporal patterns. The issue of patterns first arose with the famous work of Turing (1952). Patterns may occur in a set of similar systems (forming either a discrete or continuous family) which interact directly and/or indirectly through a shared environment. Such an ensemble could display a hierarchy of symmetries in which the most symmetric would be a "homogeneous pattern" that is capable of "splitting" to more asymmetric ones under suitable circumstances. Scriven and coworkers were the first to consider pattern formation in the chemical engineering literature. The setting here was a string of cells in which chemical reactions took place and interaction between them was facilitated through transport (Gmitro and Scriven, 1966; Othmer and Scriven, 1969, 1974). Schmitz and Tsotsis (1983) have studied pattern formation in an interacting assembly of catalyst particles, while Arce and Ramkrishna (1991) show that indirect interaction between catalyst particles through the intervening fluid can itself lead to pattern formation. Hudson et al. (1993) show pattern formation occurring in the electrodissolution of iron. Also noteworthy is the work of Shinbrot et al. (1999), who provide an interesting study of chaotic mixing in granular flows. Qin et al. (1994) show an interesting motivation for studying pattern formation by introducing a control element in it. We note in passing that the use of group theory to derive bifurcation equations for studies of pattern formation may be of interest (Sattinger, 1979).

The University of Minnesota, through the Institute of Mathematics and its Applications, has actively sponsored symposia on the application of mathematics to chemically reacting systems and has had one on pattern formation (Aris et al., 1991).

Geometric and Topological Methods

Geometry is connected with description and analysis of the shapes of objects, and topology is concerned with transformations between different geometric shapes. There have been various efforts at modeling in chemical engineering that best fit into this mathematical category, but otherwise of limited cohesiveness.

Transport in porous media

Because of the common prevalence of porous media in chemical engineering systems, we shall first consider some of the attempts to model them and transport processes occurring in them. This is an area that has accommodated widely different perspectives, some guided by simplicity of analysis, and others with a desire for fitting as much of the morphology of the porous medium as possible. Clearly, they must share different domains of applicability. Brenner has contributed significantly to this field and we cite two of his earlier publications as samples (Brenner, 1980; Adler and Brenner, 1988).

Concern with transport in disordered media spurred the introduction of percolation concepts into the chemical engineering literature. Percolation theory describes a disordered medium in terms of random connectivity between subdomains of the medium. The percolation threshold is a characteristic of the medium at which connectivity between two sides of the medium is assured and the fraction of the disordered medium at this threshold has remarkable universality properties. Davis and coworkers have spearheaded the application of percolation theory in chemical engineering. We cite two of their outstanding publications (Mohanty et al., 1982; Larson et al., 1981). For fast gas flows through porous media in which Darcy's law does not hold, Thauvin and Mohanty (1998) provide a network approach. There have been other statistical approaches to the description of porous media. One that has attracted considerable attention is the random capillary model of Gavalas (1980). Another notable article is by Sahimi et al. (1990). Noteworthy contributions have been made in this area by Sotirchos and coworkers (Burganos and Sotirchos, 1987; Tomadakis and Sotirchos, 1993).

Porous media viewed, as self-similar fractals, have provided considerable interest for some investigators. As Fickian diffusion is connected with the (stochastic) Langevin equation, the observed anomaly of diffusion in fractals has been approached by connecting it with the generalized (integro-differential) Langevin equation (Muralidhar and Ramkrishna, 1993). This is a "non-local" theory in time and explains the foregoing anomaly, which is in the progressive slowing of diffusion with time spent by the diffuser in the fractal environment. Cushman, Greenkorn and coworkers have looked at more general nonlocal theories (in space and time) of flow through porous media (Irwin et al., 2000; Sternberg et al., 1996). Toledo et al. (1992) provide scaling laws for the transport of fluids in fractal media.

A very comprehensive review by Sahimi (1993) covers the range of approaches to the description of porous media from continuous to fractal media. Many of the approaches to porous media recounted here are statistical in nature and could have been included in the section devoted to statistical modeling, but the geometric background of porous media prevailed in our choice of this section.

Topological methods

As pointed out earlier, topology is the study of continuous transformations of spatial objects. From the point of view of topology, the solution of steady-state equations may be characterized as *fixed points* of a continuous mapping. Using a combination of topological concepts such as indices of fixed points, in conjunction with homotopy theory, Gavalas (1968) analyzed equations of chemical systems with reaction and transport to make conclusions about the nature of steady states and their stability. Homotopy theory has been used by Doherty and coworkers (Doherty, 1990) in the analysis of phase diagrams for multiphase reacting mixtures, computation of azeotropes (Fidkowski et al., 1993; Wasylkiewicz et al., 1999).

We shall now briefly refer to differential geometric methods that have been used in chemical engineering. Of course, differential geometry is an inseparable feature of the fluid mechanics of fluid interfaces because of the dependence of pressure difference across the interface on surface curvature. More recently, however, in two significant articles, Kravaris and

Kantor (1990) provide a review of the use of differential geometric methods for control systems.

Discrete Mathematics: Cellular Automata

In contrast with the traditional continuum view of the world (that has been the basis of the mathematics scoped so far in this review) this field takes a discrete view of all systems. The basic ideas arose from the work of von Neumann (1956). A system is viewed as composed of cells in a lattice of one or more dimensions. The system is defined by rules describing the interaction between neighboring automata. Wolfram (1984) has conjectured that all cellular automata are contained in a limited number of classes spanning, however, a rather wide variety of behaviors including very "complex" types.

As far as we know, Zygourakis has been the sole champion of the use of cellular automata in chemical engineering; his current effort has been directed toward modeling the growth of anchorage dependent cells (Zygourakis et al., 1991a,b). Sandmann and Zygourakis (1986) show an application of cellular automata theory to the evolution of pore structure in gas solid reactions. It would appear that many more applications are possible with such discrete mathematics.

Statistics and Stochastic Processes

Statistical modeling is encountered in dealing with molecular and particulate systems. The system is described in terms of continuous distributions that are in fact quantities averaged over more detailed master density functions).

Statistical mechanics and kinetic theory

The Liouville equation in statistical mechanics deals with the distribution of N molecules in their spatial and velocity coordinates and can be used to derive averaged equations such as the equations of continuity mass, momentum, and energy, as well as the Boltzmann equation. Averaged expressions become available for various fluxes (momentum, energy, and component mass) that are encountered in transport. When suitably supplemented with intermolecular potentials, such "kinetic" theory is a source of calculation of fluid properties such as viscosity, thermal conductivity, mass diffusivity and so on. The book *Molecular Theory of Gases and Liquids* by Hirschfelder et al. (1964) has had a profound influence in the application of molecular theory to calculation of fluid properties. Since the literature is voluminous, we will be content with citing example articles such as Jagannathan et al. (1985), Pozhar and Gubbins (1993) and Bird and Ottinger (1992), the last of which is for polymeric liquids. Insights into the behavior of confined fluids (Vanderlick et al., 1989) and (Teletzke et al., 1987) are other interesting examples of the use of molecular theory. Curtiss and Bird (1996) formulate the statistical mechanics of transport phenomena for polymeric liquid mixtures. It is of interest to cite the recent text by Davis (1995) on the statistical mechanics of phases, interfaces, and thin films because of its value in educating chemical engineers of how a mathematical synthesis of interfacial phenomena (a subject of familiarity to chemical engineers from a continuum macroscopic viewpoint) is accomplished with molecular theory.

There has been considerable effort on the kinetic theory of suspensions in the literature that is of current interest. Dahler and coworkers have contributed significantly to this field during the last decade; we cite just one of their publications (Jorquera and Dahler, 1992). Another publication of interest is that of Koch (1990) in the area of gas-solid suspensions.

Population balances

Population balances have emerged as a very important part of chemical engineering modeling. Strangely, many past discourses on modeling have neglected to discuss them at length in spite of their natural preparedness for the modeling of dispersed phase systems (Ramkrishna, 1978). The *general* formulation of population balances began in the early 1960s, thanks to the effort of Hulburt and Katz (1964) and simultaneously by Randolph and Larson (1964). A similar general formulation of population balances for biological populations was published by Fredrickson et al. (1967). More specific applications of population balances had been known for several years earlier. Thus, the modeling of aggregation of particles by Brownian motion had been known much earlier (Smoluchowski, 1914). Valentas and Amundson (1966, 1968) were the first to analyze breakage and coalescence of liquid drops in a stirred liquid-liquid dispersion. It is in the capacity to include "internal" coordinates such as particle size, and other traits such as temperature, concentrations of dissolved species, and so on that makes population balances an attractive modeling implement. Population balances can be used to describe the dynamics of dispersion processes and describe the simultaneous occurrence of transport and reaction in the dispersed and continuous phases.

The book by Randolph and Larson (1971) specifically addressed the subject of crystallization systems. A review article by Ramkrishna (1985) and a recent book (Ramkrishna, 2000) treat the generic aspects of population balances and its wide applicability to transport phenomena in dispersions during the latter's formation. There have been other books on the subject of population balances for specific applications. Friedlander has made substantial contributions to modeling of aerosols, and their significance to air pollution problems is captured in Friedlander (2000). Seinfeld is another leading contributor to the aerosol literature and to climate modeling (Seinfeld, 1980; Seinfeld and Pandis, 1997). The problem of colloid stability is in the realm of population balances, featuring a diverse variety of inter-particle and hydrodynamic forces. We cite Schowalter (1984), who has addressed the stability and coagulation of colloids in shear fields, and a book on colloidal dispersions by Russel et al. (1992).

There are several interesting mathematical aspects of population balances that are of significance to applications. In particular, the property of self-similarity, first discovered by Wang and Friedlander (1967), is worthy of special mention. Its significance to the solution of inverse problems in population balance is discussed by Ramkrishna (2000). There are more contributors to population balance modeling deserving of mention that are unfortunately left out of our necessarily abridged discussion.

The statistical foundation of population balances has been addressed by Ramkrishna and Borwanker (1973), which also paves the way for *stochastic* models of population balance in which the number density is itself a stochastic variable. Its

relevance to modeling in the area of nanoparticles appears in Manjunath et al. (1994, 1996).

Most recently, the application of population balances to systems in which particle processes such as growth, aggregation, breakage and so on occur together with complex flow situations so that "external" coordinates such as particle location and velocity also become important in addition to internal coordinates. The solution of general population balance equations, which are coupled to fluid dynamic equations, are of intense interest in both academic and industrial circles.

Stochastic modeling

In an article on the statistical analysis of a stirred-tank reactor Aris and Amundson (1958b) showed how statistical properties of the reactor output could be obtained from those of the input variables at different steady states, based on a linearization of the nonlinear differential equations. Pell and Aris (1969, 1970) were apparently the first to introduce dynamic stochastic features into reactor analysis. The reactor equations were linearized about the steady states and so the linear stochastic differential equations were analyzed through their Fokker-Planck equations for the probability density. Rao et al. (1974a) were the first to derive an algorithm for solving nonlinear stochastic differential equations that converged to the proper solution of the Ito differential equation. (Ito calculus, which had several strange attributes, was relatively unknown to engineers in those times. The first step towards alleviation of this shortcoming was perhaps the appearance of the book by Wong (1971).) This algorithm was applied to the nonlinear simulation of stirred tank reactors by Rao et al. (1974b) subjected to random dynamic perturbations; they showed that reactors could seriously drift away from productive operation when the stability of the desired steady state is threatened by noise.

Algorithms for the solution of stochastic differential equations have undergone further refinement towards higher efficiencies. Talay and coworkers have published a number of important articles in this regard (Talay, 1982; Pardoux and Talay, 1985). The solution of stochastic differential equations naturally led to studies on Brownian dynamics, which became popular among the polymer community. Stochastic simulations by chemical engineers have appeared in biological applications (Sheth et al., 1977; Tranquillo and Lauffenburger, 1987), the first of which is concerned with photosynthesis in a dynamic random light intensity environment, while the second is associated with modeling of chemotaxis by Lauffenburger and coworkers. The Stokesian dynamics of particles in a suspension by Brady and Bossis (1988) also represents another example of the solution of stochastic differential systems, in this case the well-known Langevin equation of a colloidal particle which is subject to a random environment of molecular forces. Another interesting application of stochastic differential equations is contained in the concept of a "stochastic bridge," which allows the simulation of a stochastic path to span prespecified regions. The concept has been exploited by Krishnaswami et al. (1996) to simulate polymer conformations in an external field with exactly specified probabilities.

The champions of stochastic modeling in chemical engineering have been few and far between. Fredrickson's work on stochastic models of sterilization (Fredrickson, 1966) is an example of such a somewhat isolated effort. Fan and coworkers have had an extensive record of publications in the stochastic modeling area. We cite as an example Fox and Fan (1988). We cite Doraiswamy and Kulkarni (1987) for the stochastic analysis of many chemically reacting systems.

We conclude this section with observing that researchers in the systems area have made considerable use of stochastic methods in their work. For example, Kalman filtering is routinely used by researchers in the control area. A recent example of stochastic optimization is to be found in the work of Ramakrishnan et al. (1995).

Computational Methods

Without a suitable constraint, coverage of computational methods can become an overwhelming task. The area of course includes numerical methods for different types of equations (algebraic, differential, differential algebraic, partial differential, integro-differential), problems in optimization, and so on. These have engaged researchers in chemical engineering, particularly in the process synthesis area for several decades. They have been concerned with large-scale computations involving the solution of large numbers of equations. An exclusive review of work in this area will in itself be a monumental effort. We will therefore restrict our effort to covering events marked by the introduction of approaches of wide import to the solution of mathematical problems in chemical engineering other than large-scale processes. While this limitation is admittedly somewhat artificial, its imposition may be supported by much of the systems work being built on a mathematical edifice already established for modeling systems that are components of chemical processes. Yet, systems work in the current chemical engineering context has taken on very novel directions that do not support the foregoing statement. For example, there is work on conformation of large complex molecules for both fundamental and practical applications, the former in understanding the relationship between structure and properties, and the latter, for instance, in the drug discovery effort. A similar effort is under way in combinatorial catalysis. Systems researchers are gearing up for handling problems in bioinformatics where there is a substantial need for processing large amounts of metabolic flux data in ways that are constrained by reaction stoichiometry, metabolic regulatory processes, and so on. In general, without belaboring the issue, it may be stated that if systems researchers are not already playing a pronounced role in the mathematical treatment of large databases produced from high throughput combinatoric experiments, the necessary groundwork is being actively laid. With this in mind, we will consciously make the effort to recognize such published work when the opportunity arises, again with the high likelihood of missing worthy contributions in the process.

Computation in complex domains

Chemical engineering involves the solution of boundary and boundary/initial value problems featuring ordinary differential equations, partial differential equations of various types (parabolic, elliptic, hyperbolic, mixed), integro-differential equations, and so on. (There have been books published by chemical engineers on the solution ordinary and partial differential equations. The earliest from a computational viewpoint appears

to be that of Lapidus (1962). Lapidus and Seinfeld (1971) addressed the numerical solution of ordinary differential equations. Numerical solution of partial differential equations were presented in Lapidus and Pinder (1982). The application of the method of characteristics to the solution of first-order partial differential equations is presented with several applications to chemical engineering in Rhee et al. (1986b,a).)

A landmark article by Finlayson and Scriven (1966) is on the application of the method of weighted residuals (MWR) in which the solution is expressed in terms of a set of functions complete in the space in which the solution resides. The problem is basically "discretized" in the sense that a continuous variable is represented by a finite dimensional vector consisting of the coefficients of expansion that can be estimated in a variety of ways. The book of Finlayson (1980) on the subject of MWR has had notable influence on the solution of linear and nonlinear problems. Orthogonal collocation using polynomial basis functions has also been a very effective method of solving boundary/initial value problems (Villadsen and Stewart, 1978). There are various ways in which the choices of trial functions and weighting functions have been made by researchers in order to find more efficient solutions to specific problems.

The application of residual minimization techniques to complex domains leads to the so-called method of finite elements and other derivatives thereof. Scriven, Davis and coworkers have perhaps the most impressive record of computational effort in the application of finite-element methods to fluid mechanics, particularly in the area of free surface problems. (For a discussion of finite difference methods for the solution of free boundary problems see Ryskin and Leal (1984).) We cite selected publications from their group. Orr et al. (1977) have analyzed the shapes of 3-D menisci using finite-element methods. Christodulu and Scriven (1992) address finite-element methods for moving boundary flows. Basaran and Scriven (1990) present calculations for axisymmetric shapes of pendant and sessile drops in an electrical field. The two-volume compilation of Gresho and Sani (1999) deserves special mention on the use of finite-element methods for computational fluid dynamics albeit its limitation to laminar flows.

The boundary element method is popular in free boundary problems in fluid mechanics because of the reduction in dimension afforded by the formulation itself. Hume et al. (1985) discuss the relative merits of the finite-element and boundary element methods for moving boundary problems governed by a potential. Brown, Armstrong and coworkers have led a strong computational effort in rheology, particularly with respect to viscoelastic flows. Brown and coworkers have numerous publications in the area of single crystal growth of which we cite (Brown et al., 1989, 1994).

That computational fluid mechanics, particularly at finite Reynolds numbers, has progressed considerably in accuracy can be seen from comparing the work of Basaran and coworkers with their high speed photographic experiments (Wilkes et al., 1999). The analysis of a dripping faucet, recently presented by Ambravaneswaran et al. (2000), attracted considerable attention.

Concluding Remarks

Our sentiments in concluding what seemed like an endless journey through a forest of diverse mathematical effort in a profession bursting at the seams cannot possibly convey a sense of completion about our expedition. Fortunately, however, the emergence of a conclusion from such an expedition depends not as much on completeness as on extensiveness of its coverage. We hope that our coverage has not seriously lacked extensiveness.

An area that perhaps deserved better coverage was that of molecular modeling and the emergence of new methodologies in the horizon. This is in fact the subject of an entire issue of *Advances in Chemical Engineering* edited by Chakraborty (2001) that contains several outstanding articles on various aspects of molecular modeling. Product engineering is basically dependent on the ideas of molecular modeling although the relationship between structure and property may not always be clear. Cocchi and DeBenedetti (1998) provide an interesting discussion of molecular modeling issues connected with drug action. The import of various techniques from researchers in the Systems area provides one with a promising avenue. For example, the global optimization approach of Floudas and coworkers is already proving to be effective in the prediction of protein structure (Klepeis et al., 2003). The use of genetic algorithms (Venkatasubramanian et al., 1994) is also emerging in molecular design. The simulation of self-avoiding polymer conformations as performed by Ramakrishnan et al. (1995) drew on the well known work of Miller and Pekny (1991) in the exact solution of the Traveling Salesman problem. It is transparent that the heritage of mathematical modeling from the paradigm shift of the last century has firmly established itself as a methodology.

The use of quantum mechanical tools has been on the increase among chemical engineers. Sandler et al. (2001) has recently scoped this area and observes that computational power has increased to make more substantial applications of quantum mechanical calculations.

The biological revolution deserves more than the passing reference we provide in regard to its impact on the practice of mathematical modeling in chemical engineering. There have been outstanding efforts by chemical engineers in this area expounding on new opportunities in modeling. Bailey, whose background was originally in the area of nonlinear analysis and control, has had a profound influence on mathematical modeling in biochemical engineering (Bailey and Ollis, 1986) as well as in modern biotechnology (Bailey, 1998). Further, we acknowledge outstanding contributions from Stephanopoulos et al. (1998), who present opportunities in the area of metabolic engineering, Lauffenburger and Linderman (1993) for models for biological receptor mediated transport and reaction, Shuler (1989) for editing various perspective articles in biotechnology, Shuler and Kargi (1992) for a textbook on bioprocessing, and Nielsen et al. (2002) for a book on bioreaction engineering principles. Biomedical engineering is similarly endowed with numerous opportunities for modeling. New challenges in the design of biomaterials are expounded in an eloquent article by Peppas and Langer (1994).

There is evidence of great interest among industrial colleagues on the use of mathematical models as a substitute for expensive experimentation. The use of computational fluid mechanics is an example of such effort. Possibly, academic researchers addressing industrial needs more directly have favorably influenced such trends.

The use of symbolic software such as Mathematica has been

steadily rising in academic instruction of courses in mathematics. The books by Foley (2001) and Davis and Thomson (2000) are recent examples, and this trend is likely to gain strength in the coming years. The proper use of this facility can only sustain the mathematical consciousness of the profession of chemical engineering.

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