# Simple Process Equations, Fixed-Point Methods, and Chaos

The chaotic behavior of fixed-point methods for steady-state process simulation is studied. It is shown that direct substitution and Newton's method exhibit all of the rich structure of chaos (period doubling, aperiodicity, fractal basin boundaries, and related properties) on simple process examples. These examples include finding roots to the Soave-Redlich-Kwong and Underwood equations, dew point and flash calculations for heterogeneous mixtures, and a simple process flowsheet.

For single variable problems, it is shown that direct substitution follows a classical period-doubling route to chaos. On the other hand, the chaotic behavior of direct substitution and Newton's method on multivariable problems is considerably more complex, and can give the appearance that no organized route to chaos is followed. For example, for the dew point problems, truncated period doubling, odd periodic cycles, and chaotic behavior can be observed, within which are embedded narrow regions of global convergence. Many numerical results and geometric illustrations are presented.

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## Introduction

Process simulation has been an important part of preliminary chemical process design for approximately thirty years. In the face of current and perceived future demands for efficient process integration, it appears that the role of simulation using computer tools will only increase. Regardless of the architecture used (sequential modular, simultaneous modular, or equation-oriented), all process simulators rely on one or more fixed-point methods to solve nonlinear process model equations. The most widely used fixed-point methods are direct substitution, accelerated direct substitution, and various Newton-like methods.

Direct substitution is often characterized by researchers in process simulation as slow but stable, implying most importantly that it will eventually converge to some solution. Furthermore, many sequential modular simulators, such as ASPEN Plus, use directed substitution and accelerated direct substitution at the process unit and/or flowsheet levels of computation. Current parallel efforts in equation-oriented process simulation have been directed toward developing reliable and robust equation-solving algorithms, with Newton-based methods serving as the workhorse of the algorithm. These methods are intended to force convergence from (many) poor starting points and include line searching procedures, step-bounding methods, Levenberg-Marquardt methods, trust-region algorithms (Chen and Stadtherr, 1981), and homotopy-continuation methods (Wayburn and Seader, 1984). In fact, at the FOCAPD '89 conference much of the emphasis in this area was on robust methods (Swaney and Wilhelm, 1989) and methods for finding all solutions to nonlinear equations (Seader, 1989). The implications and claims contained in these papers are that the proposed equation-solving methods will not fail. While there is no doubt that progress is being made, most current efforts in process equation solving do not consider the need for good initial values of the unknown variables or the presence of chaotic regimes.

The purpose of this manuscript is to illustrate that standard fixed-point methods for process simulation, in particular direct substitution and Newton's method, can exhibit all of the rich structure of chaos (period doubling, period tripling, fractal basin boundaries, Julia sets, and related properties) on even the simplest nonlinear process model equations. Accordingly, this paper is organized in the following way. First a brief survey of relevant known results in (applied) mathematics is presented. Then simple process examples are used to show that both direct substitution and Newton's method can exhibit chaos. These examples include finding the volume roots of the Soave-Redlich-Kwong equation of state, a dew point calculation for a heterogeneous binary mixture, and a simple process flowsheet. Finally, the widespread implications of these observations to general process equation solving and flowsheetingare discussed. Many geometric illustrations are presented.

## Chaos

In this section, relevant known results from the mathematics of chaos are briefly surveyed, and the inherent relationship between chaos and fixed-point methods for equation solving is discussed. Also, some fundamental issues in the chaos of steady-state process simulation are identified.

### *Known results in chaos*

While the mathematics of chaos is primarily intended to address the dynamical behavior of nonlinear phenomena such as turbulent flow, simple nonlinear, iterative maps of a single variable are generally used to present and/or illustrate fundamental concepts. For example, in an early review article, May (1976) presents the fundamentals of chaos (period doubling, period tripling, strange attractors, and so on) using first-order difference equations that model the dynamical behavior of biological, economical, and social science systems. Feigenbaum (1978) describes period doubling and universality theory in terms of simple quadratic maps, and Mandelbrot (1980) uses a quadratic iterative process in the complex plane to explain the inherent fractal behavior of natural phenomena such as signal noise. The uniform message in these, and other related, papers is: simple iterative processes are capable of extremely complex behavior, provided nonlinearity is present.

Because the basic underlying principles of chaos are easily conveyed using functions of a single variable, consider the generic iterative process given by

$$X^{k+1} = G(X^k, p) \tag{1}$$

where $G:D \rightarrow D$ is a nonlinear function of a single variable $X$, $D \subset R$, and $p$ is a scalar parameter. The classical scenario of chaos involves the study of the global, asymptotic behavior of the iterates of Eq. 1 as a function of the parameter $p$. That is, for various values of $p$, the convergence or nonconvergence of the sequence of iterates given by Eq. 1 are studied for a sufficiently large number of initial values $X^o \in D$. Of particular interest are those values of $p$ for which there are qualitative changes in the behavior of the sequence of iterates $\{X^k\}$.

Consider the general schematic representation of a typical arbitrary iterative map given by Eq. 1, shown in Figure 1. A fixed point of $G$ is any point $X^*$ that satisfies the condition $X^* = G(X^*, p)$. Note that there are three fixed points for the function $G$ depicted in Figure 1. Furthermore, if $|G'(X^*, p)| < 1$, then $X^*$ is a stable fixed point (or an attractor), and the collection of initial values that converge to $X^*$ comprise the basin of attraction of $X^*$. Again with reference to Figure 1, there are two stable attractors, $X_1^*$ and $X_3^*$. In contrast, the fixed point in the middle, $X_2^*$, is unstable because $|G'(X_2^*)| > 1$ and, as a result, repels essentially all initial values. Moreover, the set of initial values $\{(0, X_2^*) \cup (\bar{X}, \hat{X})\}$ constitutes the basin of attraction of $X_1^*$, whereas the set $\{(X_2^*, \bar{X})\}$ comprises the basin of attraction for $X_3^*$.

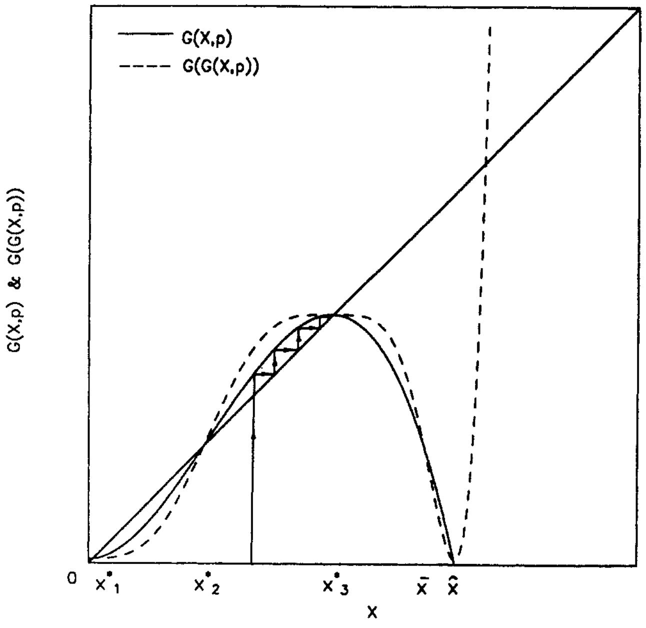

**Figure 1. Fixed points of iterative map $X = G(X, p)$.**

The most important characteristic of the nonlinear function $G$, for our discussions, is that it exhibit an extremum, and the following results are now routinely attributed to the field of chaos. It is well known that many functions follow a period-doubling route to chaos. That is, as the parameter $p$ changes, successive period-doubling bifurcations occur in the composite function $G^{2^n}(X, p)$, where

$$G^{2^n}(X, p) = G[G(\ldots G(X, p) \ldots)] \tag{2}$$

and where the composition of $G$ is repeated $2^n$ times. As a result, the iterates are attracted to the stable fixed points of $G^{2^n}(X, p)$ about $X^*$. This period doubling begins with the function $G^2(X, p)$, producing a 2 cycle about $X^*$, and successive period doubling continues as $p$ is further changed, yielding in turn, 4, 8, 16 ... cycles, until a point of accumulation is reached. Moreover, these period doubling bifurcations are characterized by the condition

$$\left|\frac{d}{dx}[G^{2^{n-1}}(X^*, p)]\right| > 1 \tag{3}$$

where $X^*$ are relevant fixed points of $G^{2^{n-1}}(X, p)$. Figure 2 shows a 2 cycle for the function $G(X, p)$ depicted in Figure 1 (for, of course, a different value of $p$).

Beyond the point of accumulation of period-doubling bifurcations, cycles with even and odd integer periods, as well as aperiodicity (quasiperiodic or chaotic), appear as the parameter $p$ continues to change and bifurcations occur. Moreover, these odd periodic cycles are usually large at first, and decrease in periodicity as $p$ is further changed until a 3 cycle is observed. At this point, cycles of all integer periods and, in particular, chaotic (or so-called strange) attractors are guaranteed to be present for some parameter values, as proved by Li and Yorke (1975) in their seminal paper. Consequently, as the parameter $p$ changes still further, stable cycles of any periodicity (or aperiodic cycles) can be observed with no apparent predictability. For a comprehensive and lucid presentation of the fundamentals of chaos, the reader is referred to the paper by May (1976).

In 1978, Feigenbaum showed that the values of $p$ that give

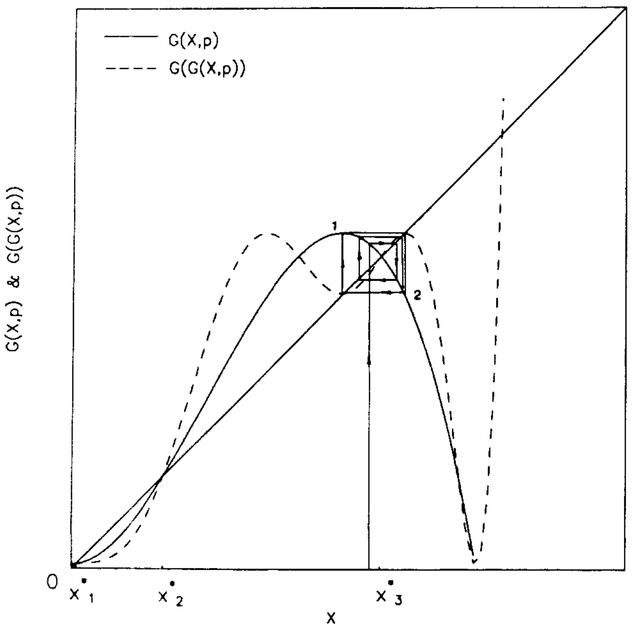

**Figure 2. Two cycle of iterative map $X = G(X, p)$.**

period-doubling bifurcations converge geometrically, and thus satisfy the condition

$$\lim_{n \to \infty} [(p_{n+1} - p_n)/(p_{n+2} - p_{n+1})] = 4.669201 \ldots \quad (4)$$

where $p_n$ denotes the parameter value at which the $2^n$ cycle appears. Furthermore, by Eq. 4, period doubling occurs at a faster rate (i.e., smaller changes in $p$ are required to go from a cycle of $2^n$ to $2^{n+1}$ . . .). Thus, in principle, the period-doubling route to chaos has a predictable component, called universality theory by Feigenbaum (1978).

Finally, we mention the work by McDonald et al. (1985) on fractal basin boundaries. This is an outgrowth of the work pioneered by Mandlebrot (1980), as it applies to dynamical systems. When a given iterative map (e.g., first-order difference equation of a dissipative dynamical system) has more than one stable attractor, different initial conditions will yield trajectories that are attracted to different attractors, and thus a separate basin of attraction or Julia set is associated with each attracting fixed point. We note here that the Julia set associated with a given iterative map is the collection of initial values that are not attracted to either a stable fixed point or a stable cycle. McDonald et al. have shown that the boundaries for dynamical systems can be either smooth or fractal, and that fractal basin boundaries can be either locally connected or locally disconnected. Moreover, fractal basin boundaries are usually striated, and do not exhibit the considerably more complex self-similarity structure of the Mandlebrot set so typical of iterative maps in the complex plane. For quite different perspectives on the nature and significance of fractal basin boundaries and Julia sets, see Mandlebrot (1980) and McDonald et al. (1985).

### *Chaos and fixed-point methods*

When the steady-state model of a physical process is nonlinear, the application of any fixed-point method such as direct substitution or Newton's method to the algebraic model equations generally results in a different, simple, nonlinear iterative process. That is, the way in which a given fixed-point method organizes the computations associated with the steady-state equation-solving task may be very different than the way the process organizes itself from a dynamical systems perspective. Clearly this is true for Newton's method and, given the variety of possible choices of tear streams usually present in any reasonably complex process with recycle, it is likely also true for direct substitution. Surprisingly, however, the potential chaotic behavior of fixed-point methods, as an interest separate from the underlying dynamical behavior of the nonlinear model equations they are being used to solve, has drawn very little research attention.

The complex behavior of fixed-point methods has a long but exceptionally sparse history. The classical problem of describing the basins of attraction for the complex roots of the equation $X^3 - 1 = 0$ dates back to Lord Cayley (1879). While some important early analysis for rational functions was also conducted (Julia, 1918; Fatou, 1919), it is largely through the recent research efforts of Mandelbrot (1980) that there is any interest in the (fractal) geometry of fixed-point methods. Nevertheless, both the number of theoretical results (Douady and Hubbard, 1985; Head, 1988) and the number of numerical investigations (Feigenbaum, 1978; Mandelbrot, 1980; Curry et al., 1983; Peitgen et al., 1984) is small, and for the most part these efforts have been devoted to simple functions of a single complex variable.

The problem in which we are specifically interested in this paper is that of describing the global, asymptotic behavior (and the associated geometric structure) of the iterates of the general fixed-point mapping

$$X^{k+1} = G(X^k, p) \quad (5)$$

where $G$ is a nonlinear function that takes $D \subseteq R^n$ into itself, and $p$ is a vector of parameters. The particular fixed-point methods that are studied in this paper are direct substitution and Newton's method, because of their obvious relevance to process simulation.

For our applications, the set $D$ is usually defined through any restrictions on the unknown variables (nonnegativity of flows, composition requirements of [0, 1], and so on), and the function $G{:}D \rightarrow D$ may be either explicitly or implicitly defined. For example, for Newton's method, $G$ is explicitly defined by

$$G(X^k, p) = X^k - [J(X^k)]^{-1}F(X^k) \quad (6)$$

where $F(X) = 0$ is the collection of nonlinear process model equations for which a solution is sought, and $J(X^k)$ is the Jacobian matrix of $F(X)$ evaluated at $X^k$. In contrast, for applications of direct substitution, say, at the process flowsheet level of a sequential modular simulator, $G$ is usually implicitly defined through the solutions of the individual process units and the stream connectivity constraints. Finally, we note that for many process simulation problems, safeguards such as step-bounding methods, line-searching procedures, trust-region methods, or homotopy-continuation methods are often used to prevent physically unrealistic iterates (negative flow rates and/or compositions, and so on), particularly if good initial values of the unknown variables are not easily determined. Without these safeguards, the iterates will occasionally leave $D$, and as a result, algorithms such as Newton's method simply fail far too frequently to be of practical value. On the other hand, many of these safeguards also have a tendency to complicate the global behavior of the iterates.

### *Open issues in chaotic process simulation*

To our knowledge, there is no study in the chemical engineering literature that is concerned with the potential chaotic behavior of equation-solving methods for steady-state process simulation. Thus, we are in the unusual position of addressing for the first time fundamental computational and theoretical issues in chaos as they pertain to process simulation. While there are many fundamental questions that can be asked, perhaps the first, and most important, concern is that of relevance. Is chaos a relevant issue in process simulation? Yes, and it is the primary objective of this paper to provide support for this position using simple chemical process equations.

If equation-solving methods for process simulation exhibit chaos, then many related theoretical and computational issues immediately arise.

1. Is the usual period-doubling route to chaos followed by these fixed-point methods, or is some other mechanism present?
2. How does the transition from even to odd periodic cycles occur, if it occurs at all?
3. What is the structure of the boundaries between basins of attraction and/or Julia sets? Are they fractal in the sense of the Mandelbrot set, displaying self-similarity at all scales, or are they striated, without any self-similarity characteristics?
4. How widespread is chaos in process simulation?
5. How do safeguards such as step-bounding methods, line-searching procedures, trust-region methods, and homotopy-continuation methods affect the structure and the integrity of the basins of attraction and the boundaries between them?

Answers to these and other questions are important because of their associated widespread implications for industrial and academic steady-state process simulation.

## Chemical Process Examples

In this section, three different chemical process examples are presented and the chaotic behavior of direct substitution and Newton's method with step bounding are studied. The basic features of each algorithm are described in the context of the illustrative examples. It is shown that both methods exhibit chaos (period doubling, fractal basin boundaries, etc.), but that, at least in one case the route to chaos is unlike that reported in other fields. In particular, it is shown that period doubling in Newton's method can be truncated, and that the even and odd periodic cycles contained in the chaotic regime can be separated by a narrow window of global convergence. The numerical experiments that were conducted on both fixed-point methods are described in detail, and many geometric illustrations are presented. All calculations were done on both an Alliant FX/8 computer and a Gould 9080 computer using sequential processing and double-precision arithmetic.

### *Volume roots of the SRK equation*

In this section, direct substitution is used to find the volume roots of the Soave-Redlich-Kwong (SRK) equation of state for a multicomponent mixture. This problem is an interesting first illustration because it involves a single unknown variable, volume, as well as a single parameter, temperature, and is commonly a repetitive subproblem in many larger chemical process flowsheeting examples. Thus, it is simple from an illustrative point of view, yet clearly relevant. However, despite this apparent simplicity, we show that direct substitution follows the classical period-doubling route to chaos on this example, and that it is a straightforward matter to use universality theory to predict the period-doubling bifurcations, once the first few are located.

The form of the SRK equation, and the associated mixing rules, chosen for this illustration were taken directly from Walas (1985, p. 53). Simple algebra gives the following explicit functional form for direct substitution

$$V^{k+1} = G(V^k, T) = -(PV^3 - RTV^2 - \alpha ab)/(\alpha a - bRT - Pb^2) \quad (7)$$

where $T$ and $P$ are the temperature and pressure, respectively, $R$ is the universal gas constant, and the quantities $\alpha$, $a$, and $b$ for the mixture depend on the critical constants for the individual species in the mixture, the accentric factor, the temperature, and a set of combining rules. See Table 1.11 in Walas (1985).

For a given mixture below critical conditions, the SRK equation will have either one or three positive real roots, depending on the particular values of $T$ and $P$. In regions where there are three real roots, the smallest root corresponds to the liquid volume, the largest root is the vapor volume, and the intermediate root has no physical significance. Furthermore, the first and second derivatives of Eq. 7 are

$$G'(V, T) = (3PV^2 - 2RTV)/(\alpha a - bRT - Pb^2) \quad (8)$$

and

$$G''(V, T) = -(6PV - 2RT)/(\alpha a - bRT - Pb^2) \quad (9)$$

respectively, and straightforward analysis shows that $G(V, T)$ exhibits a minimum at $V = 0$, and a maximum at $0 < V < V^*_{vap}$, where $V^*_{vap}$, is the vapor root of the SRK equation. Moreover, at small values of $V$ the second term in the numerator and the first term in the denominator of Eq. 8 usually dominate, and

$$G'(V, T) \approx 2RTV/\alpha a < 1 \quad (10)$$

Thus, direct substitution can be used to calculate the liquid volume and no convergence difficulties are anticipated. On the other hand, for large values of $V$ the first term in the numerator of Eq. 8 usually dominates and

$$G'(V, T) \approx -3PV^2/\alpha a \quad (11)$$

Furthermore, the condition $G'(V, T) < -1$ can occur as the temperature is increased, and as a result, the fixed point corresponding to the vapor root can become unstable. Thus, potential period doubling and chaos is anticipated in computing the vapor root of the SRK equation by direct substitution. Finally, the fixed point corresponding to the intermediate root is always unstable with respect to direct substitution and is therefore of little interest.

To illustrate that direct substitution can exhibit period

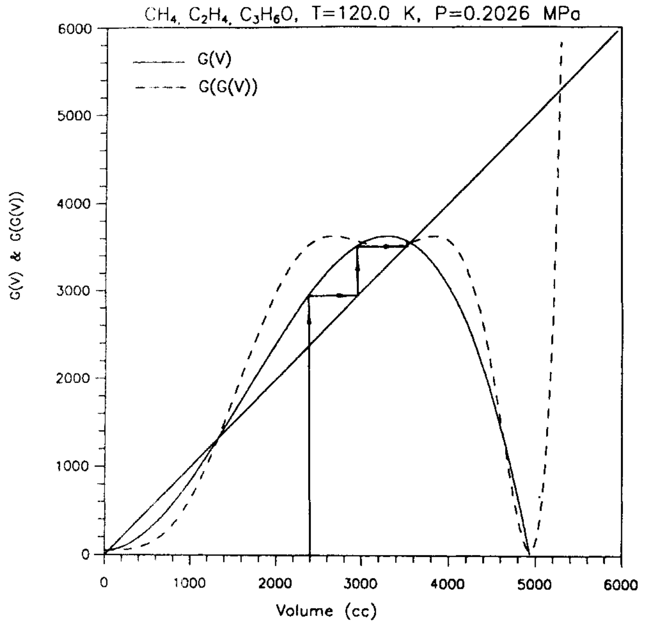

**Figure 3a. One cycle for direct substitution of SRK equation.**

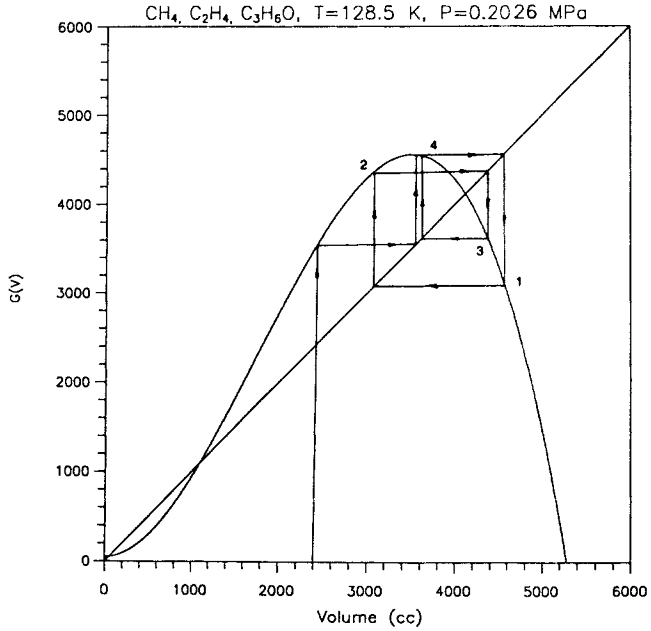

**Figure 3c. Four-cycle for direct substitution of SRK equation.**

doubling and chaos, consider a ternary mixture of 0.3 moles of methane, 0.4 moles of ethylene, and 0.3 moles of acetone at 0.2026 MPa. Figures 3a–d show the asymptotic behavior of the direct substitution iterates of the SRK equation for the given mixture at $T$ = 120, 127, 128.5, and 128.8 K, respectively. At these temperatures, stable 1, 2, 4, and 8 cycles are present, respectively. The corresponding cycle points are shown in Table 1. Note, for example for the 2 cycle, that the limiting direct substitution iterates oscillate about the vapor root, $V^* = 4{,}023.81\ \text{cm}^3$, and that the cycle points, $V = 33.6496\ \text{cm}^3$ and $V = 4371.91\ \text{cm}^3$, correspond to the stable fixed points of the function $G^2(V) = G[G(V)]$ that bracket the vapor root. Similar observations hold for any $2^n$-cycle and the corresponding function $G^{2^n}(V)$. See Feigenbaum (1978) for a lucid presentation of this.

As the temperature is further increased (slightly), period doubling continues. Table 2 shows the approximate temperature values at which the first ten period-doubling bifurcations occur. Note that successively smaller variations in temperature are required for the occurrence of the period-doubling bifurcations shown in that table.

Beyond a temperature value of 129.043268 K, both even

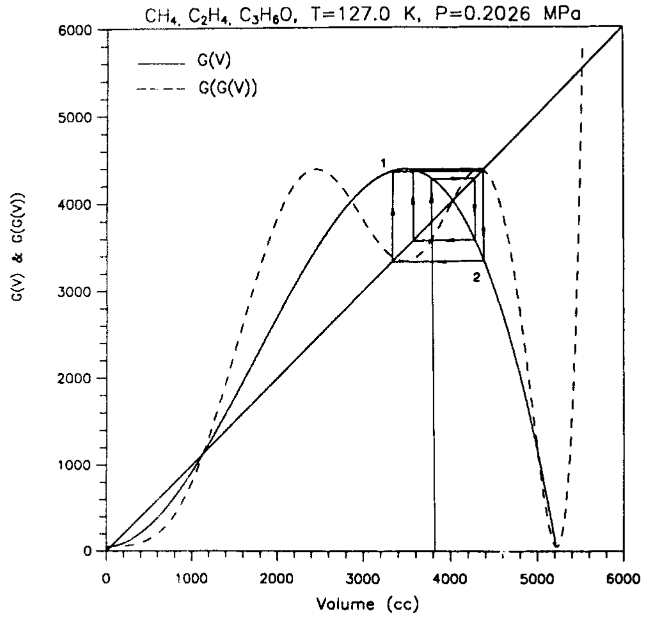

**Figure 3b. Two-cycle for direct substitution of SRK equation.**

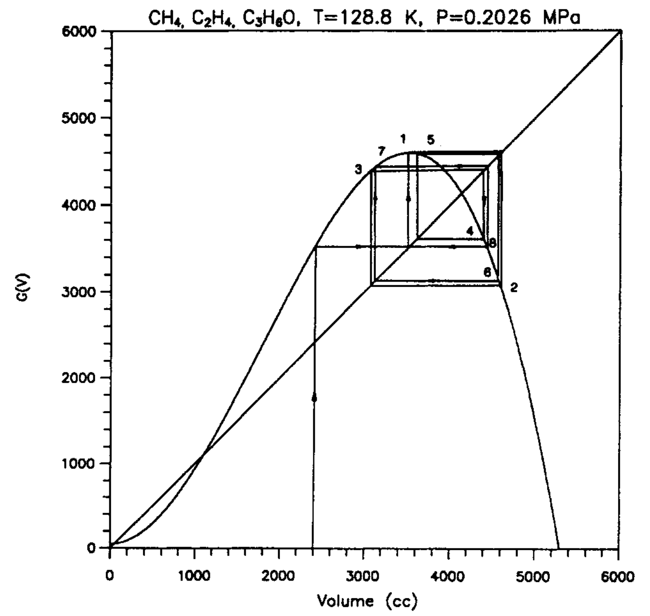

**Figure 3d. Eight-cycle for direct substitution of SRK equation.**

**Table 1. Cycle Points for Direct Substitution Iterates of SRK Equation**

| Cycle | Temp. K | Vapor Root cm$^3$ | Cycle Points cm$^3$ |
|---|---|---|---|
| 1 | 120.0 | 3,549.82 | 3,549.82 |
| 2 | 127.0 | 4,023.81 | 3,364.96<br>4,371.91 |
| 4 | 128.5 | 4,117.60 | 3,124.96<br>4,560.62<br>3,540.86<br>4,407.20 |
| 8 | 128.8 | 4,136.11 | 4,413.65<br>3,096.56<br>4,588.80<br>3,610.68<br>4,406.29<br>3,080.60<br>4,594.01<br>3,578.18 |

periodic cycles (with periods unequal to $2^n$) and aperiodic behavior exist. For example, at $T = 129.0440$ and 129.086 K, direct substitution exhibits a 640- and 820-cycle, respectively, whereas at 129.078 K, the behavior is aperiodic. This even periodic and aperiodic behavior persists for temperatures between 129.043268 and 130.1319 K, with no apparent pattern.

For temperatures above 130.1319 K, odd periodic cycles are present and in particular, a 3 cycle appears at 131.639 K. Approximate values of the bifurcation points for some of the odd cycles are shown in Table 3, and the asymptotic behavior of the 3-cycle is shown in Figure 4.

We note that provided the period-doubling bifurcations are calculated to sufficient accuracy, universality theory can be used to estimate bifurcations with reasonable confidence. For example, to seven significant digits, the bifurcation points for the 8 and 16 cycles shown in Table 2 are 128.7934986 and 128.9895931 K, respectively. Use of these values in Eq. 4 gives a predicted value of 129.0315905 K for the bifurcation point for the 32 cycle. The actual bifurcation occurs at $T = 129.0317165$ K.

### *Dew point temperature calculation for heterogeneous mixtures*

In this section, Newton's method with step bounding is used to solve a set of dew point temperature problems for a heterogeneous binary mixture. This example is more complex than the first illustration because it is a multivariable problem. In fact, it is shown that Newton's method exhibits chaotic behavior that is more complicated than that associated with classical examples. In particular, truncated period doubling and odd periodic cycles are observed, rendering universality theory useless. Furthermore, these sets of even and odd cycles are separated by a narrow parameter region in which global convergence occurs. Finally, it is illustrated that the basin boundaries are fractal and striated.

**Table 2. Approximate Period Doubling Bifurcations for Direct Substitution Iterates of SRK Equation**

| Cycle | Temp. K |
|---|---|
| 2 | 123.8 |
| 4 | 127.9 |
| 8 | 128.8 |
| 16 | 129.0 |
| 32 | 129.03 |
| 64 | 129.041 |
| 128 | 129.043 |
| 256 | 129.0431 |
| 512 | 129.04325 |
| 1,024 | 129.04326 |

**Table 3. Approximate Bifurcations for Odd Periodic Cycles of SRK Equation**

| Cycle | Temp. K |
|---|---|
| 9 | 130.1319 |
| 7 | 130.2668 |
| 5 | 130.6326 |
| 3 | 131.6393 |

Consider the problem of finding the dew point temperature and corresponding incipient liquid phase composition for any mixture. The usual model equations are given by

$$K_i x_i - y_i = 0, \quad i = 1, \ldots, n_c \tag{12}$$

$$1 - \sum_{i=1}^{n_c} x_i = 0 \tag{13}$$

where $x$ and $y$ denote the liquid and vapor phase composition, respectively, $K$ is a vector of equilibrium ratios, and $n_c$ is the number of components in the mixture. For dew point temperature calculations, the vapor composition and pressure, $P$, are fixed. Thus $K$ depends on the unknown variables, $x$ and $T$, where $T$ denotes temperature, and this dependence is usually strongly nonlinear.

One common way of solving the nonlinear model equations

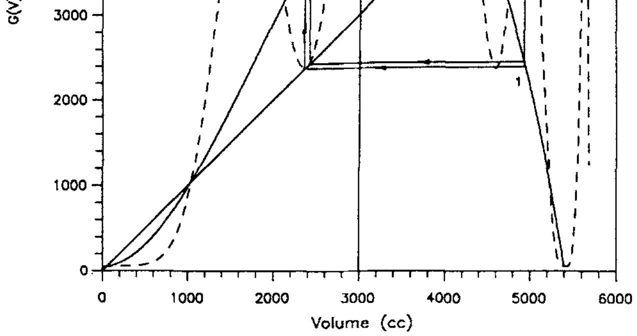

**Figure 4. Three-cycle for direct substitution of SRK equation.**

given by Eqs. 12 and 13 is to use Newton's method. Thus, if we define $X^T = (x^T, T)$ and use the notation $F(X) = 0$ to denote the collection of equations given by Eqs. 12 and 13, then the corresponding pure Newton iteration is given by Eqs. 5 and 6, where $J(X)$ in this case is the Jacobian matrix of the set of phase equilibrium and summation equations. However, because early Newton iterations often give physically unrealistic composition iterates (i.e., $x_i \notin [0, 1]$), especially from poor starting points, some safeguards are required to avoid breakdown in the K-value calculations and subsequent failure of the algorithm. We use a simple step-bounding procedure. In particular, composition steps are modified, when necessary, to satisfy the inequalities,

$$-\beta x_i^k \le \Delta x_i^k \le \beta(1 - x_i^k), \quad i = 1, \ldots, n_c \qquad (14)$$

where $\beta \in (0, 1)$, and temperature steps are bounded by the inequalities

$$-50\text{K} \le \Delta T^k \le 50\text{ K} \qquad (15)$$

As noted earlier, our numerical experience shows that this step bounding procedure avoids many failures. We used a value of $\beta = 0.999$ for all illustrations in this manuscript.

It is well known that heterogeneous mixtures (mixtures that have the potential to split into two liquid phases) exhibit multiple dew point solutions for certain compositions. This has been discussed comprehensively by Van Dongen et al. (1983), and is illustrated here in Figure 5 using a *Txy* diagram for the benzene-water system at atmospheric pressure. Note that there are three real dew point solutions for any composition under the swallowtail region; outside that composition range, there is only one solution.

In our opinion, an interesting first set of questions is: Given a composition in the swallowtail region, and a collection of initial values:

1. What is the geometric structure of the basins of attraction for Newton's method?
2. Are the basin boundaries fractal?
3. If they are fractal, what is the characteristic structure of these boundaries?

To answer these questions, we performed dew point calculations for an equimolar mixture of benzene and water at atmospheric pressure, where both the vapor and liquid phase were assumed to be nonideal and were modeled by the procedures and data given by Prausnitz et al. (1980). The three solutions to this particular problem are shown in Table 4.

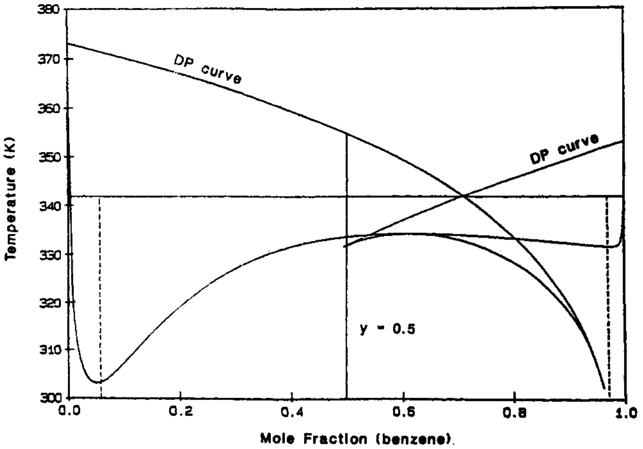

**Figure 5. *Txy* diagram for benzene and water at 0.1013 MPa.**

Consider now the collection of starting points defined by a rectangular grid in benzene composition and temperature. In particular, let the benzene composition range be 0–1, and the temperature range be 330–360 K. Moreover, let equal increments of 0.01 and 0.25 K be used to generate the grid.

Newton's method with step bounding was used to solve Eqs. 12 and 13 for this particular example to an accuracy of $\|F\|_2 \le 10^{-8}$ from each of the 13,000 starting points in the grid. In all cases, the calculations converged easily to one of the solutions shown in Table 4, and, in fact, the largest number of iterations required for any single problem was thirteen.

The basins of attraction were identified by color coding the solutions, Table 4, and assigning to each initial value the color of the solution to which it converged. The collective results for 13,000 starting points are shown in Figure 6. In this and all subsequent figures, the solutions are denoted by solid black dots.

Note that the basins of attraction for Newton's method have a rather interesting geometric structure, particularly in the middle of the figure, where small fingerlike (light gray) regions of the basin of attraction for solution 3 are dispersed in the basin of attraction for solution 2 (the large white region). There are also small, similarly shaped regions of the basin of attraction for solution 1 present in the same general area that do not appear simply because of the resolution of the graphics used to generate the figure. Furthermore, note that there is evidence of the fractal nature of the basin boundaries in Figure 6. For example, there is a thin, discontinuous white region belonging to the basin of attraction for solution 2 that appears between the large dark gray and large light gray regions associated with the basins of attraction for solutions 1 and 3, respectively.

To explore the structure of the basin boundaries, we enlarged a region between solutions 2 and 3. In particular, we constructed a second rectangular grid for the benzene composition range 0.962–0.963, and temperature range 332.1–332.2 K, using 100 equally spaced grid points in each variable, and repeated the process of solving the model equations by Newton's method with step bounding from each starting point. The same colors were chosen to identify the basins of attraction, and the results are shown in Figure 7. Note that at this scale, the striated and locally disconnected structure of the basin boundaries is clearly evident. Furthermore, this same fractal structure repeats itself, regardless of the scale of magnification, as indicated by the appearance of the crosses along the boundary between the dark gray and white area at the top of that figure. That is, whenever the basins of attraction for two solutions approach each other, a region of the basin of attraction associated with the third solution intervenes, and this pattern repeats to infinity.

**Table 4. Multiple Dew Point Solutions for Benzene-Water Mixture***

| | $x, T$ |
|---|---|
| 1 (dark gray) | (0.001568, 0.998432, 354.810 K) |
| 2 (white) | (0.988019, 0.011981, 332.130 K) |
| 3 (light gray) | (0.936852, 0.063148, 332.106 K) |

*$y = (0.5, 0.5)$

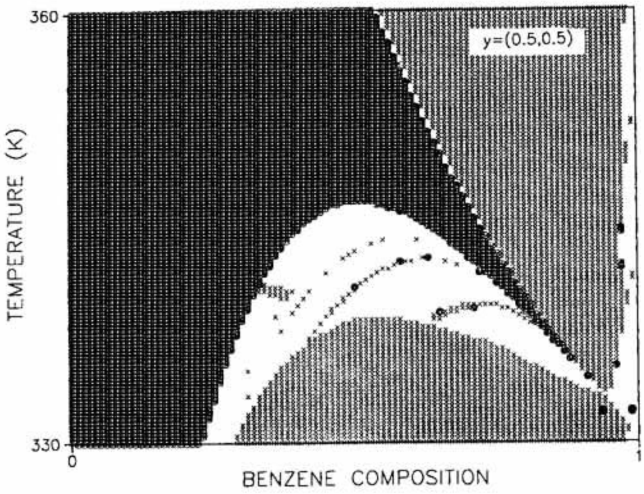

**Figure 6. Basins of attraction for Newton's method on heterogeneous dew point problem.**

Table 5. Newton Iterates for Dew Point Problem Initialized Near Basin Boundary

| Iteration | Benzene Comp. | Temp. K |
|---|---|---|
| 0 | 0.984048 | 350.0 |
| 1 | 0.985667 | 324.186 |
| 2 | 0.984492 | 330.853 |
| 3 | 0.311054 | 332.034 |
| 4 | 0.983436 | 312.903 |
| 5 | 0.981616 | 325.534 |
| 6 | 0.979554 | 331.231 |
| 7 | 0.020828 | 331.719 |
| 8 | 0.000410 | 345.344 |
| 9 | 0.001609 | 352.898 |
| 10 | 0.001569 | 354.715 |
| 11 | 0.001569 | 354.809 |
| 12 | 0.001568 | 354.810 |

Finally, it seems reasonable to attribute at least some of the structure of the basins of attraction and basin boundaries to the step bounding procedure. However, the fractal nature of the basin boundaries cannot be completely attributed to step bounding. To see this, consider the starting point given by $x^o = (0.984048, 0.015952)$ and $T^o = 350$ K. Furthermore, note that this starting point is located on the boundary between solution 2 (white region) and solution 3 (light gray region) of Figure 6. For the given starting point, Newton's method converges to solution 1 in twelve iterations, and, more important, no iterate encounters the bounds given by Eqs. 14 and 15. Thus, pure Newton steps are taken on each of the twelve iterations, and the presence of step bounding is irrelevant. The iterates for this illustration are shown in Table 5.

Suppose now the feed composition is changed slightly so that it is no longer beneath the swallowtail region. For definiteness, consider the composition $y = (0.47, 0.53)$. From Figure 5, it is clear that there is only one dew point solution, and that solution is qualitatively similar to solution 1 in Table 4. Solutions 2 and 3, which exist for $y = (0.5, 0.5)$, have bifurcated into the complex domain and, in our opinion, an interesting second set of questions is concerned with the behavior of certain sequences of Newton iterates in the face of the disappearance of these real solutions. In particular,

1. What is the asymptotic behavior of those starting points whose iterative sequences previously converged to either solutions 2 or 3? Are they attracted to a stable periodic cycle?
2. If cycling occurs, is the usual period-doubling route to chaos followed? If not, how does chaos evolve?
3. What is the geometric structure of the boundaries between basins of attraction and regions of periodic behavior?

To answer these questions, we parameterized the dew point problem in benzene vapor composition over the range 0.47 to 0.50. For each feed composition in this range, a rectangular grid of 13,000 equidistant starting points were generated, as before, and Newton's method with step bounding was used to solve Eqs. 12 and 13 to an accuracy of $\|F\|_2 \leq 10^{-8}$ from each starting point. The results of these numerical experiments were rather surprising, and are shown in Figures 8 through 13.

In Figure 8, note that the basin of attraction for the solution (dark gray region) is essentially the same as the basin of attraction for solution 1 in Figure 6 (for a benzene vapor composition of 0.50). This is not surprising since these water-

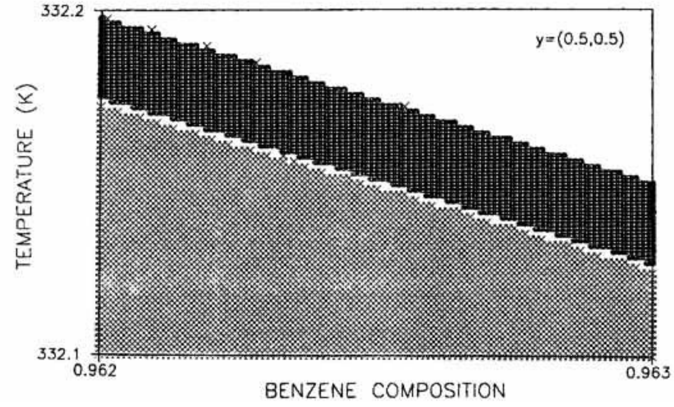

**Figure 7. Fractal basin boundaries for Newton's method on heterogeneous dew point problem.**

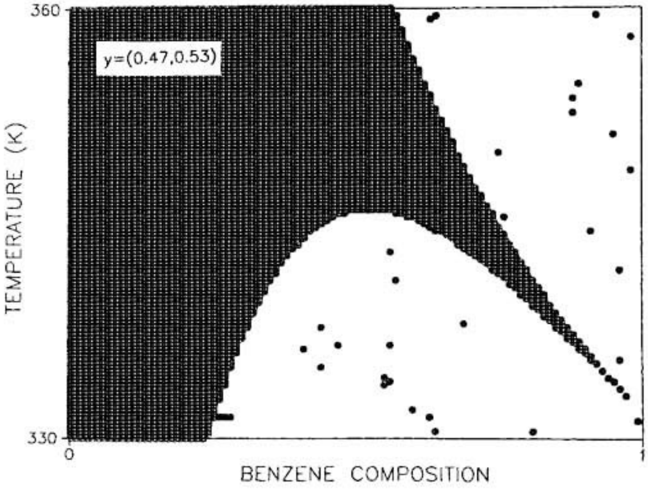

**Figure 8. Basin of attraction and 2-cycle for Newton's method on heterogeneous dew point problem.**

rich solutions are qualitatively similar. To see this, simply compare solution 1 given in Table 4 to the dew point solution $(x^T, T) = (0.001413, 0.998587, 356.257\ \text{K})$ for $y = (0.47, 0.53)$. On the other hand, what is surprising is that the basins of attraction previously associated with solutions 2 and 3 have merged into a single region in which all starting points are now attracted to a stable 2 cycle, as a consequence of the bifurcation of solutions 2 and 3 into the complex domain. This period 2 region is shown as the large white region in Figure 8 (as well as in subsequent related figures). Note also that there are initial values belonging to the basin of attraction distributed throughout this large region of stable periodic behavior. This will be of some interest as we proceed.

Figure 9 shows the basin of attraction and 4 cycle region for Newton's method for the vapor composition $y = (0.48, 0.52)$. Thus, as the benzene vapor composition is changed from 0.47 to 0.48, Newton's method goes through a second period-doubling bifurcation. Note again that the basin of attraction in this figure is qualitatively the same as the basins of attraction in Figures 6 and 8. The only difference is that there is an increase in the number of initial values belonging to the basin that are dispersed throughout the region in which stable periodic behavior occurs.

As the benzene composition is further increased, Newton's method passes through another period-doubling bifurcation. Figure 10 shows the basin of attraction and region of 8-cycle behavior for $y = (0.48087, 0.51913)$, and again the feature to note is that the density of initial values belonging to the basin of attraction that are dispersed throughout this region has increased.

Remarkably, as the vapor composition is increased to, say, $y = (0.481, 0.519)$, period doubling suddenly ceases and Newton's method with step bounding displays globally convergent behavior. This is shown in Figure 11. In fact, for all benzene vapor compositions between approximately 0.4809 and 0.4822, Newton's method is globally convergent. Moreover, while this sudden qualitative change in the global asymptotic behavior of sequences of Newton iterates is indicated by the increase in density of the basin members that are dispersed in the regions of nonconvergence for the 2, 4, and 8 cycles, respectively, this increase is nonuniform and we currently have no satisfactory explanation for the sudden appearance of a narrow region of global convergence. Other regions of global convergence have also been found.

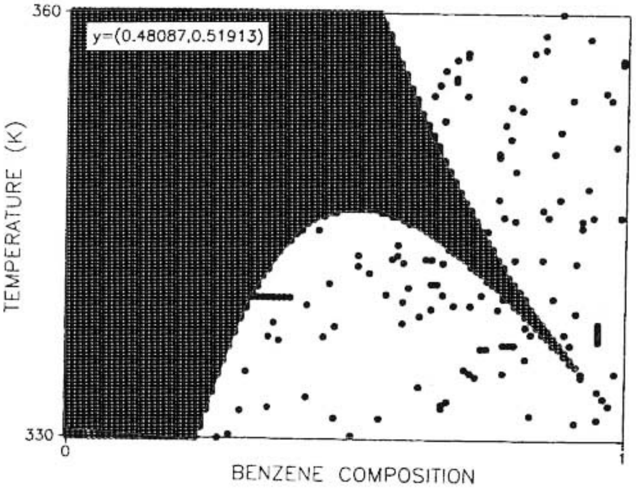

**Figure 10. Basin of attraction and 8-cycle for Newton's method on heterogeneous dew point problem.**

Continued parameterization with respect to vapor composition shows that this narrow window of global convergence disappears, and is replaced by stable odd periodic cycles. In particular, at $y = (0.4823, 0.5177)$ Newton's method exhibits a 5 cycle, and at approximately $y = (0.4839, 0.5161)$, period 3 behavior is observed. Figure 12 shows the basin of attraction and 3 cycle region for Newton's method for $y = (0.484, 0.516)$. The region of period 3 behavior extends to approximately $y = (0.488, 0.512)$, beyond which a variety of odd and even cycles are present. For example, Figure 13 shows the basin and 20 cycle region for $y = (0.492, 0.508)$. Finally, we note that aperiodicity occurs at $y = (0.4808912, 0.5191088)$, immediately following the region of truncated period doubling, and provides at least a weak indication that the route to chaos is period doubling. On the other hand, because the appearance of all nonconvergent behavior is a consequence of the bifurcation of a pair of real solutions into the complex domain, perhaps a more

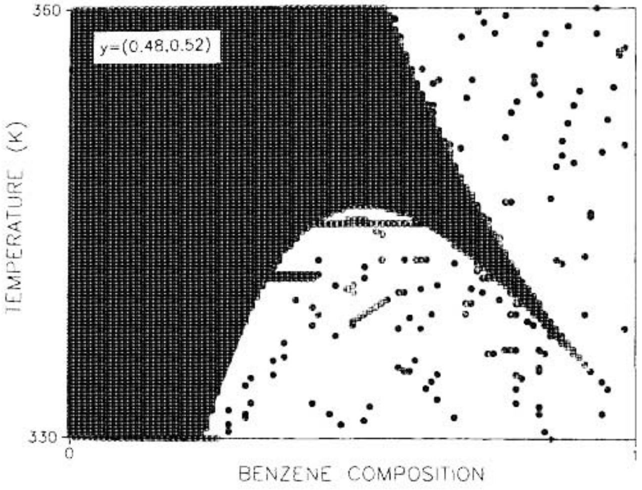

**Figure 9. Basin of attraction and 4-cycle for Newton's method on heterogeneous dew point problem.**

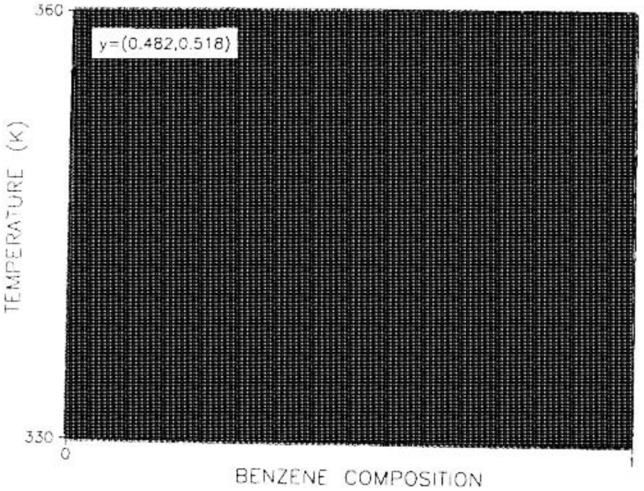

**Figure 11. Global basin of attraction for Newton's method on heterogeneous dew point problem.**

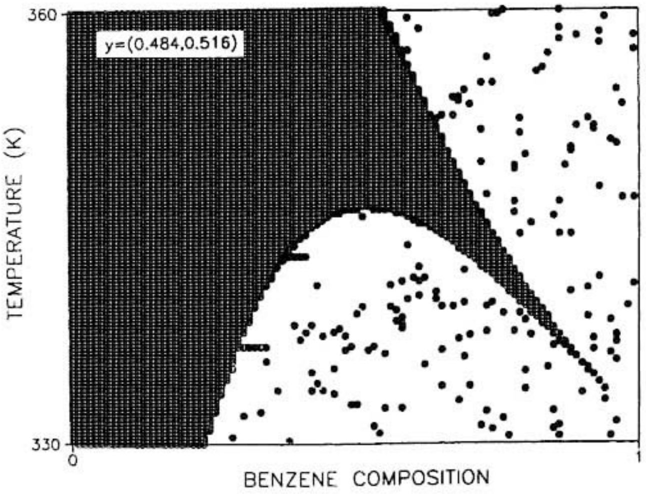

**Figure 12. Basin of attraction and 3-cycle for Newton's method on heterogeneous dew point problem.**

accurate but likely different picture of the transitions to chaotic behavior can be obtained by performing these calculations in the complex domain.

Table 6 summarizes some of the chaotic behavior of Newton's method with step bounding from a single, common starting point [$X^o = (0.984, 0.016, 350\ \text{K})$] for the benzene composition range 0.427–0.493. This will allow the reader to verify our numerical results, at least in part. However, for the benefit of those who intend to do this, the calculations must often be allowed to run for an unreasonably large number of iterations (several thousand) in order for convergence to either a fixed point or a stable cycle to occur. For the results shown in Table 6, 8,000 Newton iterations was adequate.

**Table 6. Chaotic Behavior of Newton's Method on Heterogeneous Dew Point Problem***

| Benzene Vapor Comp. | Asymptotic Behavior |
|---|---|
| 0.42751 | 2 cycle begins |
| 0.47 | 2 cycle |
| 0.47846 | 4 cycle begins |
| 0.48 | 4 cycle |
| 0.4808419 | 8 cycle begins |
| 0.4808912 | aperiodic |
| 0.481 | convergence |
| 0.482 | convergence |
| 0.4822 | convergence |
| 0.4823 | 5 cycle |
| 0.483 | 5 cycle |
| 0.4838978 | 25 cycle |
| 0.4838981 | 3 cycle begins |
| 0.484 | 3 cycle |
| 0.485 | 3 cycle |
| 0.486 | 3 cycle |
| 0.488 | 3 cycle |
| 0.489 | 7 cycle |
| 0.490 | 7 cycle |
| 0.4905 | 5 cycle |
| 0.491 | 9 cycle |
| 0.4915 | 6 cycle |
| 0.492 | 20 cycle |
| 0.4925 | 4 cycle |

*$X^o = (0.984, 0.016, 350.\text{K})$

### *A simple process flowsheet*

Here it is shown that direct substitution can exhibit chaos at the flowsheet level of computation in sequential modular simulation. To see this, consider the simple process flowsheet shown in Figure 14, which consists of two interlinked equilibrium flash drums (process units) interconnected by a single recycle stream, $v_2$. Let the specifications for each unit be the total vapor flow rate and pressure, and suppose that the model equations for each unit—the phase equilibrium, mass balance, and vapor specification equations—are solved by Newton's method, and that direct substitution is used to converge the recycle (tear) stream at the flowsheet level. Thus, the fixed-point mapping for the tear stream $v_2 = G(v_2)$, is implicitly defined by the solutions to the model equations at the process unit level and the tear stream connectivity constraints. Alternatively, this flowsheet can be considered as a two-stage separation process with specified distillate flow rate and vapor boilup.

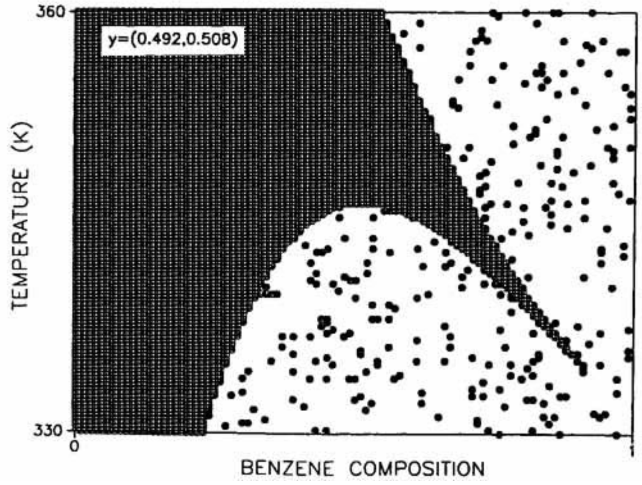

**Figure 13. Basin of attraction and 20 cycle for Newton's method on heterogeneous dew point problem.**

The specific numerical example chosen for this illustration involves the separation of acetonitrile, water, and acrylonitrile at atmospheric pressure, and is clearly defined in Table 7. It is important, however, to understand certain aspects of the (global) solution structure of this example before attempting to understand the behavior of the direct substitution iterates at the flowsheet level. In particular, when parameterized in distillate flow rate, this problem exhibits multiple two-phase (homogeneous) solutions, as well as three-phase behavior (on one or both stages of the separator). A partial illustration of this behavior is shown by the parameterized curves in Figure 15 for $V_2 = 94.5$ kmol/h. Note that despite the fact that there are only two stages and one feed stream, this problem has behavior that is at least as complicated as that of the often-studied ethanol, benzene, water distillation (Shewchuk, 1974; Magnussen et al., 1979; Prokopakis and Seider, 1983; Kovach and Seider, 1987; Kingsley and Lucia, 1988). Furthermore, it is a particularly challenging problem in an equation-tearing environment because multiple solutions and chaotic behavior exist at both the process unit level

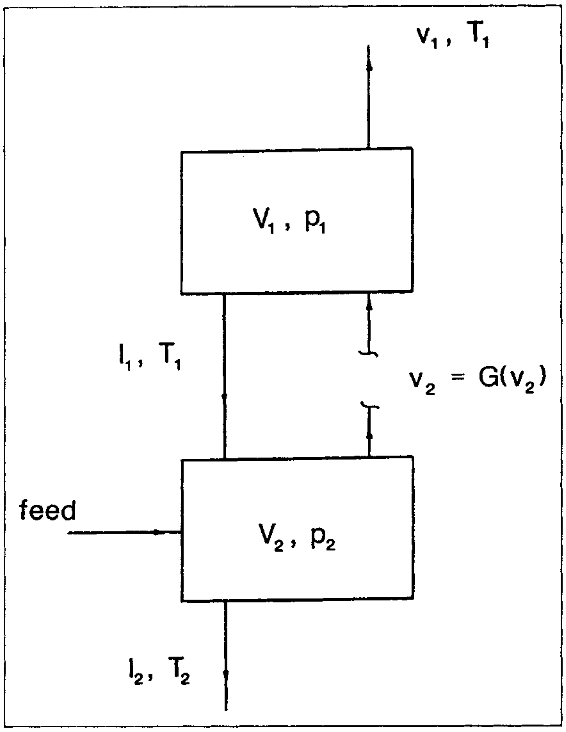

**Figure 14. A simple process flowsheet.**

and the flowsheet level of computation. We note here that the vapor-liquid and vapor-liquid-liquid equilibria were modeled using the procedures and data given by Prausnitz et al. (1980), and the solutions needed to generate Figure 15, as well as other results in this section, were obtained and/or verified by solving all model equations simultaneously using Newton-like methods and the starting point strategies described by Venkataraman and Lucia (1988) and Kingsley and Lucia (1988).

To study the chaotic behavior of direct substitution on this simple process flowsheet, we restricted our attention to finding only vapor-liquid solutions parameterized in distillate flow rate. That is, we fixed the vapor boilup rate, $V_2$, at 94.5 kmol/h, and solved the problem for distillate flow rates over the range 22–32 kmol/h. Furthermore, the inner loop was solved by Newton's method to an accuracy of $\|F\|_2 \leq 10^{-12}$ to avoid computational noise, and the convergence condition $\|v_2^{k+1} - v_2^k\|_2 \leq 10^{-4}$ was used for the outer (direct substitution) loop. Finally, we note that the single-stage variables $(v_i, l_i, T)$ were initialized by splitting the effective feed to each stage equally between the vapor and liquid phases (componentwise), and setting the temperature to 350 K for the first pass through the flowsheet. On subsequent passes, the appropriate solution from the previous pass through the stages was used to initialize the single-stage calculations, and this was done for each stage.

**Table 7. Problem Specifications for Simple Process Flowsheet**

| Stage No. | Feed Flow* kmol/h | Vapor Flow kmol/h | Pressure MPa |
|---|---|---|---|
| 1 | | 22–32 | 0.1013 |
| 2 | (4.53, 12.72, 15.56) | 85–95 | 0.1013 |

*Component order: 1, acetonitrile; 2, water; 3, acrylonitrile

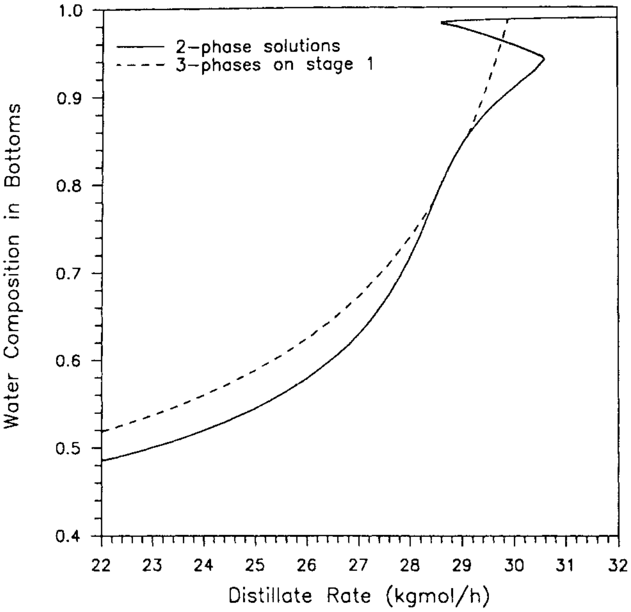

**Figure 15. Parameterized solutions to simple process flowsheet.**

From Figure 15, it is clear that there is only one vapor-liquid solution for any distillate flow rate specification below the regular turning point at $V_1 = 28.5$ kmol/h, and that corresponding solution is a relatively low-purity water solution. Furthermore, for distillate flow rates below $V_1 = 23.930$ kmol/h, direct substitution has little difficulty in finding the associated low-purity water solution from any reasonable starting point. For example, for $V_1 = 23.50$ kmol/h, direct substitution converges to the solution shown in Table 8 in 22 iterations from the starting point $v_2^o = (15, 32, 47.5)$.

At approximately $V_1 = 23.905$ kmol/h, the asymptotic behavior of direct substitution changes from convergent to nonconvergent. More specifically, the spectral radius of the Jacobian matrix, $G'(X^*)$, passes through a value of 1, the fixed point becomes unstable, and a period-doubling bifurcation occurs. As a result, direct substitution exhibits stable period 2 behavior. Moreover, while it is tempting to hastily conclude that this is the beginning of a period-doubling route to chaos, it is not. The behavior of direct substitution is far more complicated than that because of the complex interaction between the inner and outer loops. In particular, while stable period 2 behavior continues as the distillate flow rate is increased slightly (until approximately $V_1 = 23.9337$ kmol/h), for reasons that are still not entirely clear, the behavior abruptly switches to cyclic behavior with large integer period. For example, for $V_1 = 23.93376$ kmol/h, direct substitution exhibits a stable 54 cycle. While this abrupt change in periodicity is due to the presence of solution multiplicity at stage 2, the mechanism by which the switch takes place is presently unclear to us.

As the distillate flow rate is further increased the periodicity decreases, and at $V_1 = 23.95$ kmol/h a stable cycle of period 4 appears. This 4 cycle occupies a relatively large parameter window (23.96–24.8368 kmol/h), and then again, quite abruptly, cyclic behavior at stage 2, aperiodicity, and large integer periodic cycles emerge. For example, for $V_1 = 24.899$ kmol/h, the behavior of direct substitution is still aperiodic after 10,000

Table 8. Solution to Simple Process Flowsheet for $V_1 = 23.5$, $V_2 = 94.5$ kmol/h

| Stage No. | Liquid Molar Flows kmol/h | Vapor Molar Flows kmol/h | Temp. K | Heat Duty $10^2$ kJ/h |
|---|---|---|---|---|
| 1 | (12.305, 24.873, 33.822) | (2.722, 7.974, 12.804) | 345.364 | −2.3524 |
| 2 | (1.808, 4.745, 2.756) | (15.027, 32.847, 46.625) | 346.238 | 3.1246 |

outer loop iterations. There is also a stable 100-cycle at $V_1$ = 24.9023 kmol/h. A partial summary of the truly complex behavior of direct substitution on this simple process flowsheet is given in Table 9, and Figure 16 shows the behavior of a strange attractor within the parameter region of interest, which appears as a noisy 8 cycle.

### *Other chaotic process examples*

We have found other simple examples of steady-state chemical process simulation (sub)problems on which direct substitution and Newton's method exhibit chaos. These include

1. Finding the roots of the SRK equation by Newton's method
2. Finding the roots of Underwood equations by direct substitution
3. Two-phase, single-stage *VP* (vapor flow, pressure flash calculations for heterogeneous multicomponent mixtures using Newton's method

Table 9. Summary of Behavior of Direct Substitution on a Simple Process Flowsheet*

| $V_1$ kmol/h | Asymptotic Behavior |
|---|---|
| 22 | convergence |
| 23.5 | convergence |
| 23.931 | 2 cycle begins |
| 23.933 | 2 cycle |
| 23.9337 | 2 cycle |
| 23.93376 | 54 cycle |
| 23.934 | 44 cycle |
| 24.1 | 4 cycle |
| 24.4 | 4 cycle |
| 24.8 | 4 cycle |
| 24.83684 | 4 cycle |
| 24.8369 | F(4 cycle)** |
| 24.855 | F(11 cycle) |
| 24.8983 | F(15 cycle) |
| 24.899 | aperiodic |
| 24.9023 | 100 cycle |
| 24.905 | 11 cycle |
| 24.95 | 3 cycle |
| 25.20 | 3 cycle |
| 26.02 | 5 cycle |
| 26.20 | 7 cycle |
| 27.00 | 4 cycle |
| 27.50 | 5 cycle |
| 28.70 | convergence |
| 29.30 | convergence |
| 30.00 | convergence |
| 31.00 | convergence |
| 32.00 | convergence |

*$v^q$ = (15, 32, 47.5)
**Failure (inner loop behavior after 50,000 iterations)

In the neighborhood of any point at which a pair of real volume roots of the SRK equation disappear, we have observed abrupt aperiodic behavior of Newton's method. That is, despite the fact that a root of physical interest (liquid or vapor) has bifurcated into the complex plane, the Newton iterates neither converge nor diverge, but rather, wander chaotically within a bounded region in the neighborhood of the bifurcation point. They never take on physically meaningless (negative) values. They are never attracted to stable periodic cycles as the temperature is changed. They simply, and quite abruptly, show aperiodic behavior. For example, for the same mixture used earlier (0.3 methane, 0.4 ethylene, 0.3 acetone) and temperature and pressure specifications of 305.1928 K and 0.5065 MPa, respectively, the Newton iterates wander chaotically for 50,000 iterations, never once repeating a pattern. In our opinion, it would be interesting to study the behavior of Newton's method in the complex plane to determine whether chaos really exists (and if it does, what the route to chaos is), or if our observations are simply an artifact of restricting the calculations (and our attention) to the real line. Besides, complexifying the calculations seems to be a sensible way to address the computational problems associated with roots that bifurcate into the complex plane.

For the most part, the behavior of direct substitution iterates on parameterized Underwood equations is qualitatively the same as that on the SRK equation. It is a relatively simple single-variable problem on which direct substitution follows a classical period-doubling route to chaos.

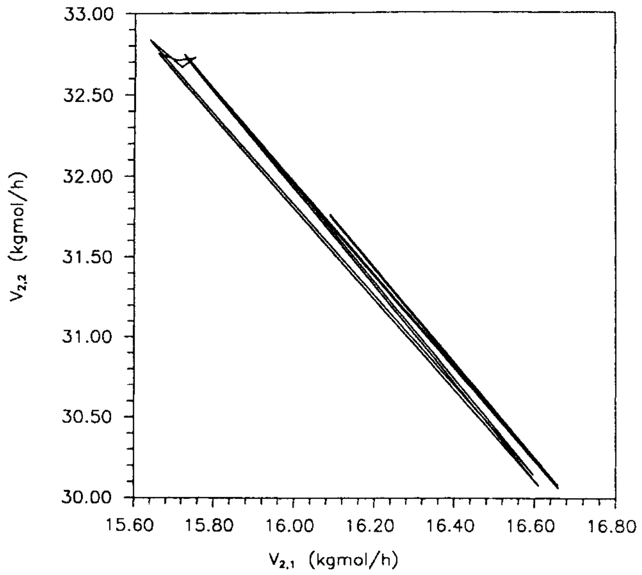

**Figure 16. Strange attractor for simple process flowsheet.**

On the other hand, we have found that Newton's method exhibits somewhat different, but equally perplexing, chaotic behavior on two-phase *VP* flash calculations involving heterogeneous multicomponent mixtures. For example, for a mixture of acetonitrile, water, and acrylonitrile at atmospheric pressure, we have parameterized *VP* flash calculations in both feed composition and total vapor flow, and have observed limited period doubling and strange windows of global convergence of Newton's method, as in the dew point calculations described earlier. However, again, truly aperiodic behavior has also been observed. For example, for a feed of 10.73, 29.54, and 59.73 kmol/h of acetonitrile, water, and acrylonitrile, respectively, assumed nonideal liquid and vapor phase behavior, a total vapor flow rate specification of $V = 95.0640$ kmol/h, and a starting point of $X^o = (l_1, l_2, l_3, v_1, v_2, v_3, T) = (0.01, 0.98, 0.01, 10.72, 28.56, 59.72, 340.\text{K})$, Newton's method exhibits aperiodic behavior without ever encountering a physical boundary, even when the calculations are continued for 50,000 iterations. This is particularly disturbing since the problem has only one real solution, $X^* = (0.7917, 1.0794, 3.0648, 9.9383, 28.4606, 56.6651, 345.323\text{ K})$, which can easily be found from a better starting point.

## Conclusions

The observation that direct substitution and Newton's method can exhibit chaotic behavior on simple process model equations has widespread implications with regard to general process equation solving and flowsheet simulation. It raises important concerns regarding the choice of equation-solving method, the use of automatic initialization strategies and stabilization procedures, and the general convergence behavior of sequential modular and equation-oriented simulators. It clearly justifies the need for further research on the potential chaotic behavior of iterative maps for steady-state process simulation, and prompts interest in building an understanding of the relationship between the dynamical behavior of chemical processes and the behavior of fixed-point methods for steady-state simulation, if there is one.

### *Choice of equation-solving method*

Although only direct substitution and Newton's method were studied in this work, in our opinion it is clear that no equation-solving method is immune to potential chaotic behavior. This includes quasi-Newton methods, hybrid methods (Venkataraman and Lucia, 1988), dogleg strategies (Chen and Stadtherr, 1981), homotopy-continuation methods (Wayburn and Seader, 1984), algorithms based on implicit enumeration (Swaney and Wilhelm, 1989), and others. Furthermore, while extensive numerical investigation is required to assert or dispel this conjecture, it is not hard to imagine, for example, a homotopy-continuation method getting caught in a periodic or aperiodic orbit in its attempts to cross a fractal basin boundary. Similarly, it is also easy to construct simple chemical process examples in which the dogleg strategy either terminates at a local minimum in the least-squares function that is bounded away from zero (in which case the model equations are not satisfied), or exhibits periodic or aperiodic behavior because the usual iterative norm-reduction criterion has been relaxed. The heterogeneous dew point problem is a simple example of this. However, these remarks are not intended to single out any particular approach or method as inferior, nor are they intended to create a sense of despair. Rather, they suggest that further research and heightened awareness of potential chaotic behavior in steady-state process simulation is needed. Clearly, methods will continue to be chosen on the basis of past performance, individual preference, and other criteria, until a better understanding of issues in chaos relevant to process simulation become available. On the other hand, it is equally clear that claims of methods that do not fail should be taken with extreme skepticism.

### *Automatic initialization strategies and stabilization procedures*

While it is always better to use good initial values of the unknown variables, when available, and to use sensible procedures to avoid physically meaningless iterates, the situation is fundamentally different for direct substitution and Newton's method. For the cases of direct substitution studied in this work, periodic and aperiodic behavior were always observed within regions in which an unstable fixed point existed. As a consequence, the asymptotic behavior of direct substitution must be nonconvergent, and no initial values, with the exception of guessing the solution to prescribed accuracy, will change that. Thus, the issue of starting points is irrelevant when the fixed point being sought is unstable with respect to direct substitution or any other iterative map. This is not true, however, for certain accelerated direct substitution methods.

On the other hand, fixed points of Newton's method are always stable, and Newton-Kantorovich theorems (Ortega and Rheinboldt, 1970, p. 421) tell us that Newton's method is guaranteed to converge, provided the initial values are close enough to the solution(s) of interest. Furthermore, this work clearly shows that, while the interpretation of "close enough" may depend on the presence of fractal basin boundaries or regions of periodic and/or chaotic behavior, it is still worthwhile investing effort in automatic ways of initializing variables in the case of Newton's method. Clearly, Figures 6–13 illustrate this point for the dew point examples.

While safeguard procedures often result in convergence on problems on which various equation-solving methods would otherwise fail, they do little to circumvent the difficulties associated with the existence of stable periodic or aperiodic cycles. For example, the step-bounding procedures used in conjunction with Newton's method in this work are often easily attracted to stable cycles. As noted earlier, while the dogleg strategy may have excellent global convergence properties, it may converge to a local minimum in the least-squares function that is bounded away from zero. Furthermore, these minima can be bounded as close to, or as far away from, zero as desired. Thus, implicit enumeration schemes (Swaney and Wilhelm, 1989) may require extremely accurate convex underestimators to reject certain subregions of the feasible region in cases where minima in the least-squares function are bounded away from, but very close to, zero. Rather, given the extreme sensitivity to initial conditions of methods that exhibit periodic and/or chaotic behavior, and the fact that it can sometimes take many thousands of iterations for convergence to a stable cycle or fixed point to occur, it is likely that no safeguard procedures will ever be completely satisfactory. Thus, we must simply come to terms with the fact that some problems can, and will, cause difficulty, and recognize that while stabilization procedures will, and should, continue to be used, they can fail.

### *General convergence behavior of steady-state process simulators*

The numerical results presented in this paper indicate that any steady-state process simulator can, and probably will, exhibit chaos, regardless of architecture. Certainly if direct substitution exhibits chaos on the SRK equation, then it will behave chaotically on some process flowsheet. Similarly, if Newton's method behaves aperiodically on a heterogeneous dewpoint problem, then it will also exhibit chaos for some equation-oriented process flowsheet simulation. Furthermore, we believe that it is likely that other workers have observed chaotic behavior of fixed-point methods in process simulation before, only perhaps they did not know it, or know what to look for, at the time.

On the other hand, it is also clear that our present knowledge of chaos and the various routes to chaos, particularly for multivariable problems, is woefully inadequate. Even for the relatively simple multivariable problems studied in this manuscript (dew point problems, *VP* flash calculations, and simple process flowsheets), there is no completely satisfactory explanation for the paths to periodic or aperiodic behavior in most cases. Some problems, like the dew point problem, display certain features of classical routes to chaos (period doubling), but then diverge sharply from that path. Others show no similarities whatsoever. Consequently, extensive numerical investigation on many, small representative process examples is required before scenarios of possible universal routes to chaos are proposed with regard to general steady-state process simulation. At present, we do not expect the situation to change very rapidly.

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## Notation

$D$ = domain
$F(X)$ = vector function
$G(X, p)$ = iterative map evaluated at $X$ and $p$
$J$ = Jacobian matrix of $F$
$K$ = vector of K values or equilibrium ratios
$l$ = vector of liquid component molar flow rates
$p$ = parameter vector
$P$ = pressure
$T$ = temperature
$v$ = vector of vapor component molar flow rates
$V$ = volume, total vapor flow rate
$x$ = liquid phase composition vector
$X, X^*$ = vector of unknown variables, fixed point
$y$ = vector of vapor phase compositions

### *Greek letters*

$\beta$ = composition step bounding parameter
$\Delta$ = change in appropriate variable

### *Subscript*

$i$ = component index

### *Superscripts*

$o$ = initial value or starting point
$k$ = iteration counter

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