

Process Simulation in the Complex Domain

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The asymptotic behavior of fixed-point methods in the complex domain is studied. Both direct substitution and Newton's method exhibit stable periodic and aperiodic behavior from real- or complex-valued starting points. Moreover, multiple stable periodic orbits can exist for direct substitution. Traditional trust region (or dogleg) methods, on the other hand, often terminate at singular points, which correspond to nonzero-valued saddlepoints in the least-squares function that can be arbitrarily far from a solution. Furthermore, the basins of attraction of these singular points are usually dispersed throughout the basin boundaries in the complex domain, clearly illustrating that singular points (via the dogleg strategy) also attract either real- or complex-valued starting points.

In light of this, an extension of the dogleg strategy to the complex domain, based on a simple norm-reducing, singular point perturbation, is proposed. This extended trust region method removes all forms of nonconvergent behavior and always terminates at a fixed point, even from critical point (worst-case) initial values. Many numerical results and geometric illustrations using chemical process simulation examples are presented.

Introduction

The behavior of iterative maps of a single complex variable has been studied in mathematical physics for many years now (see, for example, Cayley, 1879; Julia, 1918; Fatou, 1919, 1920; Brolin, 1966; Guckenheimer, 1970; Mandelbrot, 1980; Douady and Hubbard, 1982; Curry et al., 1983). From these and other studies have come many important contributions to the theory of nonlinear dynamical systems such as Julia sets, fractal geometry, bifurcation theory, strange attractors and a general understanding of the periodic and chaotic behavior, albeit in some cases indirectly. Furthermore, many of these concepts have found application in fluid mechanics, chemically reacting systems, process control, and other areas of science and engineering. On the other hand, very little, if any of this knowledge of nonlinear iterative maps has had a direct impact on the development of methods for solving sets of nonlinear algebraic equations, either within or outside chemical engineering. There are very few studies that deal with multivariable maps (for example, the Hénon map in R^2), and no studies we are aware of are concerned with multivariable iterative maps in the complex domain.

In recent articles, Lucia et al. (1990) and Lucia and Xu (1992) have studied the behavior of several commonly used nonlinear equation-solving methods in a process simulation environment.

For example, Lucia et al. (1990) show that iterative maps like direct substitution and variants of Newton's method can exhibit periodic and chaotic behavior when used to solve simple chemical process model equations (for example, the SRK equation and dewpoint and flash calculations) in the real domain. In some cases this behavior follows classical scenarios; in others it does not. For example, direct substitution follows a period-doubling route to chaos, identical to that described by Feigenbaum (1978), when used to find the volume roots of the Soave-Redlich-Kwong (SRK) equation of state. For the same problem, however, Newton's method often exhibits an abrupt transition to chaotic behavior following a bifurcation of a pair of real roots into the complex plane. In yet other multivariable examples (such as dewpoint temperature calculations), Newton's method with step bounding (due to physical limitations on some of the variables) often exhibits truncated period doubling. The dogleg strategy of Powell (1970), on the other hand, can converge to a singular point instead of a root. Finally, Lucia and Xu (1992) study the behavior of an extension of the dogleg strategy to the complex plane and show, through numerical examples, that it simultaneously avoids both periodic and chaotic behavior and convergence to a singular point. No proofs of global convergence were presented, but Lucia and

Taylor (1992) have used this complex dogleg strategy, without difficulty, to solve flash problems modeled by a single equation of state in both the real and complex domains.

The objective of this article is to study the behavior of direct substitution, Newton's method, and various dogleg strategies in the complex domain in the context of multivariable process simulation. It is shown that transitions to nonconvergent behavior, in either R^n or C^n , for Newton's method and direct substitution can be very complicated. Sometimes the route to chaotic behavior is unorganized, while in other circumstances multiple stable periodic orbits can exist. Furthermore, traditional dogleg strategies suffer from the same deficiency that they have in the single variable case (slow convergence to a singular point). To circumvent these difficulties, a multivariable extension of the dogleg strategy to the complex domain based on a norm-reducing, singular point perturbation is proposed and tested on a variety of chemical process simulation examples. Numerical results show that reliable convergence to a steady-state solution in a finite number of iterations can be obtained, but that the fractal nature of the basin boundaries makes it difficult to determine *a priori* which solution will be found.

Mathematical Background

This section briefly reviews conceptual and practical results for nonlinear iterative maps that are relevant to the equation-solving task in chemical process simulation. Definitions of common terms used in the mathematics of nonlinear iterative maps are in Appendix A for the benefit of those not actively involved in this area.

Pure methods

In this article, we are concerned with iterative maps of the form:

$$Z_{k+1} = G(Z_k, p), \quad (1)$$

where Z is a vector in some space D , p is a scalar parameter, and G is a nonlinear mapping from D into itself that often has multiple fixed points. For direct substitution, the map G is usually represented by some (often structural) algebraic rearrangement of the equations, say $F(Z, p) = 0$, whose solution is sought. For Newton's method, G is given by:

$$Z_{k+1} = Z_k - [J(Z_k, p)]^{-1} F(Z_k, p), \quad (2)$$

where $J(Z_k, p)$ is the Jacobian matrix of F evaluated at Z_k and p .

Much information is available about iterative maps in general and direct substitution and Newton's method in particular, when the domain D is either the complex plane, C , or the real domain, R^n . For example, changes in the stability of a solution or transitions to nonconvergent behavior (period doubling and chaos) are always accompanied by some type of bifurcation, and the boundaries between different basins of attraction for stable solutions and/or stable periodic or aperiodic cycles are very often fractal and of varying geometric complexity. This makes it very difficult to predict the ultimate fate of a given initial value, since slightly different initial values can converge

to widely different solutions and/or stable cycles. Furthermore, these basin boundaries can contain simple or complicated Julia sets that are directly affected by the singular points and repelling fixed points of the map in question, and this only adds to the complexity of nonconvergent behavior.

For a single complex variable mapping, periodic or aperiodic behavior can be located by applying a theorem of Julia (1918) and Fatou (1919, 1920), which initializes this unknown complex variable to a critical point [Z such that $G'(Z, p) = 0$]. Thus, critical points represent, in some sense, a set of worst starting points for any given iterative map and are a useful tool in testing algorithmic robustness. Moreover, changes in periodic or aperiodic behavior, and thus the structure of the Julia sets, can be cataloged in parameter space, at least in a local sense, by the Mandelbrot set (see Mandelbrot, 1980). However, it is important to remember that the theorem of Fatou and Julia, as well as the results of Mandelbrot, is at present applicable only to functions of a single complex variable.

Stabilization techniques

Because most mathematical models for chemical processes involve intrinsic bounds on variables, the nonlinear iterative maps that find widespread use in process simulation are necessarily more complicated than just pure Newton's method or just pure direct substitution. Because of these bounds on variables, the domain, D , is often a subset of some vector space and the iterates generated by Newton's method or direct substitution must frequently be modified so that they remain in D (so that the mathematical model remains valid). Common techniques for modifying (or stabilizing) Newton's method or direct substitution include line searching, step bounding, acceleration methods, trust regions, and continuation. These techniques are also intended to force convergence from poor starting points and thereby enlarge the basins of attraction for a given pure method. In many cases, these stabilization methods do, in fact, improve the numerical performance of Newton's method and direct substitution. However, they can also result in, for example, termination at a point which is not a solution to the model equations (Lucia and Xu, 1992), as will be described later.

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Pros and cons

In many cases, particularly with Newton's method, the appearance of periodic or aperiodic behavior in the real domain is accompanied by a bifurcation of a pair of real solutions into the complex domain. Thus, one direct way to perhaps avoid nonconvergent behavior is to simply avoid the Julia sets and perform the calculations in the complex domain, as suggested by Lucia et al. (1990). However, things are just not that simple. While complex initial values remove some of this nonconvergent behavior, Newton's method (and direct substitution) can still exhibit periodic and chaotic behavior in the complex domain (see, for example, Figure 4). Furthermore, complexifying the calculations can introduce additional complex solutions and complicate the structure of the basins of attraction. For example, for the chemical reaction problem studied by Lucia and Xu (1992), complexification resulted in the introduction of 156 additional complex solutions to a problem that had

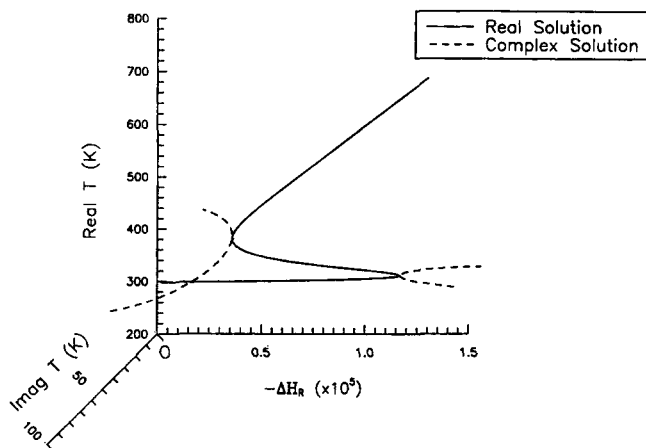


Figure 1. Bifurcation diagram for a mass/energy balance for a CSTR.

only three physically meaningful solutions in the real domain (see, Figure 9 in Lucia and Xu, 1992). Not good!

Having said all this, why complexify the calculations? There are several good reasons. First, our experience shows that performing the calculations in the complex domain (with complex initial values) never worsens, and often improves, convergence to a desired real solution (see, for example, Lucia and Taylor, 1992). Second, the use of stabilization techniques such as line searching and trust regions restricted to the real domain can never guarantee convergence to a solution because of the presence of singular points. These singular points often represent nonzero-valued local minima in the least-squares function on R^n , and therefore any method that operates on the principle of norm reduction always has the possibility of getting trapped and terminating at a point which is not a solution, regardless of its global convergence properties. Third, we have had remarkable success in using an extension of the dogleg strategy to the complex plane in the case of single variable problems. For several classes of single variable functions (polynomial and transcendental), we have been able to remove all nonconvergent behavior and always get convergence to a root. Fourth, complexification often removes points or surfaces of nondifferentiability imposed by restrictions to the real domain. For example, phase boundaries are only one-side differentiable with respect to any *a priori* choice of phases, and this can lead to rather wild behavior of algorithms in these regions. Finally, in some applications, convergence to a complex solution provides useful physical information. For example, a complex-valued liquid or vapor compressibility factor clearly signifies that the associated phase is a hypothetical thermodynamic state and is useful in determining the number of phases present at equilibrium.

Extended trust region method in the complex domain

In this section, we describe the basic features of an extension of Powell's dogleg strategy to the complex domain that is based on a simple norm-reducing singular point perturbation. The heart of the extended algorithm, however, is still the original dogleg strategy, because it has superior global convergence properties. The basic algorithm was described by Powell (1970), and the many modifications have been made (for example,

Chen and Stadtherr, 1981). The notation we use is similar to that used by Lucia and Xu (1992) for the single variable case.

The underlying idea behind the dogleg strategy is to iteratively construct a linear combination of the Cauchy (steepest descent or gradient) step in the least-squares function and the Newton step (ΔZ_N), constrained to lie within a trust region, in order to produce a monotonically decreasing sequence of function values that converge to a solution. Because the size of the trust region is also adjusted iteratively and because the rules of adjustment require the trust region radius, say Δ , to decrease when norm reduction does not occur, steepest descent steps are guaranteed to be selected in regions of difficulty and herein lies the global convergence characteristics of the dogleg strategy. However, one should be careful not to interpret global convergence (termination at a stationary point of the least-squares function) as some sort of guarantee of convergence to a solution. For smooth functions that have multiple solutions (global minima in the least-squares function), termination can also occur at local minima or saddlepoints (singular points), which are clearly not solutions. See Lucia and Xu (1992) or the examples in the next section.

To extend the basic dogleg algorithm to the complex domain, some attention must be paid to the definition of the underlying 2-norm on C^n , differentiability in terms of Cauchy-Riemann conditions and, the calculation of the scalar used to compute a linear combination of the Cauchy and Newton steps (the dogleg parameter, say β). In particular, because the norm is used throughout the algorithm (in defining the step, in accepting or rejecting the step, and in adjusting the trust region), the usual 2-norm on R^n must be replaced by $\phi = F^T \bar{F}$, where $\bar{F} = \bar{F}(Z, p)$ is the complex conjugate of $F(Z, p)$, in order to conduct the calculations in the complex domain. This, however, causes difficulties in defining a descent direction, because the associated inner product, $F^T \bar{F}$, can induce a 90-degree rotation in the Cauchy direction due to the condition $i^2 = -1$, and this is of particular concern when the imaginary parts of the function and the Jacobian matrix dominate the associated real parts. This, in turn, is a consequence of the fact that the norm does not satisfy Cauchy-Riemann conditions for differentiability.

To circumvent the difficulty of nondescent directions, we follow the idea in Lucia and Xu (1992) and approximate the Cauchy direction by the rule:

$$\phi' = J^T(Z_k, p) \text{Re}[F(Z_k, p)], \quad (3)$$

where $\text{Re}[F(Z_k, p)]$ denotes the vector formed from the real parts of the complex-valued vector $F(Z_k, p)$. In tandem with this, we force the dogleg parameter, β , to be real-valued by using the rules given by Lucia and Xu (1992, p. 550).

At this point, while the extended dogleg strategy is capable of using real- or complex-valued starting points and finding real or complex solutions (when $\|F\|_2 \leq \epsilon$), it can still terminate at a singular point (when $\|\phi'\|_2 \leq 10^2 \epsilon$ and $\|\Delta Z_N\|_2 \geq 10^5 \epsilon$ and $\|F\|_2 \geq \epsilon$ are satisfied). In the neighborhood of a singular point, the Newton step is large (always outside the trust region) and the Cauchy step tends to zero, thus making convergence slow because all steps are usually gradient steps. Thus we do not use a tight convergence tolerance to detect a singular point in order to avoid an excessively large number of function calls due to the linear rate of convergence that results from asymp-

otic Cauchy steps. Furthermore, these singular points can be either real or complex. However, they often represent saddle-points of the two norm on C^n and therefore contain directions of negative curvature from which norm-reducing perturbations can be made to move from a singular point to a solution. In fact, the direction of negative curvature is often confined to the subspace of C^n in which the real part of all components of the vector are zero.

To force convergence from a singular point to a solution, we generalize the ideas by Lucia and Xu (1992, p. 551). That is, the algorithm first identifies a direction of negative curvature by considering directions, in turn, that are orthogonal to the normalized approximate Cauchy step at the singular point. This is easily done using the fact that C^n is isomorphic to R^{2n} and any number of orthogonalization procedures (such as Gram-Schmidt, Jacobi rotations). Successive perturbations in each direction are made until a point with a lower value of the 2-norm is found. That way, the first direction that gives a decrease in the 2-norm is accepted. Once such a point is found, the algorithm returns to the complex domain trust region method until another stationary point is located (a solution or another singular point) and this strategy is repeated until a solution (a global minimum) is found. Sample calculations illustrating the steps of the extended dogleg method are given in Appendix B.

Numerical Performance

In this section, we study the behavior of direct substitution, Newton's method, and traditional and extended dogleg strategies in the complex domain. Particular emphasis is placed on the presence of periodic and chaotic regimes, singular points and repelling fixed points, and algorithmic reliability and efficiency. Results for two chemical process engineering examples and a variety of geometric illustrations are presented.

Continuous stirred-tank reactor

The particular chemical reaction system studied in this section is a classical example taken directly from Smith (1981). It involves a first-order, irreversible reaction with an exothermic heat of reaction and takes place in an adiabatic continuous-stirred tank reactor (CSTR). The mathematical model that describes the behavior of any single-phase reaction of this type consists of the mass and energy balances around the reactor, which are

$$X - \frac{\theta A e^{-(E/RT)}}{1 + \theta A e^{-(E/RT)}} = 0 \quad (4)$$

and

$$X + \frac{\rho C_p}{C_0 \Delta H_R} (T - T_0) = 0, \quad (5)$$

respectively, where ρ is the fluid density, C_p is the specific heat, C_0 and T_0 are the inlet concentration and temperature of the reactant respectively, ΔH_R is the heat of reaction, θ is the average residence time for the reactor, A is the frequency factor, and E is the activation energy. The unknown variables in these equations are the reactor outlet concentration and

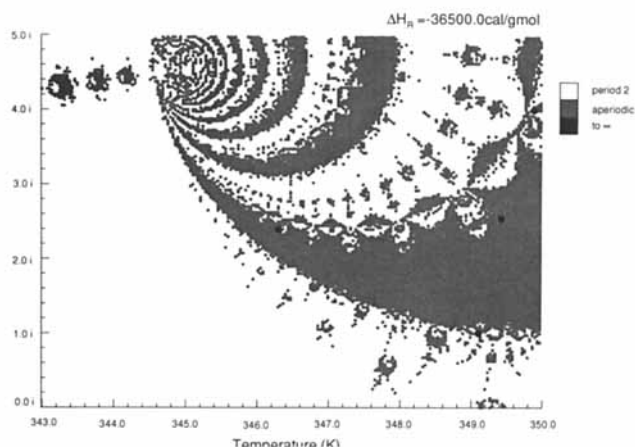


Figure 2. Basins of attraction for direct substitution on CSTR equations.

temperature, X and T . Furthermore, because the energy balance equation is linear in both T and X , either T or X can be eliminated, and the behavior of the model can be studied as a (combined mass/energy balance) function of a single complex variable, as described by Lucia and Xu (1992). A bifurcation diagram for the single complex variable problem parameterized in the heat of reaction is shown in Figure 1. Note that there is a region in which there are three real solutions and regions in which either the high- or low-temperature (and conversion) solutions are complex.

Here, we study the behavior of various two-dimensional nonlinear maps associated with solving Eqs. 4 and 5, also parameterized in the heat of reaction. In this regard, all illustrations and numerical results in the sections that follow were based on the problem data given in Table 1. Furthermore, numerical results were compiled for heats of reaction ranging from $-120,000$ to -50 cal/mol, and all numerical experiments were run on a SPARC II workstation in double-precision arithmetic for both real and complex variables.

Direct Substitution. Simple rearrangement of Eqs. 4 and 5 gives the nonlinear map for direct substitution defined by:

$$Z_{k+1} = \begin{cases} X_{k+1} = \frac{\theta A e^{-(E/RT_k)} - X_k}{\theta A e^{-(E/RT_k)}} \\ T_{k+1} = T_0 - \frac{C_0 (\Delta H_R)}{\rho C_p} X_k \end{cases} = G(Z_k, \Delta H_R), \quad (6)$$

where $Z = (X, T)$. This is the direct substitution iteration used in this work. It is not unique, however. Other algebraic rearrangements are possible, but all are nonlinear and coupled.

Table 1. Numerical Data for CSTR Example

Quantity	Value
ρ (mol/cm ³)	1.0
C_p (cal/mol·K)	1.0
C_0 (mol/cm ³)	0.003
T_0 (K)	298.0
θ (s)	300.0
A (L/s)	4.48×10^{-6}
E (cal/mol)	15,000.0

Table 2. Nonconvergent Behavior of Direct Substitution on a Two-Dimensional CSTR Model*

$-\Delta H_R$ (cal/mol)	Cycle
36,622	2
36,560	24
36,550	aperiodic
36,500	aperiodic
36,430	2
36,390	60
36,340	2
36,290	48
36,200	2
36,100	aperiodic
36,000	**
35,000	20
34,000	aperiodic
33,000	12
32,000	aperiodic
31,000	10
30,000	10
25,150	46
25,140	38
25,130	33

*Critical point starting value

**Converges to fixed point at ∞

For the parameter range of interest and the iteration defined by Eq. 6, direct substitution exhibits convergent behavior from a critical-manifold initial value for all values of ΔH_R less than $-36,623$ cal/mol. At this point, the high-conversion solution becomes unstable, the corresponding spectral radius of $G'(Z, \Delta H_R)$ passes through a value of $1 + 0i$ and the solution bifurcates into a 2-cycle with cycle points that are complex conjugates. For example, for a slightly larger parameter value of $-36,622$ cal/mol, the cycle points are $(X, T) = (0.8484 + 0.000407i, 391.215 - 0.0447i)$ and $(X, T) = (0.8484 - 0.000407i, 391.215 + 0.0447i)$. Unfortunately, as the heat of reaction is increased, other periodic and aperiodic behavior emerges, but no organized pattern unfolds, as shown in Table 2.

Perhaps the most interesting aspect of the behavior of direct substitution on this particular problem is that we have found more than one stable cycle for the same heat of reaction. For example, for a parameter value of $-36,500$ cal/mol, there is

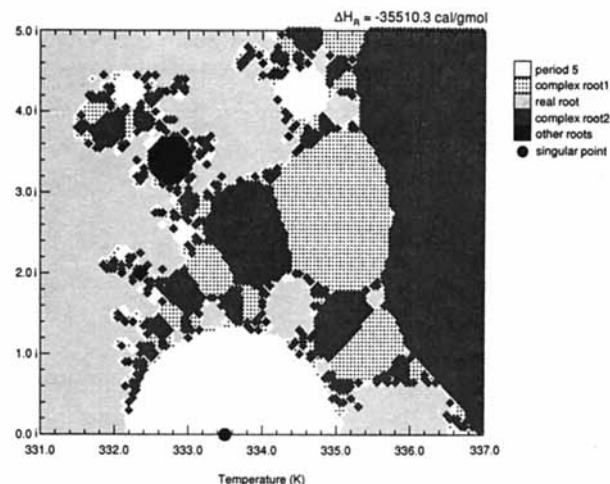


Figure 4. Basins of attraction for Newton's method on CSTR equations.

a stable two cycle with complex conjugate cycle points and aperiodic behavior confined to R^2 , which of course is a subspace of C^2 . Thus clearly the 2-cycle and chaotic cycle are unrelated. The basins of attraction in temperature for a fixed initial conversion of $X_0 = 0.5 + 3i$ for this pair of stable cycles is shown in Figure 2. Similar behavior can be found for other values of the heat of reaction. For example, for $\Delta H_R = -35,560$ cal/mol and the same initial conversion, there is a stable complex-valued 2-cycle and a stable real-valued 24-cycle, as shown in Figure 3. The cycle points for the 2-cycle in Figure 3 are $(X, T) = (0.8499 - 0.0288i, 391.061 + 3.154i)$ and $(X, T) = (0.8499 + 0.0288i, 391.061 - 3.154i)$. Note also that all periodic and/or aperiodic cycles attract both real or complex-valued starting points and that the basin boundaries are fractal.

In our opinion, the existence of multiple stable periodic cycles is due to the fact that the direct substitution map has more than one critical manifold. Thus, if extensions of the theorem of Julia (1918) and Fatou (1919, 1920) exist for iterated maps of several complex variables, then it seems plausible that different critical points can be attracted to different stable cycles. In fact, even the rigorous theorems of Julia and Fatou do not preclude this behavior for iterated-rational maps of a single complex variable. However, no proofs of this conjecture exist.

Newton's Method. Since Newton-like methods are the equation-solving techniques of preference in chemical process simulation, we solved the same two-dimensional reactor problem over the same parameter range using Newton's method. For the most part, the qualitative behavior of Newton's method is the same as that for direct substitution. In particular, the onset of nonconvergent behavior is accompanied by the bifurcation of the high-conversion solution into the complex domain, and no simple organized route to chaotic behavior seems to exist. This is partially summarized by the numerical results shown in Table 3.

Furthermore, stable periodic or aperiodic cycles often attract both real- and complex-valued starting points. For example, Figure 4 shows the basins of attraction in temperature for Newton's method for a heat of reaction of $-35,510.3$ cal/mol and an initial conversion that satisfies Eq. 5. Note that there is a basin of attraction for each of the three physically mean-

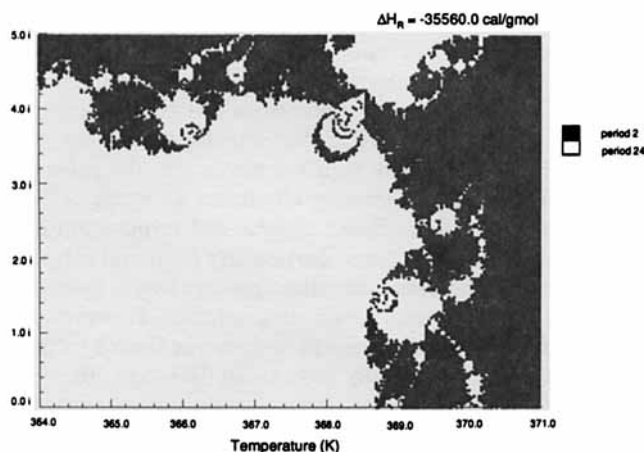


Figure 3. Basins of attraction for direct substitution on CSTR equations.

Table 3. Behavior for Newton's Method on a Two-Dimensional CSTR Model*

$-\Delta H$ (cal/mol)	Cycle
35,836	5
35,803	22
35,711	aperiodic
35,705	72
35,577	14
35,478	56
35,461	4
35,442	aperiodic
35,074	aperiodic
34,593	8
34,407	5
34,000	8
33,011	25
32,707	32
32,704	16
32,702	aperiodic
32,701	8
32,291	39
32,261	38
32,243	17

*Saddlepoint starting value $(X, T) = (X, 355.952)$, where the conversion can take on any value.

ingful solutions of interest, albeit two of them complex-valued, as well as basins of attraction for other complex-valued solutions and a stable cycle of period 5. Clearly, Figure 4 shows that the basin boundaries for Newton's method are fractal, and stable periodic cycles can attract both real- and complex-valued starting points. The particular solutions and cycle points associated with Figure 4 are shown in Table 4. Note also that for this example, one of the cycle points is physically unrealistic ($X \gg 1$ and an extremely large value of T). While this is not uncommon for Newton's method because of the proximity of a singular point [$(X, T) = (0.3332, 333.519)$] and a cycle point (4th cycle point in Table 4), it is by no means always the case. We have also observed stable cyclic behavior that is totally confined to a physically meaningful region.

Unlike direct substitution, Newton's method does not seem to possess regions in which there is more than one stable cycle.

Table 4. Solutions and Cycle Points for Newton's Method for Two-Dimensional CSTR Model

(X, T)	
Solutions	$(0.7734 + 0.0737i, 380.390 + 7.854i)$
	$(0.7734 - 0.0737i, 380.390 - 7.854i)$
	$(0.0151, 299.609)$
Cycle	$(0.9999, 404.531)$
	$(0.8587, 389.476)$
	$(0.7805, 381.144)$
	$(0.3354, 333.730)$
	$(20.561, 2,488.39)$

However, this may be due in part to the fact that there is a two-dimensional manifold of critical points for the Newton map that correspond to the unique saddlepoint temperature of $F(X, T) = 0$, which occurs at 355.952 K and is independent of ΔH_R . In general, however, parameter-independent saddlepoints should not be considered a common occurrence.

Like direct substitution, the behavior of Newton's method in the complex domain is not entirely satisfactory from an equation-solving perspective, since it can be attracted to stable periodic/aperiodic cycles.

Traditional Dogleg Methods. Figure 5 shows the basins of attraction in temperature for the original dogleg strategy of Powell (1970) for the same problem specifications used to generate Figure 1 for Newton's method and an initial trust region radius of 100. Note that Figures 4 and 5 are quite different and that there is a basin of attraction in Figure 5 associated with a real-valued (high conversion) singular point that occurs at $(X, T) = (0.7702, 380.478)$, clearly showing that the dogleg strategy can terminate at a singular point, arbitrarily far from a solution. Note also that basin for this singular point has replaced the basin for the 5-cycle for Newton's method, but that it is dispersed throughout the solution basin boundaries and again can attract both real- and complex-valued starting points.

On average, Powell's dogleg strategy requires relatively few function calls (less than 50) to find the singular point, irrespective of starting point. Despite this, however, the numerical performance of traditional trust region methods also is not completely satisfactory since they can terminate at points which are not solutions.

Trust Region Methods in the Complex Domain. Figure 6 shows the basins of attraction in temperature for the extension of the dogleg strategy to the complex domain described earlier, again for the same problem specifications used to generate Figure 4. The initial trust region radius was 100 and the perturbation in imaginary parts of the singular point were $(\Delta X, \Delta T) = (0.1i, 2.5i)$. Clearly Figure 6 shows that the proposed complex domain dogleg strategy eliminates all forms of non-convergent behavior, periodic, chaotic and termination at a singular point. In many cases, particularly for initial values in the basin boundaries, the calculations proceed first to a singular point and then, by perturbation, to a solution. However, the number of function calls required to converge from a singular point to a solution is usually quite small (less than 10).

Dewpoint temperature calculations for a heterogeneous mixture

The calculation of the dewpoint temperature and incipient

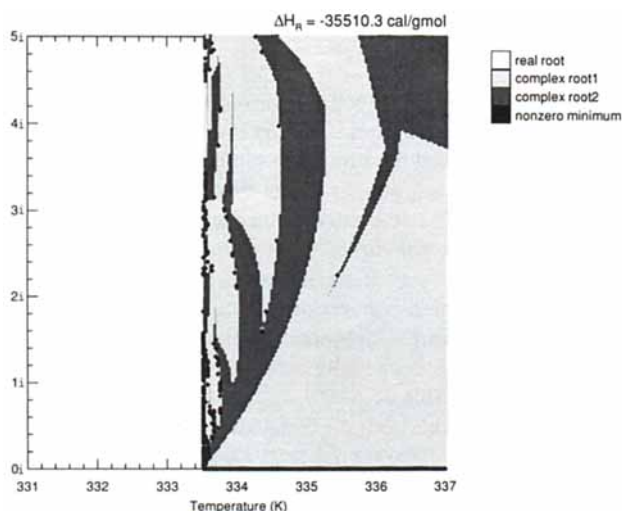


Figure 5. Basins of attraction for original dogleg strategy on CSTR equations.

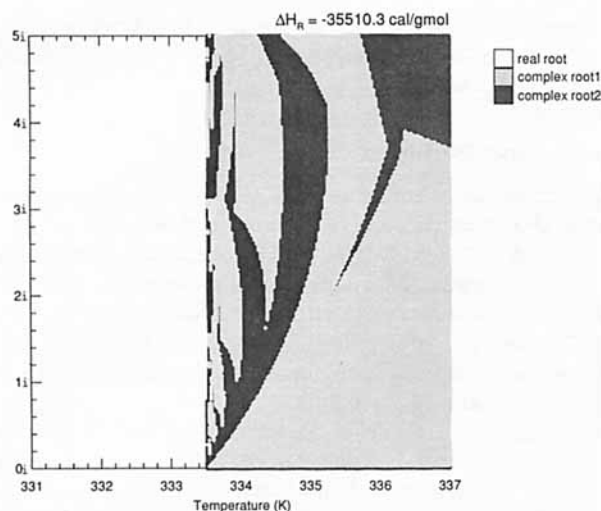


Figure 6. Basins of attraction of extended trust region method on CSTR equations.

liquid-phase composition for partially miscible liquids is a process simulation problem in which there is often more than one real-valued solution (see Van Dongen et al., 1983). Furthermore, Lucia et al. (1990) have shown that Newton's method with step bounding (and restricted to the real domain) can exhibit both truncated period doubling and chaotic behavior in solving the model equations:

$$K_i x_i - y_i = 0, \quad i = 1, 2, \dots, n_c \quad (7)$$

and

$$\sum x_i - 1 = 0, \quad (8)$$

where K_i is the i th component K value, y_i and x_i are the vapor and liquid mole fractions, respectively, and n_c is the number of components. Here, the vapor-phase composition and total

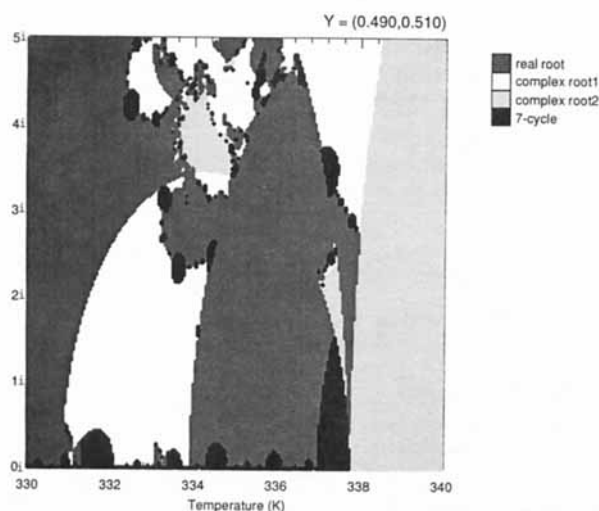


Figure 7. Basins of attraction for Newton's method on dewpoint problem.

pressure of the system are usually fixed, and thus the K_i 's are nonlinear functions of temperature and liquid composition, which are computed iteratively by applying some fixed-point method to Eqs. 7 and 8.

In the sections that follow, we study the behavior of various Newton-like methods on dewpoint problems in the complex domain using the benzene-water system at atmospheric pressure and the accompanying physical properties models (UNIQUAC, the virial equation, and so on) and data given in Prausnitz et al. (1980). Again, all computations were performed on a SPARC II workstation in double-precision arithmetic.

Newton's Method. For parametric values of benzene vapor-phase compositions in the range (0.495, 0.960), there are three real-valued solutions to Eqs. 7 and 8, and the basin boundaries for Newton's method with step bounding are fractal but striated (see, for example, Table 4 and Figures 5, 6 and 7 in Lucia et al., 1990). Outside this range, two of the solutions are complex-valued, indicating that the liquid phase represents a hypothetical thermodynamic state; as a consequence, computations restricted to the real domain can become periodic or chaotic.

Figure 7 shows the basins of attraction in temperature for pure Newton's method in the complex domain for the dewpoint temperature calculations for a benzene vapor mole fraction of 0.490 at atmospheric pressure. The initial liquid mole fractions were kept fixed at 0.3 and 0.7 for benzene and water, respectively. The associated fixed points for these conditions are shown in Table 5. We also remark here that in performing calculations in the complex domain, no restrictions were placed on the iterative values of the liquid mole fractions since negative mole fractions do not present the same difficulties (undefined K values) that they do in the real domain. Thus, mole fractions were permitted to be real- or complex-valued and have real parts outside the interval [0, 1]. Of course, the K values were also complex-valued.

Note that Newton's method can exhibit periodic behavior and that the basin of attraction for this periodic cycle is dispersed throughout the basins of attraction for the solutions. Furthermore, we have observed similar behavior for other parameter values. Thus, complexification alone will not improve the reliability of Newton's method on this class of problems, since again both real- or complex-valued starting points can be attracted to stable periodic/apperiodic cycles.

Traditional Dogleg Methods. For the same parametric benzene vapor composition, Figure 8 shows that there is a basin of attraction associated with a real-valued stationary point [a singular point that occurs at $(x, T) = (0.9801, 0.0197, 331.579)$] that is dispersed throughout the basin boundaries. The initial trust region radius used in these computations was 100. Despite the fact that the dogleg strategy removes the periodic behavior associated with Newton's method and usu-

Table 5. Solutions for Dewpoint Temperature Calculation for $y = 0.490$

x (Benzene)	T (K)
0.00152	355.300
$0.9822 + 0.0170i$	$331.591 - 0.0063i$
$0.9822 - 0.0170i$	$331.591 + 0.0063i$

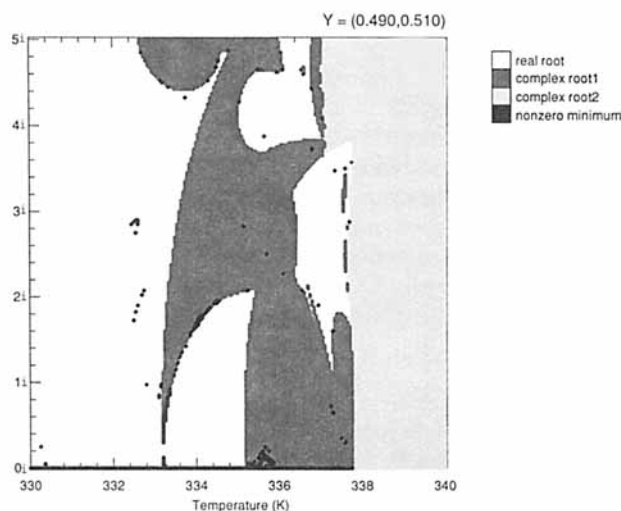


Figure 8. Basins of attraction for original dogleg strategy on dewpoint problem.

ally terminates in under 50 function calls, it actually reduces the size of the basins of attraction of the solutions and therefore performs slightly less reliably than pure Newton's method on this problem. Similar behavior was observed for other parameter values.

Trust Region Methods in the Complex Domain. Figure 9, on the other hand, shows the basins of attraction for the extended trust region method for the same parameter (benzene vapor composition) for an initial trust region radius of 100 and three successive singular point perturbations of $(\Delta x, \Delta T) = (0 + 0.001i, 0 - 0.001i, 0 + 0.001i)$. See the sample calculations in Appendix B. Note that the proposed extension of the dogleg strategy results in the removal of all forms of non-convergent behavior, but again, the fractal nature of the basin boundaries makes it difficult to predict the ultimate fate of any given initial value. We also remark that the number of function calls required for convergence is usually within an acceptable limit, say 100, and that convergence from a singular point to a solution is quite fast (under 10 function calls). Clearly

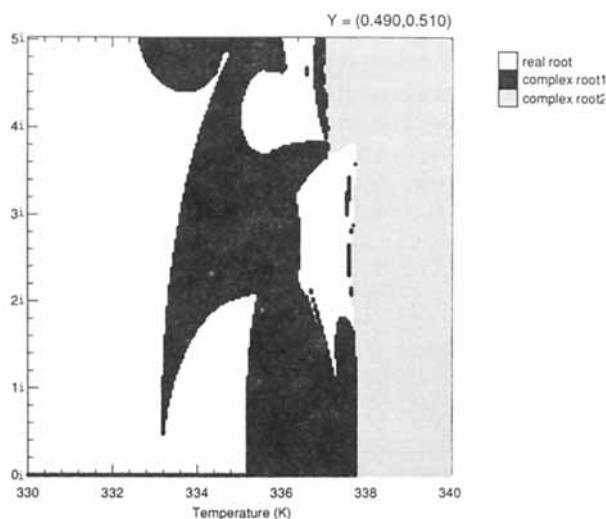


Figure 9. Basins of attraction for extended trust region method on dewpoint problem.

the numerical results show that the proposed extended trust region method is more reliable than Newton's method or the original dogleg strategy.

Concluding Remarks

In this article, chemical process simulation examples were used to show that classical fixed-point methods such as direct substitution and Newton's method can be readily extended to the complex domain. Complexification, however, does not preclude the occurrence of periodic or chaotic behavior from complex-valued starting points. On the other hand, while traditional dogleg strategies can remove cyclic behavior, they can still terminate at singular points.

An extension of Powell's dogleg strategy to the complex domain, which is based on simple norm-reducing singular point perturbation, was proposed and tested on two simple chemical process simulation examples. A large number of numerical results illustrate that the proposed extension is clearly more reliable than either direct substitution, Newton's method or the original dogleg strategy and always appears to converge to a solution to the model equations. However, because of the fractal nature of the basin boundaries, it is difficult to predict the ultimate fate of a given set of initial values in advance.

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Notation

A	= frequency factor
C_p	= specific heat
C, C_0	= concentration, inlet concentration
D	= domain
E	= activation energy
$F(Z, p)$	= complex-valued vector function
$G(Z, p)$	= complex-valued fixed-point mapping
ΔH	= heat of reaction
K	= vector of complex-valued K values
p	= parameter value
T, T_0	= temperature, inlet temperature
x	= vector of complex-valued mole fractions
X	= conversion
y	= vapor phase mole fractions
Z	= vector of complex variables

Greek letters

β	= dogleg parameter
ρ	= density
θ	= residence time

Subscripts

i	= component index
k	= iteration counter

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Appendix A: Glossary of Mathematical Terms

This appendix contains definitions of common terminology used in the study of nonlinear iterative maps of the general form:

$$Z_{k+1} = G(Z_k, p)$$

for finding a solution to $F(Z, p) = 0$, where Z is a vector in some space D , p is a scalar parameter, and F is twice continuously differentiable function defined on D .

aperiodic behavior—any bounded set of iterates for which there is no asymptotically repeating pattern

basin of attraction—set of initial values that are attracted to (or ultimately wind up) either at a fixed-point or in a periodic/chaotic cycle

Cauchy step—direction given by $\phi'(Z, p)$, where ϕ is the function $\phi = F'\bar{F}$ and \bar{F} denotes the complex conjugate of F . The gradient and Cauchy step are synonymous; the steepest descent step is the negative of the Cauchy direction.

chaotic behavior—same as aperiodic behavior.

composite map— $G^2(Z, p) = G[G(Z, p)]$, $G^3(Z, p) = G\{G \times [G(Z, p)]\}$, and so on

critical point—any point Z such that $G'(Z, p) = 0$, where G is a function of a single complex variable

critical manifold—a space generated from Z such that $\det[G'(Z, p)] = 0$, where $G'(Z, p)$ is the Jacobian matrix of G

fixed point—any point, say Z^* , such that $Z^* = G(Z^*, p)$

fractal geometry—a nonEuclidean geometry in which the (Hausdorff) dimension of the space can take on fractional values

Julia set—set of initial values (basin of attraction) attracted to a periodic or chaotic cycle

periodic behavior—a finite set of asymptotically repetitive values, say $\{Z_1, Z_2, \dots, Z_m\}$, such that $Z_2 = G(Z_1, p)$, $Z_3 = G(Z_2, p)$, ..., $Z_1 = G(Z_m, p)$. Alternately, for any m cycle, there exists an integer $K < \infty$ such that $Z_{im+K+j-1} = Z_{(i-1)m+K+j-1} = G^{(i-1)m+K+j-2}(Z, p)$, for $i = 1, \dots$ and $j = 1, \dots, m$

saddlepoint—any point Z such that $F''(Z, p) = 0$, where F is a function of a single complex variable

singular point—any point Z such that $F'(Z, p) = 0$ or $\det[J(Z, p)] = 0$, where J is the Jacobian matrix of F

spectral radius—eigenvalue of largest absolute value: that is, $\rho[G'(Z, p)] = \max_{1 \leq i \leq n} |\lambda_i[G'(Z, p)]|$, where λ_i is an eigenvalue of $G'(Z, p)$

stable—any iterative map for which the spectral radius of the associated Jacobian matrix of that map is less than one at a point (or points) of interest. For example, if $Z^* = G(Z^*, p)$ and $\rho[G'(Z^*, p)] < 1$, then Z^* is a stable (or attracting) fixed-point. Otherwise, Z^* is an unstable (or repelling) fixed-point. If Z_1 and Z_2 are the asymptotic values of a 2-cycle, and $\rho[G^2(Z_1, p)] < 1$ and $\rho[G^2(Z_2, p)] < 1$, then the 2-cycle is stable, and so on

stationary point—any point Z such that $\phi'(Z, p) = 0$. Stationary points can be minima, maxima or saddlepoints. Note that a critical point is necessarily a stationary point of the iterative map G in the single variable case

trust region—region in which the affine (linear + translation) approximation of $F(Z, p) = F(Z_k, p) + J(Z_k, p)(Z - Z_k)$ is trusted. The size of the trust region is usually denoted by the trust region radius Δ

two-norm—for any vector Z , $\|Z\|_2 = \left(\sum_{i=1}^n Z_i^2\right)^{1/2}$, where Z_i

is the i th component of the vector.

Appendix B: Sample Calculations in the Complex Domain

Iterative output is presented here for a sample dewpoint

Table B1. Iterative Values of Unknowns for Dewpoint Temperature Calculation for $y = 0.490$

Iteration No.	Temperature (K)	Liquid Composition*	Step
0	333.100 + 0.00i	0.30000 + 0.00i	dogleg
1	313.952 + 0.00i	0.96858 + 0.00i	Newton
2	325.838 + 0.00i	0.87418 + 0.00i	Newton
3	330.906 + 0.00i	0.89327 + 0.00i	Newton
4	331.577 + 0.00i	0.93093 + 0.00i	Newton
5	331.589 + 0.00i	0.96101 + 0.00i	Newton
6	331.588 + 0.00i	0.97987 + 0.00i	dogleg
7	331.585 + 0.00i	0.98415 + 0.00i	dogleg
8	331.589 + 0.00i	0.98010 + 0.00i	perturbation
9	331.589 + 0.00100i	0.98010 - 0.001i	perturbation
10	331.589 + 0.00200i	0.98010 - 0.002i	perturbation
11	331.589 + 0.00300i	0.98010 - 0.003i	dogleg
12	331.589 + 0.00892i	0.98130 - 0.013i	Newton
13	331.591 + 0.00667i	0.98230 - 0.017i	Newton
14	331.591 + 0.00634i	0.98223 - 1.698i	

Table B2. Iterative Function and K Values for Dewpoint Temperature Calculation

Iteration No.	Function Values			K Values*	
				Benzene	Water
0	0.49475 + 0.00000i	-0.26530 + 0.00000i	0.00000 + 0.00000i	3.28250 + 0.00000i	0.34957 + 0.00000i
1	-0.20780 + 0.00000i	-0.29206 + 0.00000i	-0.10657 + 0.00000i	0.29135 + 0.00000i	1.57943 + 0.00000i
2	-0.08787 + 0.00000i	-0.15719 + 0.00000i	0.00000 + 0.00000i	0.46001 + 0.00000i	2.80415 + 0.00000i
3	-0.00901 + 0.00000i	-0.05522 + 0.00000i	0.00000 + 0.00000i	0.53846 + 0.00000i	4.26096 + 0.00000i
4	0.00071 + 0.00000i	-0.02360 + 0.00000i	0.00000 + 0.00000i	0.52647 + 0.00000i	7.16267 + 0.00000i
5	0.00025 + 0.00000i	-0.01183 + 0.00000i	0.00000 + 0.00000i	0.51014 + 0.00000i	12.7783 + 0.00000i
6	0.00017 + 0.00000i	-0.01044 + 0.00000i	0.00000 + 0.00000i	0.50024 + 0.00000i	24.8222 + 0.00000i
7	0.00011 + 0.00000i	-0.01421 + 0.00000i	0.00016 + 0.00000i	0.49800 + 0.00000i	31.6137 + 0.00000i
8	0.00011 + 0.00000i	-0.01069 + 0.00000i	0.00016 + 0.00000i	0.50006 + 0.00000i	25.2982 + 0.00000i
9	0.00011 + 0.00000i	-0.01063 + 0.00053i	0.00016 + 0.00000i	0.50006 + 0.00052i	25.2380 - 1.25201i
10	0.00011 + 0.00001i	-0.01044 + 0.00103i	0.00016 + 0.00000i	0.50005 + 0.00104i	25.0591 - 2.48702i
11	0.00011 + 0.00002i	-0.01013 + 0.00149i	0.00016 + 0.00000i	0.50005 + 0.00155i	24.7661 - 3.68873i
12	-0.00003 + 0.00005i	-0.00263 + 0.00170i	0.00013 + 0.00002i	0.49921 + 0.00707i	17.6634 - 13.0137i
13	-0.00001 + 0.00001i	-0.00021 + 0.00017i	0.00000 + 0.00000i	0.49867 + 0.00877i	14.7706 - 14.4206i
14	0.00000 + 0.00000i	0.00000 + 0.00000i	0.00000 + 0.00000i	0.49872 + 0.00862i	15.0047 - 14.3339i

*Calculated using models and data in Prausnitz et al. (1980).

temperature calculation for the extended dogleg method. In particular, given a vapor mixture of 49% benzene and 51% water at atmospheric pressure, we wish to calculate the dewpoint temperature and incipient liquid-phase composition, assuming both phases are nonideal. In addition, the initial trust region radius is set equal to 10^2 and the convergence tolerance, ϵ , is 10^{-6} .

This problem has three solutions, one real-valued and two complex conjugate, as shown in Table 5. Here, we present results for one of the complex solutions. Iterative values of dewpoint temperature and liquid composition are shown in Table B1. Corresponding function values (see Eqs. 7 and 8) and equilibrium ratios are given in Table B2. At iteration 8, $\|\phi'\|_2 = 6.096 \times 10^{-5} < 10^{-4} = 10^2\epsilon$, $\|\Delta Z_N\|_2 = 1.937 > 10^{-1} = 10^5\epsilon$ and $\|F\|_2 = 5.031 \times 10^{-4} > 10^{-6} = \epsilon$; as a consequence, the algorithm identifies the 8th iterate as an approximate singular

point. The trust region radius has also been reduced to a value of $\Delta_g = 1.851$. Perturbations of a magnitude of 10^{-3} are made in the imaginary components of the variables in an effort to find a point whose corresponding function values have a two-norm less than 5.031×10^{-4} . After three perturbations of $0 + 10^{-3}i$, $0 - 10^{-3}i$ and $0 + 10^{-3}i$ in benzene composition, water composition and temperature respectively, $\|F\|_2$ was reduced to a value of 5.011×10^{-4} . Also note that these perturbations are orthogonal to the Cauchy direction at the approximate singular point since it is real-valued. The perturbations and the remaining iterates are summarized in the continuation of Table B1. It is a simple matter of substitution to verify that the last iterate in Table B1 satisfies the model equations (Eqs. 7 and 8) for the dewpoint temperature calculation.

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