Numerical Methods & Modeling for Chemical Engineers

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Preface

This book is an introduction to the quantitative treatment of differential equations that arise from modeling physical phenomena in the area of chemical engineering. It evolved from a set of notes developed for courses taught at Virginia Polytechnic Institue and State University.

An engineer working on a mathematical project is typically not interested in sophisticated theoretical treatments, but rather in the solution of a model and the physical insight that the solution can give. A recent and important tool in regard to this objective is mathematical software—preprogrammed, reliable computer subroutines for solving mathematical problems. Since numerical methods are not infallible, a "black-box" approach of using these subroutines can be dangerous. To utilize software effectively, one must be aware of its capabilities and especially its limitations. This implies that the user must have at least an intuitive understanding of how the software is designed and implemented. Thus, although the subjects covered in this book are the same as in other texts, the treatment is different in that it emphasizes the methods implemented in commercial software. The aim is to provide an understanding of how the subroutines work in order to help the engineer gain maximum benefit from them.

This book outlines numerical techniques for differential equations that either illustrate a computational property of interest or are the underlying methods of a computer software package. The intent is to provide the reader with sufficient background to effectively utilize mathematical software. The reader is assumed to have a basic knowledge of mathematics, and results that require extensive mathematical literacy are stated with proper references. Those who desire to delve deeper into a particular subject can then follow the leads given in the references and bibliographies.

Each chapter is provided with examples that further elaborate on the text. Problems at the end of each chapter are aimed at mimicking industrial mathematics projects and, when possible, are extensions of the examples in the text. These problems have been grouped into two classes:

Class 1: Problems that illustrate direct numerical application of the formulas in the text.

Class 2: Problems that should be solved with software of the type described in the text (designated by an asterisk after the problem number).

The level of this book is introductory, although the latest techniques are presented. The book can serve as a text for a senior or first-year graduate level course. At Virginia Polytechnic Institute and State University I have successfully used this material for a two-quarter sequence of first-year graduate courses. In the first quarter ordinary differential equations, Chapter 1 to 3, are covered. The second quarter examines partial differential equations using Chapters 4 and 5.

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I dedicate this book to my wife, who uncomplainingly gave up a portion of her life for its completion.

Mark E. Davis

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Initial-Value Problems for Ordinary Differential Equations

INTRODUCTION

The goal of this book is to expose the reader to modern computational tools for solving differential equation models that arise in chemical engineering, e.g., diffusion-reaction, mass-heat transfer, and fluid flow. The emphasis is placed on the understanding and proper use of software packages. In each chapter we outline numerical techniques that either illustrate a computational property of interest or are the underlying methods of a computer package. At the close of each chapter a survey of computer packages is accompanied by examples of their use.

BACKGROUND

Many problems in engineering and science can be formulated in terms of differential equations. A differential equation is an equation involving a relation between an unknown function and one or more of its derivatives. Equations involving derivatives of only one independent variable are called ordinary differential equations and may be classified as either initial-value problems (IVP) or boundary-value problems (BVP). Examples of the two types are:

$$\text{IVP:}\quad y'' = -yx \tag{1.1a}$$

$$y(0) = 2, \qquad y'(0) = 1 \tag{1.1b}$$

$$\text{BVP:}\quad y'' = -yx \tag{1.2a}$$

$$y(0) = 2, \qquad y(1) = 1 \tag{1.2b}$$

where the prime denotes differentiation with respect to x. The distinction between the two classifications lies in the location where the extra conditions [Eqs. (1.1b) and (1.2b)] are specified. For an IVP, the conditions are given at the same value of x, whereas in the case of the BVP, they are prescribed at two different values of x.

Since there are relatively few differential equations arising from practical problems for which analytical solutions are known, one must resort to numerical methods. In this situation it turns out that the numerical methods for each type of problem, IVP or BVP, are quite different and require separate treatment. In this chapter we discuss IVPs, leaving BVPs to Chapters 2 and 3.

Consider the problem of solving the mth-order differential equation

$$y^{(m)} = f(x, y, y', y'', \ldots, y^{(m-1)}) \tag{1.3}$$

with initial conditions

$$\begin{aligned} y(x_0) &= y_0 \\ y'(x_0) &= y_0' \\ &\vdots \\ y^{(m-1)}(x_0) &= y_0^{(m-1)} \end{aligned}$$

where f is a known function and $y_0, y_0', \ldots, y_0^{(m-1)}$ are constants. It is customary to rewrite (1.3) as an equivalent system of m first-order equations. To do so, we define a new set of dependent variables $y_1(x), y_2(x), \ldots, y_m(x)$ by

$$\begin{aligned} y_1 &= y \\ y_2 &= y' \\ y_3 &= y'' \\ &\vdots \\ y_m &= y^{(m-1)} \end{aligned} \tag{1.4}$$

and transform (1.3) into

$$\begin{aligned} y_1' &= y_2 && = f_1(x, y_1, y_2, \ldots, y_m) \\ y_2' &= y_3 && = f_2(x, y_1, y_2, \ldots, y_m) \\ &\vdots && \vdots \\ y_m' &= f(x, y_1, y_2, \ldots, y_m) && = f_m(x, y_1, y_2, \ldots, y_m) \end{aligned} \tag{1.5}$$

with

$$\begin{aligned} y_1(x_0) &= y_0 \\ y_2(x_0) &= y_0' \\ &\vdots \\ y_m(x_0) &= y_0^{(m-1)} \end{aligned}$$

In vector notation (1.5) becomes

$$\mathbf{y}'(x) = \mathbf{f}(x, \mathbf{y}) \qquad \textbf{(1.6)}$$
$$\mathbf{y}(x_0) = \mathbf{y}_0$$

where

$$\mathbf{y}(x) = \begin{bmatrix} y_1(x) \\ y_2(x) \\ \vdots \\ y_m(x) \end{bmatrix}, \qquad \mathbf{f}(x, \mathbf{y}) = \begin{bmatrix} f_1(x, \mathbf{y}) \\ f_2(x, \mathbf{y}) \\ \vdots \\ f_m(x, \mathbf{y}) \end{bmatrix}, \qquad \mathbf{y}_0 = \begin{bmatrix} y_0 \\ y_0' \\ \vdots \\ y_0^{(m-1)} \end{bmatrix}$$

It is easy to see that (1.6) can represent either an mth-order differential equation, a system of equations of mixed order but with total order of m, or a system of m first-order equations. In general, subroutines for solving IVPs assume that the problem is in the form (1.6). In order to simplify the analysis, we begin by examining a single first-order IVP, after which we extend the discussion to include systems of the form (1.6).

Consider the initial-value problem

$$y' = f(x, y), \qquad y(x_0) = y_0 \qquad \textbf{(1.7)}$$
$$x_0 \leqslant x \leqslant x_N$$

We assume that $\partial f/\partial y$ is continuous on the strip $x_0 \leqslant x \leqslant x_N$, thus guaranteeing that (1.7) possesses a unique solution [1]. If $y(x)$ is the exact solution to (1.7), its graph is a curve in the xy-plane passing through the point (x_0, y_0). A discrete numerical solution of (1.7) is defined to be a set of points $[(x_i, u_i)]_{i=0}^{N}$, where $u_0 = y_0$ and each point (x_i, u_i) is an approximation to the corresponding point $(x_i, y(x_i))$ on the solution curve. Note that the numerical solution is only a set of points, and nothing is said about values between the points. In the remainder of this chapter we describe various methods for obtaining a numerical solution $[(x_i, u_i)]_{i=0}^{N}$.

EXPLICIT METHODS

We again consider (1.7) as the model differential equation and begin by dividing the interval $[x_0, x_N]$ into N equally spaced subintervals such that

$$h = \frac{x_N - x_0}{N} \qquad \textbf{(1.8)}$$
$$x_i = x_0 + ih, \qquad i = 0, 1, 2, \ldots, N$$

The parameter h is called the step-size and does not necessarily have to be uniform over the interval. (Variable step-sizes are considered later.)

If $y(x)$ is the exact solution of (1.7), then by expanding $y(x)$ about the point x_i using Taylor's theorem with remainder we obtain:

$$\begin{aligned} y(x_{i+1}) &= y(x_i) + (x_{i+1} - x_i)y'(x_i) \\ &\quad + \frac{(x_{i+1} - x_i)^2}{2!} y''(\xi_i), \qquad x_i \leqslant \xi_i \leqslant x_{i+1} \end{aligned} \tag{1.9}$$

The substitution of (1.7) into (1.9) gives

$$y(x_{i+1}) = y(x_i) + hf(x_i, y(x_i)) + \frac{h^2}{2!} f'(\xi_i, y(\xi_i)) \tag{1.10}$$

The simplest numerical method is obtained by truncating (1.10) after the second term. Thus with $u_i \simeq y(x_i)$,

$$\begin{aligned} u_{i+1} &= u_i + hf(x_i, u_i), \qquad i = 0, 1, \ldots, N - 1, \\ u_0 &= y_0 \end{aligned} \tag{1.11}$$

This method is called the Euler method.

By assuming that the value of u_i is exact, we find that the application of (1.11) to compute u_{i+1} creates an error in the value of u_{i+1}. This error is called the local truncation error, e_{i+1}. Define the local solution, $z(x)$, by

$$z'(x) = f(x, z), \qquad z(x_i) = u_i \tag{1.12}$$

An expression for the local truncation error, $e_{i+1} = z(x_{i+1}) - u_{i+1}$, can be obtained by comparing the formula for u_{i+1} with the Taylor's series expansion of the local solution about the point x_i. Since

$$z(x_i + h) = z(x_i) + hf(x_i, z(x_i)) + \frac{h^2}{2!} z''(\bar{\xi}_i)$$

or

$$z(x_i + h) = u_i + hf(x_i, u_i) + \frac{h^2}{2!} z''(\bar{\xi}_i), \qquad x_i \leqslant \bar{\xi}_i \leqslant x_{i+1} \tag{1.13}$$

it follows that

$$e_{i+1} = \frac{h^2}{2!} z''(\bar{\xi}_i) = 0(h^2) \tag{1.14}$$

The notation 0( ) denotes terms of order ( ), i.e., $f(h) = 0(h^L)$ if $|f(h)| \leqslant Ah^l$ as $h \rightarrow 0$, where A and l are constants [1]. The global error is defined as

$$\mathcal{E}_{i+1} = y(x_{i+1}) - u_{i+1} \tag{1.15}$$

and is thus the difference between the true solution and the numerical solution at $x = x_{i+1}$. Notice the distinction between e_{i+1} and $\mathcal{E}_{i+1}$. The relationships between e_{i+1} and $\mathcal{E}_{i+1}$ will be discussed later in the chapter.

We say that a method is pth-order accurate if

$$e_{i+1} = 0(h^{p+1}) \tag{1.16}$$

and from (1.14) and (1.16) the Euler method is first-order accurate. From the previous discussions one can see that the local truncation error in each step can be made as small as one wishes provided the step-size is chosen sufficiently small.

The Euler method is explicit since the function f is evaluated with known information (i.e., at the left-hand side of the subinterval). The method is pictured in Figure 1.1. The question now arises as to whether the Euler method is able to provide an accurate approximation to (1.7). To partially answer this question, we consider Example 1, which illustrates the properties of the Euler method.

EXAMPLE 1

Kehoe and Butt [2] have studied the kinetics of benzene hydrogenation on a supported Ni/kieselguhr catalyst. In the presence of a large excess of hydrogen, the reaction is pseudo-first-order at temperatures below 200°C with the rate given by

$$-r = P_{H_2}k_0K_0T \exp\left[\frac{(-Q - E_a)}{R_gT}\right] C_B \qquad \text{mole/(g of catalyst·s)}$$

where

$$\begin{aligned} R_g &= \text{gas constant, } 1.987 \text{ cal/(mole·K)} \\ -Q - E_a &= 2700 \text{ cal/mole} \\ P_{H_2} &= \text{hydrogen partial pressure (torr)} \\ k_0 &= 4.22 \text{ mole/(gcat·s·torr)} \\ K_0 &= 2.63 \times 10^{-6} \text{ cm}^3\text{/(mole·K)} \\ T &= \text{absolute temperature (K)} \\ C_B &= \text{concentration of benzene (mole/cm}^3\text{).} \end{aligned}$$

Price and Butt [3] studied this reaction in a tubular reactor. If the reactor is assumed to be isothermal, we can calculate the dimensionless concentration profile of benzene in their reactor given plug flow operation in the absence of inter- and intraphase gradients. Using a typical run,

$$\begin{aligned} P_{H_2} &= 685 \text{ torr} \\ \rho_B &= \text{density of the reactor bed, } 1.2 \text{ gcat/cm}^3 \\ \theta &= \text{contact time, } 0.226 \text{ s} \\ T &= 150°\text{C} \end{aligned}$$

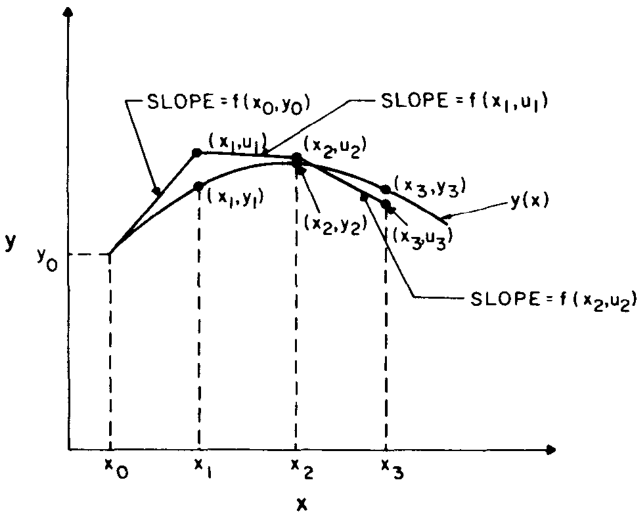

FIGURE 1.1 Euler method.

SOLUTION

Define

C_B^0 = feed concentration of benzene (mole/cm^3)

z = axial reactor coordinate (cm)

L = reactor length

y = dimensionless concentration of benzene (C_B/C_B^0)

x = dimensionless axial coordinate (z/L).

The one-dimensional steady-state material balance for the reactor that expresses the fact that the change in the axial convection of benzene is equal to the amount converted by reaction is

$$\frac{d}{dx}\left(\frac{C_B}{\theta}\right) = r$$

with

$$C_B = C_B^0 \quad \text{at} \quad x = 0$$

Since θ is constant,

$$\frac{dy}{dx} = -\rho_B\theta P_{H_2}k_0K_0T \exp\left[\frac{(-Q - E_a)}{R_gT}\right] y$$

Let

$$\phi = \rho_B\theta P_{H_2}k_0K_0T \exp\left[\frac{(-Q - E_a)}{R_gT}\right]$$

Using the data provided, we have $\phi = 21.6$. Therefore, the material balance equation becomes

$$\frac{dy}{dx} = -21.6y$$

with

$$y = 1 \quad \text{at} \quad x = 0$$

and analytical solution

$$y = \exp(-21.6x)$$

Now we solve the material balance equation using the Euler method [Eq. (1.11)]:

$$u_{i+1} = u_i - 21.6hu_i, \qquad i = 0, 1, 2, \ldots, N - 1$$

where

$$h = \frac{1}{N}$$

Table 1.1 shows the generated results. Notice that for $N = 10$ the differences between the analytical solution and the numerical approximation increase with x. In a problem where the analytical solution decreases with increasing values of the independent variable, a numerical method is unstable if the global error grows with increasing values of the independent variable (for a rigorous definition of stability, see [4]). Therefore, for this problem the Euler method is unstable when $N = 10$. For $N = 20$ the global error decreases with x, but the solution oscillates in sign. If the error decreases with increasing x, the method is said to be stable. Thus with $N = 20$ the Euler method is stable (for this problem), but the solution contains oscillations. For all $N > 20$, the method is stable and produces no oscillations in the solution.

From a practical standpoint, the "effective" reaction zone would be approximately $0 \leq x \leq 0.2$. If the reactor length is reduced to $0.2L$, then a more realistic problem is produced. The material balance equation becomes

$$\frac{dy}{dx} = -4.32y$$

$$y = 1 \quad \text{at} \quad x = 0$$

Results for the "short" reactor are shown in Table 1.2. As with Table 1.1, we see that a large number of steps are required to achieve a "good" approximation to the analytical solution. An explanation of the observed behavior is provided in the next section.

Physically, the solutions are easily rationalized. Since benzene is a reactant, thus being converted to products as the fluid progresses toward the reactor outlet ($x = 1$), y should decrease with x. Also, a longer reactor would allow for greater conversion, i.e., smaller y values at $x = 1$.

TABLE 1.1 Results of Euler Method on $\frac{dy}{dx} = -21.6y$, $y = 1$ at $x = 0$

x	Analytical Solution†	$N = 10$	$N = 20$	$N = 100$	$N = 8000$
0.00	1.00000	1.0000	1.00000	1.00000	1.00000
0.05	0.33960	—	−0.80000(−1)	0.29620	0.33910
0.10	0.11533	−1.1600	0.64000(−2)	0.87733(−1)	0.11499
0.15	0.39164(−1)	—	−0.51200(−3)	0.25986(−1)	0.38993(−1)
0.20	0.13300(−1)	1.3456	0.40960(−4)	0.76970(−2)	0.13222(−1)
0.25	0.45166(−2)	—	−0.32768(−5)	0.22798(−2)	0.44837(−2)
0.30	0.15338(−2)	−1.5609	0.26214(−6)	0.67528(−3)	0.15204(−2)
0.35	0.52088(−3)	—	−0.20972(−7)	0.20000(−3)	0.51558(−3)
0.40	0.17689(−3)	1.8106	0.16777(−8)	0.59244(−4)	0.17483(−3)
0.45	0.60070(−4)	—	−0.13422(−9)	0.17548(−4)	0.59286(−4)
0.50	0.20400(−4)	−2.1003	0.10737(−10)	0.51976(−5)	0.20104(−4)
0.55	0.69276(−5)	—	−0.85899(−12)	0.15395(−5)	0.68172(−5)
0.60	0.23526(−5)	2.4364	0.68719(−13)	0.45600(−6)	0.23117(−5)
0.65	0.79892(−6)	—	−0.54976(−14)	0.13507(−6)	0.78390(−6)
0.70	0.27131(−6)	−2.8262	0.43980(−15)	0.40006(−7)	0.26582(−6)
0.75	0.92136(−7)	—	−0.35184(−16)	0.11850(−7)	0.90139(−7)
0.80	0.31289(−7)	3.2784	0.28147(−17)	0.35098(−8)	0.30566(−7)
0.85	0.10626(−7)	—	−0.22518(−18)	0.10396(−8)	0.10365(−7)
0.90	0.36084(−8)	−3.8030	0.18014(−19)	0.30793(−9)	0.35148(−8)
0.95	0.12254(−8)	—	−0.14412(−20)	0.91207(−10)	0.11919(−8)
1.00	0.41614(−9)	4.4114	0.11529(−21)	0.27015(−10)	0.40416(−9)

† (−3) denotes 1.0×10^{-3}.

STABILITY

In Example 1 it was seen that for some choices of the step-size, the approximate solution was unstable, or stable with oscillations. To see why this happens, we will examine the question of stability using the test equation

$$\frac{dy}{dx} = \lambda y \qquad y(0) = y_0 \tag{1.17}$$

where λ is a complex constant. Application of the Euler method to (1.17) gives

$$u_{i+1} = u_i + \lambda h u_i \tag{1.18}$$

or

$$u_{i+1} = (1 + h\lambda)u_i = (1 + h\lambda)^2 u_{i-1} = \ldots = (1 + h\lambda)^{i+1} u_0 \tag{1.19}$$

The analytical solution of (1.17) is

$$y(x_{i+1}) = y_0 e^{\lambda x_{i+1}} = y_0 e^{(i+1)h\lambda} \tag{1.20}$$

Comparing (1.20) with (1.19) shows that the application of Euler's method to (1.17) is equivalent to using the expression $(1 + h\lambda)$ as an approximation for