A Course in

MATHEMATICAL METHODS IN CHEMICAL ENGINEERING

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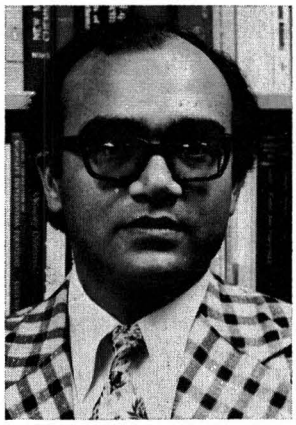
A TWO-SEMESTER, three lectures per week graduate course dealing with Mathematical Methods in Chemical Engineering is offered every year at Notre Dame. The course originated with Merlin Howerton in Fall 1949 when he joined the department. It was initially a one-semester course, and was taken largely by graduate students at the master's level (the doctoral program in ChE at Notre Dame did not begin 'til the arrival of Julius T. Banchero from Michigan as Chairman in 1959), although some seniors also took the course as a technical elective. Two of our current (and senior) faculty members, James J. Carberry and James P. Kohn, took the course together in Fall 1950, the second time it was offered; the former as a master's student, and the latter as a senior. Howerton taught the course 'til 1954, using the early book of Marshall and Pigford [8] on differential equations as text. He left the department for the University of Denver in June 1955; Howerton was particularly close to John Treacy who had died that year in an explosion while conducting a kinetics experiment with organo-nitrides used for propellants.



Arvind Varma is currently an Associate Professor of Chemical Engineering at the University of Notre Dame. His degrees are all in Chemical Engineering; B.S. from Panjab University, India, M.S. from the University of New Brunswick, Canada, and Ph.D. from the University of Minnesota (1972). After staying on the faculty at Minnesota for a year, he was with Union Carbide for two years, and joined Notre Dame in 1975. His research interests include chemical and catalytic reaction engineering, modeling and simulation. His friendship with the renowned Aris McPherson Rutherford began while he was a graduate student, and was nurtured by their common interests in Amundson's early work on distillation—the fruits of which they both enjoy.

Fortunately, Jim Kohn joined the faculty in Fall 1955 after completing graduate work at Michigan and Kansas, and took over the course, expanding it immediately to a two-semester sequence. His course was particularly oriented towards modeling. Although he used the second edition of Applied Mathematics in Chemical Engineering [11] as text for one year, it did not prove satisfactory and Kohn started developing his own notes on the subject. Except for the years 1964-67 when Francis Wehner taught it, using the first edition of Jenson and Jeffrys [7], Kohn taught the course for twenty years.

Because it was unique in the college of engineering, Kohn's course consistently attracted students as well as faculty from the other engineering departments. In Fall 1963 enrollment in the course was at its highest; 45, including 15 seniors. The course has been taught by the author since Fall 1976. Enrollment in the course started dropping during the middle sixties as other engineering departments began their own courses, and the department began a one-semester undergraduate course in applied mathematics at the junior level. This last course was dropped in 1967 in favor of a similar college-wide core course.

Our present course is taken by all first-year graduate students in the department, and the class typically consists of twelve to fifteen students, always including a few from other branches of engineering, chemistry or physics. Although technically it is open to seniors, only one has elected to take it in the last three years.

Notre Dame has been at a disadvantage for some time with respect to instruction in applied mathematics within our mathematics department, since it is more oriented towards "pure" mathematics. That department is a distinguished one, but most scholarly research is in areas such as algebra, topology, logic and group theory. These topics are not the most useful for our graduate students, either in their research or in coping with other graduate courses, so we must teach them, within the department, what we would like them to know in applied mathematics. Apart from this need, I am certain we would teach our own mathematical methods course even if there were courses available within the mathematics department. The reason is that the course not only teaches techniques for solving mathematical problems once they are formulated, but also stresses model-building. In this sense, my ideas of teaching applied mathematics to chemical engineers closely match those of my mentor Neal Amundson. Indeed, our current course bears a striking similarity to his at Minnesota in the late sixties [1].

COURSE FORMAT

THE COURSE MEETS THREE times a week for fifty minute lectures. Homework problems are assigned almost every week, and are graded and returned to the student. Somewhere between 25-30 homework problems are assigned each semester. I also give two mid-semester exams and a final each semester, all closed-book. Lengthy formulae are not required to be memorized, and are provided for the examinations.

Approximately one-third of the homework problems require use of the university computer (IBM 370). No instruction in programming or numerical techniques is given as part of this course and almost all of our entering graduate students take the separate Numerical Methods course offered annually in the fall semester within the department.

TABLE 1
Topical Course Outline

1. **Matrices and their Application.**
2. **First Order Nonlinear Ordinary Differential Equations and Stability Theory.**
3. **Linear Ordinary Differential Equations: Initial-value, Boundary-value and Eigenvalue Problems.**
4. **Series Solutions and Special Functions.**
5. **Linear Partial Differential Equations.**
6. **Laplace Transforms.**

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An unusual characteristic of the course is that the lectures are given on transparencies shown by an overhead projector. Students receive copies of the transparencies in chapter form, at cost, well in advance. I prefer this method because teaching mathematics usually requires lengthy manipulations which consume a good amount of class time if performed on the blackboard. The additional, and main, advantage is that students are not busy transcribing material from the blackboard (an operation which can occur, bypassing the mind) and thus can concentrate on understanding the material. Students invariably like this approach. Since classes are small, there are frequent interruptions for questions, both by students and the instructor.

COURSE DESCRIPTION

A TOPICAL OUTLINE OF the course is shown in Table 1. The following is a detailed description.

The first five to six weeks in the fall semester are devoted to matrices and their application, covering portions of Amundson's book [2]. This includes material on determinants, solution of linear simultaneous algebraic equations, matrix eigenvalues and eigenvectors, expansion of an arbitrary vector in terms of the eigenvectors, solving a system of coupled first order linear ordinary differential equations (ODEs) by the method of eigenvalues and eigenvectors, similarity transforms, quadratic forms, and functions defined on matrices. Several non-trivial examples from the book are covered in detail; they have usually included transient analyses of staged separation processes, and a sequence of isothermal first order reactions occurring in a batch reactor or in a series of continuous-flow stirred tank reactors.

The balance of the course deals with ordinary and partial differential equations. The first aspect in this area deals with first order nonlinear ODEs and stability theory, and usually takes six to seven weeks. Topics covered include the existence and uniqueness result for initial-value problems, continuous dependence of the solution

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on a parameter or initial conditions, qualitative behavior of nonlinear ODEs, linearization, Liapunov's theorem for the local stability of nonlinear systems, classification of the phase plane for two-dimensional systems, higher order systems, and stability by Liapunov's Direct Method. This portion is perhaps the most interesting part of the course, for it brings out the essential differences between linear and nonlinear dynamic systems. Linear systems arising in nature invariably possess a unique steady state which is asymptotically approached in time by all initial conditions (global asymptotic stability). Nonlinear systems, of course, can have a multiplicity of steady states (some stable, others unstable) and frequently one encounters cases where either a unique steady state or all the multiple steady states are unstable—in which case the dynamic behavior is a self-sustained oscillation. Examples from reactor analysis and population balances are covered to illustrate these features. In this context, I hope to include in future offerings, recently developed material on first-order nonlinear *difference* equations which, although simple and deterministic, can exhibit very surprising dynamic behavior, from stable steady states to stable periodic solutions, and eventually to apparently random fluctuations implying "chaos." Such equations have been used to great advantage in analyzing biological populations [9, 10]. Also recent experimental [14] and theoretical studies [cf., 13] suggest that complex reactions in flow reactors can also exhibit the same exotic features even under isothermal conditions.

The theory of linear ODEs is treated next. Topics in this category naturally subdivide into three classes: initial-value, boundary-value, and eigenvalue problems. Although second-order differential operators are emphasized since they arise most frequently in applications such as mass-diffusion and heat-conduction, higher order operators are also considered because of their role in elasticity problems. In fact, general n-th order linear differential operators are treated throughout initial-value problems. The concept of linear independence of solutions of homogeneous equations is instilled early, and tests for it by the Wronskian determinant are developed. This leads to solution of non-homogeneous equations by the method of variation of parameters, and the resulting one-sided Green's function for initial-value problems. Normally the fall semester ends with a discussion of the adjoint operator and the adjoint differential equation.

The spring semester begins with a treatment of boundary-value problems, and in it, a discussion of boundary conditions (BCs). Some time is spent on how BCs actually arise in physical problems, and what they mean. They are a mathematical representation of interaction of the system with the surroundings. As Amundson has often said, "BCs arise from nature, and not mathematics." To understand this further, it is profitable to take the approach of two observers near the boundary, one just within the boundary and the other just outside. The flux arriving at the boundary from within the system is established using the same principles employed in deriving the model (i.e., the ODE) itself. However, the observer just outside the boundary "sees" a flux that depends on what is happening in the surroundings. Thus in the context of a heat-conduction problem, external convection may be excellent, poor, or only fair, leading to first (Dirichlet), second (Neumann or 'insulation'), or third (Robin or 'natural') kind BCs, respectively. All these may be thought of arising as a consequence of the magnitude of h/k, the ratio of external heat transfer coefficient to the material thermal conductivity. Depending on whether the ratio is large, near zero, or finite, one gets the appropriate BC, which physically imply that the surface temperature equals that of the surroundings, the surface is insulated, or Newtonian heat transfer at the surface, respectively. These BCs are all linear. Nonlinear ones can also arise in the same manner if radiative exchange occurs at the surface; in this case the surface flux from the viewpoint of the internal observer remains unaltered, but the external observer sees a radiative flux. There is no counterpart of the nonlinear BC in a mass-diffusion problem, except when a nonlinear reaction occurs on the surface.

After a discussion of the BCs, the concept of

a self-adjoint differential operator and of self-adjoint boundary-value problems (i.e., the operator plus the BCs) is developed. The Green's function for solving non-homogeneous boundary-value problems is derived from the one-sided Green's function for initial-value problems, and a physical interpretation is attached to it.

The origin of eigenvalue problems is discussed, and following introductory examples, the general Sturm-Liouville problem is treated for self-adjoint operators with self-adjoint BCs. Several examples are treated in this context, and the fact that such problems possess an infinite number of real eigenvalues, each with an eigenfunction belonging to it, is brought out. Completeness and orthogonality of the eigenfunctions is responsible for generalized eigenfunction expansions of functions, and lead to finite Fourier transforms and thus the solution of boundary-value problems by this technique. The method of finite Fourier transforms also plays a centrol role in solving partial differential equations, and is thoroughly discussed.

The topic of power series solutions and special functions is covered next, in about three weeks. The distinction between ODEs with analytic coefficients and those with regular singular points is made. Orthogonal polynomials associated with Legendre and Hermite arise as solutions of specific ODEs in the former class, and are developed. The extended power series method of Frobenius is considered for the latter class, and is applied in detail to develop the various Bessel functions. Relationships among Bessel functions and variety of ODEs having Bessel function solutions are reported. The topic concludes with several physical and chemical examples in cylindrical geometry which have solutions in terms of Bessel functions, such as the temperature profile with internal heat generation, heat transfer in a fin, and diffusion-first order reaction in a catalyst pellet. The remaining orthogonal polynomials, those of Laguerre and Chebyshev, are normally developed as homework problems, as special cases of the confluent hypergeometric function—the solution of the confluent hypergeometric equation. The various orthogonal polynomials play a central role in numerical quadrature [4, 15].

The remaining weeks are devoted to second-order partial differential equations (PDE's) and Laplace transforms. Armed with the powerful method of finite Fourier transforms, it becomes a relatively straightforward matter to routinely solve PDEs in many space variables and time. In applying the method, a differential operator and associated homogeneous BCs need to be identified corresponding to each of the space variables. In most physically motivated problems, these are or can be made self-adjoint. The corresponding eigenvalue problems are then solved, and successive transforms of the PDE are taken to eventually yield an ODE in the last independent variable. This ODE can usually be directly solved, and inverse transforms performed to yield the solution in series form. A good rule to remember is that the number of series summations is one less than the number of independent variables; the solution of a problem in three space variables and time will thus be a triply infinite series. Nonhomogeneities in the BCs and the equation itself are readily accommodated by the technique of impulse response, for which a physically-based but mathematically sound derivation is provided.

In Laplace transforms, other than basic relationships, we usually cover Heaviside expansion theorem for finding inverse transforms, and the solution of ordinary and partial differential equations by the technique using examples.

CONCLUDING REMARKS

AS THE PREVIOUS DESCRIPTION indicates, we do a significant amount of applied mathematics in our course. The mathematical content is quite oldfashioned, but the aim is to insure that our graduates have a thorough mastery of at least the old-fashioned mathematics. To make the course more modern and to provide another set of techniques, I plan to include some material on perturbation methods [cf., 12] in future offerings. These methods are powerful in giving solutions of nonlinear problems in limiting cases, and have been used in fluid mechanics as well as in reaction engineering. They are currently introduced in one of our advanced elective courses in reaction engineering, but all students do not take that course.

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There are no textbooks available for the course, although Ince [6] covers the theory of linear ODEs in depth, some aspects of stability theory can be found in Davis [5] and in Boyce and DiPrima [3], and Weinberger [16] gives a good

exposition of the method of finite Fourier transforms. As mentioned before, we distribute a set of notes to the students. These notes were developed in collaboration with Professor Amundson, and we plan to refine and publish them in textbook form in the future. The use of overhead transparencies is very helpful in covering the relatively broad set of topics in the mathematical detail necessary, and provides the student with a feel for mathematics and its use. A great deal of class time is spent on "talking about" problems, and on the role and use of mathematics in chemical engineering in general.

A fundamental question arises as to whether all this should be done in a chemical engineering department. Some reasons for our doing so were noted in the introductory section. In addition, it is my observation that mathematics courses offered in mathematics departments, even if they are titled "applied", tend to be rather theoretical in nature. Also, in general, mathematicians do not care about solving problems, much less model-building. The type of course we offer not only gives the student a good mathematical background, but also gives him confidence in formulating and solving problems. At the end of the course he is conversant with standard mathematical techniques, knows their limitations, and can readily use them to solve non-trivial problems in practice. Student feedback has been uniformly positive. □

ACKNOWLEDGMENT

It is a pleasure to thank my colleagues, James J. Carberry and James P. Kohn for providing historical information regarding the course.

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