

# APPLIED MATHEMATICS

## *Opportunities for Chemical Engineers*

DORAISWAMI RAMKRISHNA

*Purdue University  
West Lafayette, IN 47907*

**I**N ALL THE furor over new technologies and the wealth of opportunities they hold for chemical engineers, the biggest change in mathematics as a source of opportunity is probably the development of new applications. The remarkable computing potential of current hardware and software presents new alternatives for the use of mathematics. A belief that the reputation of analysis has suffered in recent years (at least in expression, if not in practice) is the main reason for this article. More specifically, the objective of this article is to deliberate on certain areas of applied mathematics that may be old but which are most useful, and others that are new but which hold great promise.

In meeting this objective, we are faced with two dilemmas. First, mathematics is so diverse and fragmented that even mathematicians find communication between themselves hampered by specialized machinery. This makes writing a coherent article on the application of mathematics difficult because of constraints on one's familiarity and because of the discomfort that comes from the limited rationale of one's selection. Yet, a compromise possibly lies in the selection of an area of mathematics which has wide applications in chemical engineering and the examination of how that area fulfills various requirements of the discipline.

This brings up the second dilemma. Engineering applications, too, are diverse and difficult to categorize. How can one devise a coherent scheme for

covering such disparate applications? Figure 1 presents an attempt in this direction which, with suitable interpretation, could embrace the newer areas. It views chemical engineering analysis as being broadly concerned with the application of two physical theories—continuum and statistical, the latter of molecular and particulate states of matter (which purport to include heterogeneous media, etc.) to chemical process systems (or other systems in which matter undergoes similar experiences). Methods of averaging used in the treatment of heterogeneous media may be absorbed in continuum analysis. Commentary on Figure 1 also presents the opportunity to briefly (and superficially) cover general areas of mathematics which are useful to chemical engineering whether or not they are in current use.

### GENERAL OVERVIEW

Figure 1 depicts the methodology of chemical engineering in a sequence through which a mathematical model of a system matures to the stage at which it serves to guide the design and control of the operating system. Formulation represents the stage of its birth in which constitutive equations are proposed based on material behavior observed experimentally and on certain principles. In this regard, the framework of rational thermodynamics by Truesdell and coworkers [1-3], in spite of being germane, has received little attention from chemical engineers. (This is particularly true with respect to guidelines for constitutive equations in multicomponent systems which contain results at variance from irreversible thermodynamics and which could possibly be of significance.) Caruthers and coworkers [4,5] have recently exploited the framework to formulate constitutive equations for viscoelastic polymers. This formulative stage employs vector and tensor calculus, algebra, and topology.

The next stage is model validation, which must interact mutually with formulation. Validation could

*Doraiswami Ramkrishna is professor of chemical engineering at Purdue University. He received his BS from Bombay University and his PhD from the University of Minnesota. This article was compiled while he was the George T. Piercy Distinguished Visiting Professor at the University of Minnesota during the fall of 1988. His research interests cover applied mathematics, dispersed phase systems, and biochemical engineering.*



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be a long drawn-out process exceeding the bounds indicated in which the investigation of solution structure (a favorite term of Amundson) could be a participant. Here the implements do, or could, originate from statistics, stochastic filtering theory, inverse scattering theory, functional analysis, etc.

A model which emerges from the validation state (but not necessarily weathered to that of acceptance) is ready to be probed for its mathematical solution structure. This stage is preliminary to detailed computation and is one in which several analytical and semi-analytical tools of functional analysis (including nonlinear bifurcation and stability theories, catastrophe, and singularity theories), topology, differential, and algebraic geometry (relatively unfamiliar to chemical engineers), etc., are, and have been shown to be, very useful. Indeed, this stage may substantially overlap with the validation stage because of its capacity to create subtle situations for discriminating between models. Particular attention

is called to recent successes of differential geometry in the solution of partial differential equations [6]. Since the resolution of singularities is an integral aspect of algebraic geometry, it has many potential applications in the analysis of chemical reaction systems.

Engineering analysis consists of obtaining detailed solutions of model equations by examining system behavior under various circumstances. Numerical methods form the backbone of this effort, even in implementing analytical solutions. The method of finite elements has established itself as a tool of central importance in the analysis of complex models. In view of the many free boundary problems in chemical engineering, and the facility of algebraic geometry to describe geometric shapes, attention is called to the use of *rational* basis functions in finite element methodology [7].

Finally, the synthesis stage represents the ultimate accomplishment of mathematical models in realizing engineering objectives. Here, control theory and the methods of operations research form the bulwark of process systems engineering. Of special interest in operations research are recent developments in the application of projective geometric methods to linear programming [8].

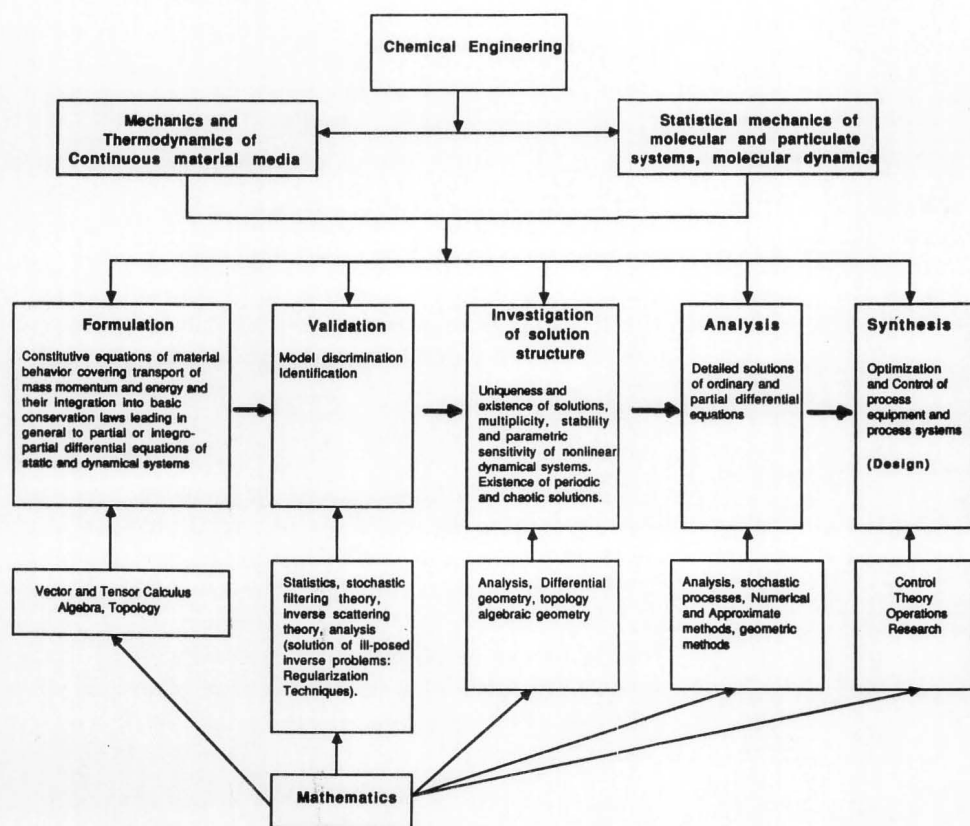


FIGURE 1

The above is a general overview of the development and application of mathematical models in chemical engineering in which areas of mathematics are identified with significant roles in the different stages shown in Figure 1. We now return to the main objective of this article, which is to present opportunities in an area with broad applications. The subject of linear operator theory fits this requirement for a number of reasons. Chiefly, it not only serves the cause of the many linear problems that occur naturally in applications, but

also forms the basis of several aspects of nonlinear analysis. There are even more reasons which will be left for subsequent discussions.

## LINEAR PROBLEMS

There are several linear problems of interest to chemical engineers which we will briefly cover. While their selection was based on their engineering importance, they also have mathematical traits which are generally unfamiliar. In the discussion that follows, it will become clear that modeling engineering systems usually calls for a blend of different mathematical implements. This feature does make modeling somewhat difficult.

### *Solid-Fluid Contacting*

Many operations in chemical engineering involve solid-fluid contacting, which is normally accomplished by passing a fluid through a bed of particles. The packed bed, catalytic reactor is a very important example. It is well-known that when modeling a packed bed reactor, one must take account of diffusional resistance within particles. A consequence of

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this awareness is the concept of the effectiveness factor. However, much reactor analysis has depended on the pseudo-homogeneous reactor model which neglects particles.

Let us briefly consider the reactor in which the fluid phase undergoes some form of convective mixing (possibly axial dispersion), and there is diffusion in every particle in the bed. The equations are easily written down. The reaction-free linear operator can be readily identified [9] and written in terms of the isolated "fluid" operator  $\mathbf{F}$ , the isolated "particle" operator  $\mathbf{S}$ , and an interaction operator  $\mathbf{A}$  accounting for transport across the particle surface to the fluid as shown below.

$$\mathbf{L} = \begin{pmatrix} \mathbf{F} & \mathbf{A} \\ \mathbf{O} & \mathbf{S} \end{pmatrix}$$

The above operator  $\mathbf{L}$  has a discrete spectrum containing an infinite set of sequences of eigenvalues, each converging to an eigenvalue of the particle operator. The eigenvalues can be characterized in terms

of the eigenvalues of the isolated fluid and particle operators. Limiting cases representing various simplifications of a physical nature can be studied from the behavior of the spectrum. Thus, conditions under which the fluid phase controls the dynamics can be determined.

From this analysis [10] it emerges that the quasi-static assumption for the particle phase can be made only when the effectiveness factor is too small to permit significant production. In other words, the "empty" tubular reactor does not exist from the transient viewpoint. It would appear then that much of the reactor analysis with pseudo-homogeneous models concerning steady state multiplicity, stability, and other transient features would be more appropriately performed with heterogeneous (two-phase) models.

It is here that the linear operator above becomes a very important tool. Furthermore, it has been customary to stipulate the extent to which particle steady states can vary in the reactor. A heterogeneous model of the foregoing type which includes only "indirect" interaction between particles because of mixing in the fluid phase can allow discontinuous changes in particle states. Modeling direct interaction between particles by some form of heat conduction and/or diffusion could eliminate such discontinuities but not prevent very fine variations presenting a reactor exploding with patterns [11]!

### *Singular Spectral Theory*

Sturm-Liouville operators (representing transport and reaction) on infinite domains have behaviors quite different from those on bounded domains. The theory, not covered in most engineering courses on applied mathematics, is extremely useful in dealing with transport in media of infinite (indefinite) extent. For a treatment of this material, see Jørgens [12] or Naimark [13]. While some applications have been made [14,15], there are several other interesting possibilities.

Consider, for example, the concept of surface renewal for mass transfer in turbulent gas-liquid systems. It would seem that a similar approach would be of interest in liquid-liquid systems. The application of this concept to liquid-liquid systems is complicated by two problems.\* One is if renewal occurs on either side of the interface, it is not clear what an "eddy" on arrival at the interface from one side would "see" on the other side. The other is that the

\*Stewart, Angelo, and Lightfoot [32] present an application of surface renewal concepts to such a situation in which the surface elements are not renewed but are merely stretched because of deformation of the interface.

methodology for solving diffusion equations in infinite contiguous media (for arbitrary initial conditions) is not available from standard treatments of boundary value problems.

On either count, a solution is made possible as follows. In regard to the first, assume an "expected" concentration profile on each side of the interface to which a freshly arriving eddy from the opposite side would be exposed. During its life at the interface, a random number of renewals may occur on the other side (with specifiable probabilities). Transport during this time can be described by using continuous spectral transforms. Averaging over all possible renewal combinations, the expected concentration profile of the eddy is computed on either side of the interface in terms of the concentration profile in the other. Two coupled integral equations result for the expected concentration profiles, the solution of which will lead to the calculation of mass transfer rates between the two phases. This particular example should give the right flavor of the nature of applications under this category.

### Inverse Scattering Theory

A very interesting problem, which was addressed as early as 1951 by Gelfand and Levitan [16], is the inverse Sturm-Liouville problem [13] which poses the question of how to determine a linear operator when given its spectral information. The spectral information, broadly stated, consists of the eigenvalues and the spectral distribution function of the operator. (The problem arose in quantum mechanics when the potential function was of interest given spectral information of the Schrodinger operator.) The spectral distribution function arises as the coefficient of the eigenfunction written at large distance (essentially normalization constants) and must be determined experimentally. The strategy for determining the potential function (*i.e.*, the operator), as developed by Gelfand and Levitan [16], involves the solution of a certain integral equation derived from the spectral data [17]. When the potential function is a constant, this step is greatly simplified.

The elegant treatment of first order reaction systems by Wei and Prater [18] may be considered as a rudimentary example of the methodology of inverse scattering theory. Except for the work of Kravaris and Seinfeld [19], the author is unaware of instances of the application of scattering theory in the chemical engineering literature. There are many applications possible in the validation-identification area, particularly in determining transport coefficients in multi-component systems. Besides the effort of Krishna, *et*

*al.* [20], who were more concerned with transfer coefficients than diffusivities, few instances can be cited in the literature where multicomponent systems have been subjected to identification experiments. An experiment which appears attractive is to allow the diffusion of species from a well-mixed section across a rigid membrane of known transport properties into a long quiescent medium. Concentration measurements in the well-mixed section could be made as a function of time from which the spectral distribution of the operator, and thence the diffusion coefficients, could be calculated. The convenient feature of this setup is that the concentration range can be controlled to use "constant" diffusion coefficients.

There have also been alternative inverse problem formulations without involving the spectral transform. Rundell [21] has investigated the solution of the parabolic equation

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - q(x)u \quad 0 < x < 1$$

in a bounded domain. Given measurements of  $u(0,t)$ ,  $u(1,t)$ ,  $u(x,0)$ , and  $u(x,t_0)$ ,  $t_0 > 0$ , the problem of determining  $q(x)$  becomes a well-posed problem, and one can constructively march to the solution. However, note that this well-posed problem has been obtained by measuring an entire concentration profile at one fixed time during the diffusion process.

The subject of inverse problems is also important in other formulations in chemical engineering. Thus, population balance models of dispersed phase systems are often based on rate functions (such as those of break-up and agglomeration of individual particles, or of particle "growth," *etc.*) that must be determined by inverse problem formulation. For example, the determination of the coalescence rate of liquid droplets as a function of drop sizes in a stirred liquid-liquid dispersion, denoted by  $q(v,v')$ , may be determined by transient measurements of the cumulative drop size distribution,  $F(v,\tau)$ , through the solution of the inverse problem

$$\frac{\partial F(v,\tau)}{\partial \tau} = - \int_0^v \partial F(v',\tau) \int_{v-v'}^{\infty} \partial F(v'',\tau) q(v',v'') / v''$$

The problem above is ill-posed, and a regularization method due to Tikhonov and Arsenin [22] is required to solve the problem. Muralidhar and Ramkrishna [23,24] have solved this problem by using similarity theory to convert the integro-differential equation to a Volterra integral equation and applying regularization techniques to the latter. Regularization techniques have been used by others

(e.g., [25]), but generally they are not common knowledge among chemical engineers.

## NONLINEAR PROBLEMS

### *Inverse Scattering Transform and Nonlinear Evolution*

A most interesting development of the inverse scattering theory referred to earlier is its connection to the solution of certain families of nonlinear partial differential equations. This development has occurred over the last decade. Briefly, the method works like any linear integral transform used to solve linear differential equations. The remarkable aspect of the technique is that while the dependent variable evolves in time through a nonlinear equation, its transform evolves through a linear equation! Shelving, for the present, the nature of the association of the linear problem which defines the transform and the nonlinear equation, let us denote the linear operator as

$$-\frac{d^2}{dx^2} + q(x, t) \quad -\infty < x < \infty$$

where  $t$  is to be regarded as a parameter, and  $q$  is in fact the dependent variable in the nonlinear evolution equation. The self-adjoint operator above defines a spectral transform depending obviously on parameter  $t$ . What we are interested in is solving a certain nonlinear partial differential equation in  $q(x, t)$  subject to some initial condition  $q(x, 0) = q_0(x)$ . The transform is well-defined at time  $t = 0$  since  $q_0$  is known then. This transform may have a continuous and discrete part (if there are discrete eigenvalues). We denote the partial differential equation satisfied by  $q(x, t)$  by

$$\frac{\partial q(x, t)}{\partial t} = 2\beta(\mathbf{L}, t) \frac{\partial q(x, t)}{\partial x}$$

where  $\mathbf{L}$  is the linear operator

$$\mathbf{L} = \frac{\partial^2}{\partial x^2} - 4q(x, t) + 2 \frac{\partial q(x, t)}{\partial x} \int_x^\infty dy(\ )$$

in which specific attention is called to the presence of the dependent variable  $q(x, t)$  here also. The function  $\beta(z, t)$  appearing in the nonlinear operator can be any entire function of  $z$ , and it determines the linear evolution equation in the spectral (inverse scattering) transform. Inverting the spectral transform for the solution requires the solution of a linear integral equation, which is not always easy. On inversion, the continuous transform provides for "dispersive" waves, while the discrete part gives rise to solitary waves or "solitons." The solitons survive at large times and can be calculated analytically because when there is only a discrete transform the integral equation to be solved for inversion contains a degenerate kernel. Thus the

most interesting attribute of this technique seems to be the calculation of soliton solutions of nonlinear evolution equations. For an interesting account, see Degasperis [26] and Drazin [27]. Some of the equations that have been analytically solved for solitons are the KdV equation in the production of shallow water waves given by

$$u_t - 6uu_x + u_{xxx} = 0$$

and Fischer's equation in nonlinear diffusion

$$u_t = u_{xx} + \alpha^2 u(1 - u)$$

and Burger's equation

$$u_t + uu_x = \nu u_{xx}$$

etc. All of the foregoing examples could be obtained by specific choices of the function  $\beta$  in the general formulation

Lax [28] has provided an operator formulation of the above in which the association between the nonlinear and the linear problem is less mysterious. Consider the nonlinear operator  $\mathbf{N}: \mathbf{H} \rightarrow \mathbf{H}$  where  $\mathbf{H}$  is a Hilbert space, and the nonlinear evolution equation

$$u_t = \mathbf{N}(u) \quad (1)$$

The problem is to find a linear operator  $\mathbf{L}$  which generates a transform applicable to the solution of the nonlinear problem (Eq. 1) in the sense described above. (In linear problems, this step was immediately obvious.) Lax requires that one must determine two linear operators,  $\mathbf{L}$  and  $\mathbf{B}$ , on  $\mathbf{H}$ —both depending on  $\mathbf{u}$  such that  $\mathbf{L}$  is symmetric and of the type considered earlier in the inverse scattering transform above with  $\mathbf{u}$  in place of  $q$ , and such that Eq. (1) somehow implies that

$$\mathbf{L}_t = \mathbf{B}\mathbf{L} - \mathbf{L}\mathbf{B} \quad (2)$$

The eigenvalues of  $\mathbf{L}$  will obviously depend on the parameter  $t$ . It turns out that the necessary and sufficient condition for the eigenvalues of  $\mathbf{L}$  to be independent of  $t$  is that the nonlinear Eq. (1) be satisfied. In other words, the interesting conclusion emerges that the eigenvalues of  $\mathbf{L}$  (which depend on  $u(x, t)$ ) will be independent of  $t$  if and only if  $u(x, t)$  satisfies a suitable nonlinear evolution equation.

In applications, one is of course confronted with a given nonlinear equation and the utility of the foregoing methods is clearly not straightforward. On the other hand, the above methods can generate a dictionary of solvable equations through a tool that can admit some "tuning" to accommodate a given problem. For example, it is not inconceivable that the combination of chemical reaction and diffusion could produce solitary waves in flowing systems.

### Direct Methods for Nonlinear Evolution

The nonlinear equations which can be solved for the solitons by using the inverse scattering transform appear to be also solvable by more direct methods [29]. In this approach, where the main advantage is that it also becomes available for those not conversant with inverse scattering theory, a traveling frame of reference is introduced in terms of a wave velocity to be subsequently determined. The solution is expressed in terms of a convergent power series of decaying exponentials (of the transformed variable) and the entire form of the solution is obtained by direct substitution into the equation. Soliton solutions emerge as exactly summable expansions in this direct approach.

### Other Methods – Differential Geometry

It appears that exactly solvable nonlinear systems are amenable to seemingly different approaches. One such approach is provided by the methods of differential geometry in which a second order partial differential equation is converted by appropriate transformation into a linear system of first order partial differential equations. The first order system is, in turn, associated with what are known as *exterior differential forms* in a manner that provides for either analytical solutions or computationally efficient solutions [4,30,31].

### SUMMARY

This article has attempted a brief survey of the offshoots of linear operator theory and their potential to various aspects of chemical engineering analysis, including the solution of nonlinear problems.

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