Smoothing Methods for Complementarity Problems in Process Engineering

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Complementarity is central to all constrained optimization problems. However, direct enforcement of complementarity conditions is difficult because of the inherent nondifferentiability associated with them. Here, a class of smoothing methods for solving the complementarity problem by using a continuation algorithm to solve nonlinear equations is studied. The applicability of smoothing methods to approximate complicated nested derivative discontinuities is investigated using simple functions with a single smoothing parameter. In addition, an equation-based formulation for solving the phase equilibrium problem with complementarity conditions is formulated. This approach can model the appearance and disappearance of phases directly in phase equilibrium problems. Moreover, it is shown how smoothing methods can be used to solve limiting distillation cases, such as dry and vaporless trays, modeled within an equation-based formulation.

Introduction

Chemical process industries require the solution of (constrained) nonlinear programming problems as part of current process-synthesis, design, optimization, and control activities. A variety of implementations based on successive quadratic programming (SQP) (Biegler et al., 1995) and reduced-gradient methods (Murtagh and Saunders, 1982) have been developed for the solution of the nonlinear programming problems. An interesting problem in this class is the efficient treatment of the complementarity conditions arising from the direct solution of the Karush-Kuhn-Tucker (KKT) conditions of the optimization problem. However, direct enforcement of the complementarity conditions could be problematic because of the inherent nondifferentiability and singularities associated with these functions.

In related work (Albuquerque et al., 1997), we investigated the applicability of interior point methods to overcome the computational complexity associated with active-set methods to process optimization. To summarize, primal–dual interior point methods solve the complementarity conditions (Eq. 1) approximately, where at each iteration an approximation to complementarity, (Eq. 2) is solved for $K > 0$. K is reduced at each iteration until the original problem is solved:

$$x_k y_k = 0 \qquad k = 1. \ldots, n$$
$$x, y \geq 0 \tag{1}$$
$$x_k y_k = K \qquad k = 1, \ldots, n$$
$$x, y > 0. \tag{2}$$

Looking at this exercise from a different angle, interior-point methods solve the complementarity problem, which is nonsmooth at the origin, by solving a sequence of smooth approximations to it. From that standpoint, primary–dual interior-point methods can be considered as a special case of a larger class of smoothing methods used in process engineering. Moreover, interior-point methods and their potential to solve a variety of problems (Albuquerque et al., 1999; Gopal and Biegler, 1998; Wright, 1997) motivated us to look at smoothing methods in general and their applicability to process engineering. In this article, we focus our attention on the properties and the applicability of smoothing methods to address the following issues in chemical process engineering:

- Complementarity conditions modeling implicit discontinuities
- Nondifferentiabilities, especially in nested functions
- Specialization to phase-equilibrium problems.

Complementarity is central to all constrained optimization problems because it defines active constraints at the opti-

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mum point. An efficient method for the solution of the complementarity problem has wide implications in process engineering. Moreover, a broad variety of applications of complementarity problems in engineering and economics is described in Ferris and Pang (1995).

Consider, for example a general nonlinear programming problem of the form (Eq. 3):

$$\begin{aligned} \text{Min} \quad & f(x) \\ \text{s.t.} \quad & h(x) = 0 \\ & g(x) \geq 0 \end{aligned} \tag{3}$$

$x \in \Re^n$, $h \in \Re^m$, $g \in \Re^r$. The KKT conditions of Eq. 3 are given by Eq. 4. $\lambda \in \Re^m$, $\upsilon \in \Re^r$:

$$\begin{aligned} \nabla f(x) - \nabla h(x)\lambda - \nabla g(x)\nu &= 0 \\ h(x) &= 0 \\ g(x) &\geq 0 \\ \nu_k g_k(x) &= 0 \qquad k = 1, \ldots, r \\ \nu &\geq 0 \end{aligned} \tag{4}$$

Direct solution of the KKT conditions requires an efficient way of handling the complementarity conditions $\nu_k g_k = 0$ and the nonnegativity constraints ν, $g(x) \geq 0$.

In this article, the focus will be on formulating and solving the complementarity conditions that model applications outlined in our previous work (Gopal and Biegler, 1997). In the next section we show that reformulation of the complementarity constraints along with smoothing forms an efficient framework for the solution of this problem, while taking care of the nonnegativity constraints implicitly. The interior-point method described in Albuquerque et al. (1997) could be considered as a special class of smoothing methods, for the solution of the complementarity problem in the solution of the KKT conditions. The third section presents several formulations that substitute for nondifferentiable functions and involve smoothing functions. In the fourth section, we describe the applicability of smoothing methods to the solution of flash and distillation models, and the fifth section concludes the article.

Complementarity and Smoothing Functions

Consider the general complementarity and nonnegativity conditions of the form Eq. 1. Equation 1 could be represented by the following notation:

$$0 \leq x \perp y \geq 0, \tag{5}$$

and from Chen and Mangasarian (1996), Eq. 5 could be expressed equivalently as Eq. 6,

$$x_k = (x_k - y_k)_+, \tag{6}$$

where the $+$ function is defined as

$$\xi_+ = \max(0, \xi). \tag{7}$$

Note that the nonnegativity conditions are implicitly enforced within Eq. 6. Hence no additional procedure is required in the algorithm to keep x and y nonnegative. However, the $+$ function is nondifferentiable, as it involves the nonsmooth max operator. To deal with the nondifferentiability of this operator, Chen and Mangasarian (1996) describe a class of smoothing methods for the treatment of complementarity conditions, which we briefly outline below.

Properties of smoothing functions

Consider a piecewise-continuous distribution function $d(x)$ that satisfies the properties (Eq. 8):

$$d(x) \geq 0 \qquad \text{and} \qquad \int_{-\infty}^{+\infty} d(x)\, dx = 1. \tag{8}$$

The density function $d(x)$ can be used to derive smooth approximations $\hat{t}(x)$ for the Dirac Delta function $\delta(x)$ (Eq. 9). Also, we have $\hat{s}(x)$ for the step function $\sigma(x)$ (Eq. 10), and $\hat{p}(x)$ for the plus function $(x)_+$ (Eq. 11). Here β is a small positive parameter in these equations, and the approximations approach their nonsmooth counterparts as β approaches zero:

$$\hat{t}(x, \beta) = \frac{1}{\beta} d\left(\frac{x}{\beta}\right) \approx \delta(x) \tag{9}$$

$$\hat{s}(x, \beta) = \int_{-\infty}^{\infty} \hat{t}(t, \beta)\, dt \approx \sigma(x) \tag{10}$$

$$\hat{p}(x, \beta) = \int_{-\infty}^{\infty} \hat{s}(t, \beta)\, dt \approx (x)_+. \tag{11}$$

To deal with the complementarity problem, the smooth approximation to the complementarity condition (Eq. 6) is given by Eq. 12:

$$x_k - \hat{p}(x_k - y_k, \beta) = 0. \tag{12}$$

We now consider some of the key theoretical properties of the smooth formulation. Lemma 1 and Proposition 2 look at properties of the smooth function $\hat{p}(x, \beta)$. They also establish error bounds on the residual of the smooth approximation of the complementarity condition. The proofs are given in the cited references.

Lemma 1. (Chen and Mangasarian, 1996). Let $d(x)$ be a probability density function that satisfies the following:

(A**1**) $d(x)$ is piecewise continuous with a finite number of pieces and satisfies Eq. 8.

(A**2′**) $\mathrm{E}[|x|]_{d(x)} = \int_{-\infty}^{+\infty} |x| d(x)\, dx < +\infty$ and $\hat{t}(x, \beta)$ is defined as in Eq. 9. Then

- (P**1**) $\hat{p}(x, \beta)$ is continuously differentiable.
- (P**2′**) $-D_2 \beta \leq \hat{p}(x, \beta) - (x)_+ \leq D_1 \beta$, where

$$D_1 = \int_{-\infty}^{0} |x| d(x)\, dx$$

$$D_2 = \max\left\{\int_{-\infty}^{+\infty} x d(x)\, dx, 0\right\}. \tag{13}$$

• (P3′) $\hat{p}(x,\beta)$ is nondecreasing and convex.

• (A3) If the support, supp $d(x)=\Re$, then (P3) $\hat{p}(x,\beta)$ is strictly increasing and strictly convex.

• (P5) $\| x-(x-F(x))_+ \|_p \le \| x-\hat{p}(x-F(x),\ \beta)\ \|_p + \gamma_p \max\{D_1,\ D_2\}\beta$, where γ_p is a constant based on the vector norm.

Property (P5) shows that the residual of the nonlinear complementarity problem is bounded by that of the smooth equation. Chen and Harker (1997) introduced additional conditions (A2), (A4), on $d(x)$ and identified a subclass of these functions that satisfy properties (P2) and (P4) below:

(A2) $\lim_{x\to\infty} x^3 d(x) < \infty$ and $\lim_{x\to\infty} x^3 d(-x) < \infty$.

(A4) $\int_{-\infty}^{+\infty} x d(x)dx = 0$.

(P2) $0 \le \hat{p}(x,\beta) - (x)_+ \le b(\beta)$, where $b(0)=0$ and $\lim_{\beta\to\infty} b(\beta)=\infty$.

(P4) $\lim_{x\to\infty}(\hat{p}(x,\beta)+\hat{p}(-x,\beta)-x)x<\infty \qquad 0<\beta<\infty$.

Chen and Harker (1997) showed that (A2) $\Rightarrow$ (A2′) and (P2) becomes (P2′) with $D_2=0$ and $b(\beta)=D_1\beta$. They also show that any $\hat{p}(x,\beta)$ satisfying properties (P2)–(P4) can be described in terms of a density function satisfying Eq. 8. Proposition 1 shows the boundedness and uniqueness of the solution trajectory.

Proposition 1. (Chen and Harker, 1997). Let the function $\hat{p}(x,\beta)$ satisfy (P2)–(P4). Then

• Let $x=\hat{p}(x-y,\beta)$ for some $0\le\beta<\infty$. Then $x\ge 0$, $y\ge 0$ and $xy\le B$, for some $0\le B<\infty$.

• Given any $x\ge 0$, $y\ge 0$, there exists a unique $\beta\ge 0$ such that $x=\hat{p}(x-y,\beta)$.

Examples of smoothing functions

The preceding subsection summarizes some of the key properties of smooth approximations, derived from distribution functions from Chen and Harker (1997) and Chen and Mangasarian (1996), for the complementarity problem. In this subsection we consider two specific classes of smoothing functions that could be described in terms of distribution functions satisfying Eq. 8. They will be used to solve application problems in the subsequent sections.

Sigmoidal Function. The sigmoidal distribution function (Eq. 14), frequently used with neural networks, is analyzed in detail in Chen and Mangasarian (1996). For this function $D_1=\log 2$ and $D_2=0$ in Eq. 13, and the smooth plus function is given by Eq. 15:

$$d(x)=\frac{e^{-x}}{(1+e^{-x})^2} \tag{14}$$

$$\max(0,\ x)\approx \hat{p}(x,\ \beta)=x+\beta\ln(1+e^{-(x/\beta)}). \tag{15}$$

Theorem 1 establishes an arbitrarily accurate solution to the smooth nonlinear equation arising from the sigmoidal function for any solvable linear, nonlinear, or mixed complementarity problem.

Theorem 1. (Chen and Mangasarian, 1996): If $x,y\in R$ satisfy

$$-\frac{\delta_1}{\beta}\le x-p(x-y,\ \beta)\le 0, \tag{16}$$

where $\delta_1\ge 0$. Then

$$(-x)_+\le\delta_1\beta, \qquad (-y)_+\le\delta_1\beta,$$
$$(xy)_+\le\max\{2,\ (e^{\delta_1}-1)\log^2(e^{\delta_1}-1)\}\beta^2.$$

For all $\delta_1\ge D_1$, Eq. 16 has a solution for $\beta>0$. Hence a solution of this system of inequalities is an approximate solution to the complementarity problem.

Interior-Point Smooth Approximation. Consider the smooth approximation by Balakrishna and Biegler (1992). Here

$$d(x)=\frac{1}{2(x^2+1)^{3/2}} \tag{17}$$

$$\max(0,\ x)\approx\hat{p}(x,\ \beta)=\frac{x+(x^2+\beta^2)^{1/2}}{2}. \tag{18}$$

For this function $D_1=1/2$ and $D_2=0$. This smooth function is similar in form to those described in (Chen and Harker, 1997; Kanzow, 1994; Smale, 1987). It can be shown along the lines of Kanzow (1994) that the smooth approximation (Eq. 19) to the complementarity condition will be satisfied if and only if Eq. 20 is satisfied. Hence, this is referred to as the *interior-point* smooth approximation.

$$x=\frac{x-y+\left((x-y)^2+\beta^2\right)^{1/2}}{2} \tag{19}$$

$$x>0, \qquad y>0, \qquad xy=\beta^2/4. \tag{20}$$

Both smoothing functions are shown in Figure 1a and 1b for $\beta=1$ and $\beta=0.01$, respectively. Note that the deviation at the origin is less for the interior-point function ($\beta/2$) than for the sigmoidal function ($\beta\log 2$), but the deviation for the sigmoidal function decays more rapidly away from the origin.

Implementation

We consider two algorithms for the solution of systems of nonlinear equations (NLPs) with the smoothing functions described previously.

A Continuation Method. A continuation method reduces the parameter β in the smooth equations gradually until the original complementarity problem is solved within certain error criteria. A general framework for the implementation of a continuation method is as follows (Chen and Harker, 1997; Chen and Mangasarian, 1996):

Algorithm 1. Let $r(x^i)$ be the residual of the original complementarity problem and $R(x^i,\beta^i)$ be that of the smoothed equations with a tolerance ϵ, a positive constant K and $\eta\in(0,\ 1)$. Set the iteration counter i to zero.

1. If $\| r(x^i)\ \| \le \epsilon$, then x^i is an approximate solution to the complementarity problem.

2. Determine search direction Δx^i from the smooth equation and find next point x^{i+1} using an equation-solving technique (for example, Newton)

3. If $\| R(x^{i+1},\ \beta i)\ \| \le K\|\beta^i\|$, then
$\beta^{i+1}=\eta\beta^i$. Else, $\beta^{i+1}=\beta^i$.
$i=i+1$. Goto 1.

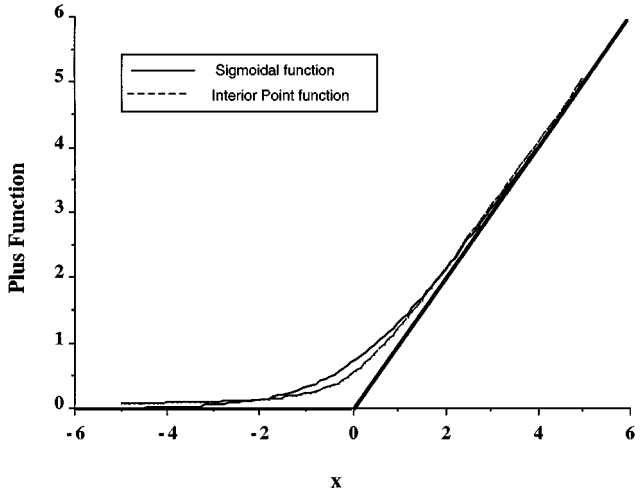

Figure 1a. Smoothing functions for $\beta = 1$.

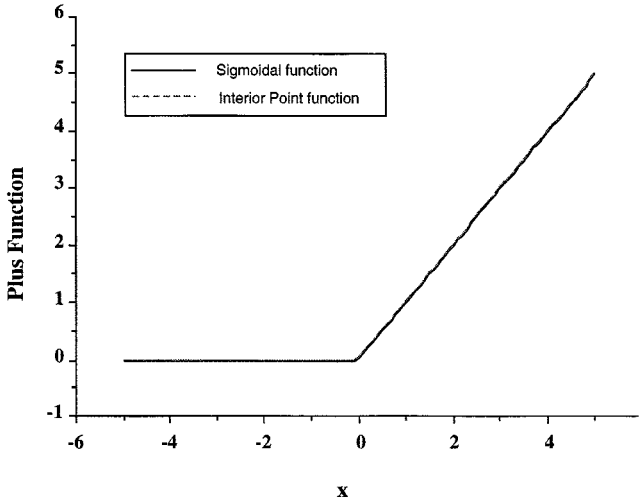

Figure 1b. Smoothing functions for $\beta = 0.01$.

Modified Framework. In the modified framework, an approximate solution of the smooth equations ($\| R(x, \beta^i) \| \leq \epsilon$) is determined for a fixed value of β in step 2. Here a loose tolerance, ϵ, is progressively tightened as β is reduced. Using the solution from step 2 as an initial point, β is reduced systematically in step 3 until the original set of equations is satisfied with a certain error. As a result, the Newton method in step 2 of the continuation method is substituted by a more general equation solver.

Although the continuation method of Algorithm 1 is expected to give more efficient performance, the modified framework was considered for ease of implementation within modeling languages like GAMS. The error criterion for termination of the subproblem for a fixed β is set proportional to β. This leads to better treatment of nonstrict complementarity problems, which arise in example problems in the Example section. In case of nonstrict complementarity, where both terms in Eq. 1 go to zero, the smoothed equations (Eq. 12) cannot be satisfied exactly for nonzero values of β. An approximate solution at nonzero β overcomes this problem. In the next section, we consider the solution of nonlinear equations with explicit nondifferentiabilities using smoothing function. We defer the solution of complementarity problems to the fourth section.

Representation of Nondifferentiabilities Using Smoothing Functions

Functions with discontinuous derivatives or *kinks* occur frequently in process problems in chemical engineering. Typical examples are equations of the form of Eq. 21:

$$h\left\{ x,\ \max_j \left[f_j(x) \right] \right\} = 0. \tag{21}$$

Several reformulation strategies of the nondifferentiabilities have been suggested to solve problems of the form of Eq. 21. The smoothing approximations could be used to deal with such nondifferentiable functions appearing in engineering applications. Duran (1984) used a smoothing approximation for approximating functions of the form max[0, $f(x)$]. Below we consider the applicability of the sigmoidal smoothing function described in the section titled ''Sigmoidal Functions.'' The advantage is that the sigmoidal function gives compact closed formulations for a wide variety of these functions that are easily implementable. First, we consider two commonly used functions, the absolute-value operator and the max of n functions.

Absolute-value operator

Let

$$y_{\text{abs}} = \text{abs}(x). \tag{22}$$

Define

$$\alpha = \frac{1}{\beta}. \tag{23}$$

From Eq. 22, we have for the sigmoidal function:

$$\begin{aligned} y_{\text{abs}} &= \max(x, -x) \\ &= \max(0, x) + \max(0, -x) \\ &\approx x + \frac{1}{\alpha}\ln(1 + e^{-\alpha x}) - x + \frac{1}{\alpha}\ln(1 + e^{\alpha x}) \\ &= \frac{1}{\alpha}\ln(2 + e^{\alpha x} + e^{-\alpha x}). \end{aligned} \tag{24}$$

Similarly for the interior point function, the absolute-value function is approximated by

$$\begin{aligned} y_{\text{abs}} &= \max(x, -x) \\ &= \max(0, x) + \max(0, -x) \\ &\approx \left(x^2 + \beta^2\right)^{1/2}. \end{aligned} \tag{25}$$

Max of n functions

Let

$$y_{\max} + \max(f_1, f_2, \ldots, f_k, \ldots, f_n). \tag{26}$$

The preceding function could have many nondifferentiable points instead of just one nondifferentiable point, the origin, as in Eqs. 7 and 22. However, a smooth approximation could be derived for the preceding max function based on just one smoothing parameter.

Proposition 2. Using the sigmoidal function, a smooth approximation to Eq. 26 is given by

$$\max(f_1, f_2, \ldots, f_k, \ldots, f_n) \approx f_k + \frac{1}{\alpha}\ln\left(1 + \sum_{i=1, i\neq k}^{n} e^{-\alpha(f_k - f_i)}\right) \tag{27}$$

for any $1 \le k \le n$.

Proof. See Appendix A.

This result leads immediately to two important cases.

- Using this property, the absolute value operator (Eq. 22) could also be expressed using Eq. 88 as

$$y_{\text{abs}} = \text{abs}(x) \approx x + \frac{1}{\alpha}\ln(1 + e^{-2\alpha x}). \tag{28}$$

Note the approximation error in Eq. 28 is better than in Eq. 24. For example, the error at the origin is $(\ln 2/\alpha)$ in Eq. 28 as opposed to $(\ln 4/\alpha)$ in Eq. 24.

- Min of *n* functions can also be expressed similarly:

$$\begin{aligned}\min(f_1, f_2, \ldots, f_k, \ldots, f_n) &= -\max(-f_1, -f_2, \ldots, -f_k, \ldots, -f_n)\\ &\overset{\text{(Eq. 27)}}{\approx} -\left[-f_k + \frac{1}{\alpha}\ln\left(1 + \sum_{i=1, i\neq k}^{n} e^{-\alpha(-f_k + f_i)}\right)\right]\\ &= f_k - \frac{1}{\alpha}\ln\left(1 + \sum_{i=1, i\neq k}^{n} e^{-\alpha(f_i - f_k)}\right).\end{aligned} \tag{29}$$

Nested min-max functions

Nested min-max functions, which are otherwise too complicated to represent within an equation-oriented framework, can also be approximated using the preceding smooth formulation, using fairly simple functions. Consider the following form:

- $\max[f_1, f_2, \ldots, f_k, \ldots, f_n, \min(f_{n+1}, \ldots, f_m)]$

$$\begin{aligned}&\max[f_1, f_2, \ldots, f_k, \ldots, f_n, \min(f_{n+1}, \ldots, f_m)]\\ &\approx \max[f_1, f_2, \ldots, f_k, \ldots, f_n, f_K\\ &\quad - \frac{1}{\alpha}\ln\left(1 + \sum_{i=n+1, i\neq K}^{m} e^{-\alpha(f_i - f_K)}\right)\Bigg]\\ &\quad n+1 \le K \le m\\ &\approx f_k + \frac{1}{\alpha}\ln\Bigg[1 + \sum_{j=1, j\neq k}^{n} e^{-\alpha(f_k - f_j)}\\ &\quad + e^{-\alpha\left[f_k - f_K + \frac{1}{\alpha}\ln\left(1 + \sum_{i=n+1, i\neq K}^{m} e^{-\alpha(f_i - f_K)}\right)\right]}\Bigg]\\ &\quad 1 \le k \le n, n+1 \le K \le m\\ &= f_k + \frac{1}{\alpha}\ln\Bigg[1 + \sum_{j=1, j\neq k}^{n} e^{-\alpha(f_k - f_j)}\\ &\quad + \frac{e^{-\alpha(f_k - f_K)}}{1 + \sum_{i=n+1, i\neq K}^{m} e^{-\alpha(f_i - f_K)}}\Bigg]\\ &\quad 1 \le k \le n, n+1 \le K \le m.\end{aligned}$$

Note that the interior-point function can also be applied to these nested nondifferentiable functions, but it leads to approximations that are much more difficult to express in closed form.

Example

To demonstrate the applicability of the smooth approximations to discontinuous functions, the following example problem from Bullard and Biegler (1991) was solved.

Pipeline Network Problem. The pipeline network in Figure 2 has 22 nodes, 38 pipes, and 5 check valves. The set of equations (Eqs. 32) describe the pipeline network.

$$P_i - P_j = H_{ij} \qquad \forall i, j$$

$$KQ_{ij}^2 = \max(0, H_{ij}) \qquad \forall i, j \quad \text{with valves} \tag{30}$$

$$H_{ij} = K\,\text{sign}(Q_{ij})\,Q_{ij}^2 \qquad \forall i, j \quad \text{with no valves} \tag{31}$$

$$\sum_j Q_{ij} + \sum_j Q_{ji} = w_i \qquad \forall i. \tag{32}$$

The presence of the check valves makes the solution of the problem difficult, mainly because of the *open/closed* nature of the valves that introduces nondifferentiabilities. Traditional methods for solving these problems often require an *if−then−else* iterative procedure that solves the problem assuming certain valve positions and resolves them with different valve positions if any conditionals are violated. This pro-

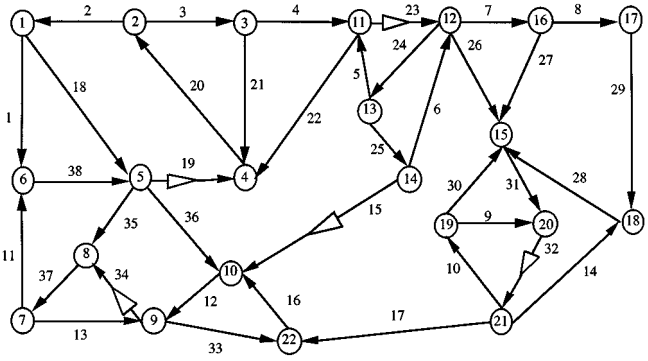

Figure 2. Pipe network with checkvalves.

cedure could be cumbersome and could fail to converge for large systems. Bullard and Biegler (1992) introduced continuous and mixed-integer formulations that handle switching of valve positions through inequality constraints. This approach is more appropriate in an optimization framework; in a pure equation-solving environment, one would like to avoid inequality constraints. Smoothing methods can be used to achieve this objective.

Here Eq. 30 could be approximated using Eq. 15 as

$$KQ_{ij}^2 = H_{ij} + \frac{1}{\alpha}\ln\left(1 + e^{-\alpha H_{ij}}\right), \tag{33}$$

while Eq. 31 has a derivative discontinuity for the second derivative at $Q_{ij} = 0$. For methods using second-order information, it could be approximated as

$$H_{ij} = K\,\text{sign}\left(Q_{ij}\right)Q_{ij}^2 = KQ_{ij}\text{abs}\left(Q_{ij}\right) \approx KQ_{ij}\left[Q_{ij} + \frac{1}{\alpha}\ln\left(1 + e^{-2\alpha Q_{ij}}\right)\right] \tag{34}$$

The data and the listing of the initial guesses could be found in Bullard and Biegler (1992). All the valves were specified as open as initial conditions, although valves in pipes 15, 32, and 34 are closed at the solution of the problem. For the pipeline network with five valves and with $\alpha = 1/\beta = 10^4$, the smoothing method solved the problem in 16 Newton iterations. The solution to this problem is identical to the one reported in Bullard and Biegler and compares well to the 14 (more expensive) successive MILP and 19 SLP iterations required in that study. Finally, MINOS took 82 iterations to solve the original nonsmooth problem.

Flash and Distillation Models

In Gopal and Biegler (1997) we consider the phase-equilibrium problem as an important class of implicit discontinuities occurring in process simulation. These implicit discontinuities arise from the complementarity conditions that result from the solution of a nonlinear program. Simplified NLP formulations and SLP algorithms for phase equilibrium have been explored in Bullard and Biegler (1993) and Gopal and Biegler (1997). These have also been extended more recently by Han and Rangaiah (1997), Kendlbacher (1993) and Swaney and Kendlbacher (1994). Instead, in this section, we formulate the phase-equilibrium problem as a complementarity problem and solve it using the smoothing techniques described earlier.

Strictly speaking, the solution of phase-equilibrium problems requires a global optimization strategy and the checking of stability criteria. For this purpose, specialized strategies for global optimization have been developed by McDonald and Floudas (1994) and Stadtherr et al. (1995), and these apply bounding strategies that are often more expensive than the application of local methods. We caution that the approach developed here is only a local method and cannot guarantee convergence to a global minimum of the Gibbs free-energy function. However, it is very efficient in finding local solutions, and this can be useful for a variety of applications. First, for flash and separation problems where the problem is well initialized or the Gibbs function is convex (with ideal or Wilson activity coefficient models), it is reasonably certain that our local smoothing approach will obtain the *global solution*. Second, the smoothing approach can also be incorporated within more complex global methods (McDonald and Floudas, 1994; Stadtherr et al., 1995) as an efficient local solver that determines upper bounds for the solution of phase-equilibrium problems.

Phase-equilibrium problems with phase changes

As pointed out in Gopal and Biegler (1997), a basic problem associated with the phase-equilibrium calculations in equation-oriented simulation environments is switching between different phases. Here, different sets of equations are valid depending on the number of phases present at equilibrium. For example, in a two-phase flash, the equilibrium equations are not valid in either of the single-phase regions. To solve this problem, the classic sequential modular approach first guesses the number and nature of the phases present at equilibrium and then solves the corresponding set of equations. If there is no solution, another choice is made. For an equation-oriented environment, on the other hand, such a *procedure-based* approach is not efficient since large systems are solved simultaneously.

In Gopal and Biegler (1997), we addressed this problem for multiphase systems using an optimization formulation (Eq. 35):

$$\begin{aligned}
&\text{Min} \sum_p \delta_p \\
&F - \sum_p M_p = 0 \\
&Fz_i - \sum_p M_p x_i^p = 0 \qquad i = 1,\, n_c \\
&x_i^{p_{\text{ref}}} - \gamma_p K_i^p x_i^p = 0 \qquad p = 1,\, n_p, \qquad p \neq p_{\text{ref}} \qquad i = 1,\, n_c \\
&\sum_i x_i^{p_{ref}} - \sum_i x_i^p = 0 \qquad p = 1,\, n_p, \qquad p \neq p_{\text{ref}} \\
&\delta_p \geq \gamma_p - 1 \qquad p = 1,\, n_p, \qquad p \neq p_{\text{ref}} \\
&\delta_p \geq 1 - \gamma_p \qquad p = 1, n_p, \qquad p \neq p_{\text{ref}} \\
&\delta_p \geq 0 \\
&0 \leq x_i^p \leq 1 \\
&0 \leq M_p \leq F.
\end{aligned} \tag{35}$$

Here M_p is the molar flow rate of phase p, x_i^p is the mole fraction of component i in phase p, and p_{ref} is a reference phase based on which the equilibrium expressions are defined. $\bar{K}_i^p$ is a "pseudo" equilibrium constant, which is defined as $\bar{K}_i^p = \gamma_p K_i^p$, where K_i^p is the equilibrium constant computed at the specified temperature and pressure. The key idea used in the formulation in Gopal and Biegler (1997) is that if two phases do not coexist at equilibrium, then the corresponding equilibrium expression could be relaxed. This was

done by relaxing the equilibrium constant K_i^p in the equilibrium expression (Eq. 36) by introducing the variable γ_p:

$$x_i^{p_{\text{ref}}} - \gamma_p K_i^p x_i^p = 0 \qquad p = 1,\ n_p, \qquad p \neq p_{\text{ref}}. \quad (36)$$

$\delta_p \geq 0$ is defined as the deviation of γ_p from unity through Eq. 37, and the objective function of the optimization formulation is given by $\sum_p \delta_p$:

$$\begin{aligned} \delta_p &\geq \gamma_p - 1 \qquad p = 1,\ n_p, \qquad p \neq p_{\text{ref}} \\ \delta_p &\geq 1 - \gamma_p \qquad p = 1,\ n_p, \qquad p \neq p_{\text{ref}}. \end{aligned} \quad (37)$$

In Gopal and Biegler (1997) this formulation is shown to be equivalent to the KKT conditions for a Gibbs free-energy minimization.

For the two-phase problem, Eq. 35 could be simplified to Eq. 38:

$$\begin{aligned} &\text{Min } \delta \\ \text{s.t.} \quad & F - L - V = 0 \\ & Fz_i - Lx_i - Vy_i = 0 \qquad i = 1,\ n \\ & y_i - \gamma K_i(P,\ T,\ x)\, x_i = 0 \qquad i = 1,\ n \\ & \sum_i y_i - \sum_i x_i = 0 \\ & \delta \geq \gamma - 1 \\ & \delta \geq 1 - \gamma \\ & \delta \geq 0 \\ & 0 \leq x_i,\ y_i \leq 1 \\ & 0 \leq L,\ V \leq F. \end{aligned} \quad (38)$$

The equilibrium expression is given by Eq. 39, where δ, the objective function, is defined using inequalities 40:

$$y_i - \gamma K_i(P,\ T,\ x)\, x_i = 0 \qquad i = 1,\ n \quad (39)$$

$$\begin{aligned} \delta &\geq \gamma - 1 \\ \delta &\geq 1 - \gamma. \end{aligned} \quad (40)$$

In Gopal and Biegler (1997), the optimization formulations (Eq. 35), for the multiphase case, and Eq. 38, for the two-phase case, were successfully tested on dynamic simulation example problems from the LLV and LV systems where the number of phases changes with time.

We now consider a simplified equation-based system equivalent to this optimization formulation, that is, we would like to have an equation-based formulation for solving (locally) the phase equilibrium problem, without prior knowledge of the number of phases at equilibrium, or in the likelihood of the phase change in a dynamic problem. The motivation for solving this problem comes from the following:

- Phase-equilibrium problems can be described locally as an equation-based complementarity problem.
- There is a need to enhance currently used equation-based models for phase-equilibrium calculations in process simulators with the capability of addressing the issue of phase transitions.

Equation-based models used in most commercial simulators are formulated for a certain prespecified number and nature of phases. Companies that use these models report failure when there is a change in the phase combinations present. A classic example is dry or vaporless trays in two-phase distillation columns. Models that enforce the existence of both phases are unable to describe such cases and lead to a failure of the simulation or optimization exercise. Therefore, in addition to addressing the more complex problem of finding global solutions, developers are also considering the issue of phase transitions by modifying existing models while still maintaining their basic structure.

We address these issues for two- and three-phase systems in the following subsections.

Two-phase formulation

In this subsection we develop an equation-based formulation for the two-phase system. The following analysis develops the equation-based formulation from the results obtained from the optimization formulation.

Here Eq. 40 can be written as Eq. 41 by introducing slacks s_+, s_- to convert them to equalities:

$$\begin{aligned} -\delta + \gamma - 1 + s_+ &= 0 \\ -\delta - \gamma + 1 + s_- &= 0. \end{aligned} \quad (41)$$

In Gopal and Biegler (1997) we showed that the optimality conditions of Eqs. 38 can be expressed equivalently as the set of equations (Eqs. 42–52):

$$F - L - V = 0 \quad (42)$$

$$Fz_i - Lx_i - Vy_i = 0 \qquad i = 1,n \quad (43)$$

$$y_i - \gamma K_i(P,\ T,\ x)\, x_i = 0 \qquad i = 1,n \quad (44)$$

$$\sum_i y_i - \sum_i x_i = 0 \quad (45)$$

$$-\delta + \gamma - 1 + s_+ = 0 \quad (46)$$

$$-\delta - \gamma + 1 + s_- = 0 \quad (47)$$

$$s_+ L = 0 \quad (48)$$

$$s_- V = 0 \quad (49)$$

$$\delta, s_+, s_- \geq 0 \quad (50)$$

$$0 \leq x_i, y_i \leq 1 \quad (51)$$

$$0 \leq L, V \leq F. \quad (52)$$

In that study, we also showed that Eqs. 42–52 are equivalent to the following relations:

- $\gamma = 1 \Rightarrow \text{L}, \text{V} > 0$
- $\gamma > 1 \Rightarrow \text{V} = 0$
- $\gamma < 1 \Rightarrow \text{L} = 0.$

The key constraints are the complementarity conditions expressed in Eqs. 48 and 49. They could be derived intuitively as follows. Eliminating δ from Eqs. 46 and 47 leads to Eq. 53:

$$\gamma - 1 = (s_- - s_+)/2. \quad (53)$$

Now, from Eq. 53, when $\gamma > 1$, $s_- > 0$, $s_+ = 0$ and $\gamma > 1$ corresponds to the case $V = 0$. Also, when $\gamma < 1$, $s_- = 0$, $s_+ > 0$, which corresponds to $L = 0$. From before, we can see that the pairs (s_-, V) and (s_+, L) are complementary. The final formulation by eliminating δ is given by Eqs. 54–63:

$$F - L - V = 0 \tag{54}$$

$$Fz_i - Lx_i - Vy_i = 0 \qquad i = 1,n \tag{55}$$

$$y_i - \gamma K_i(P, T, x)\, x_i = 0 \qquad i = 1,n \tag{56}$$

$$\sum_i y_i - \sum_i x_i = 0 \tag{57}$$

$$\gamma - 1 = s_- - s_+ \tag{58}$$

$$s_+ L = 0 \tag{59}$$

$$s_- V = 0 \tag{60}$$

$$s_+, s_- \geq 0 \tag{61}$$

$$0 \leq x_i, y_i \leq 1 \tag{62}$$

$$0 \leq L, V \leq F. \tag{63}$$

The methodologies for the efficient treatment of complementarity conditions described in the second section can be used for the solution of the system of equations, Eqs. 54–63.

Formulation of Eqs., 54–63, where the relevant set of equations automatically fall into place for either single-phase or two-phase solutions, is helpful in dealing with these transitions without additional procedures, in the larger context of equation-based process and plant simulation and optimization. A typical equation-oriented simulator or optimizer will have flash models described by Eqs. 54–57 (with γ set to 1). Addition of three equations (Eq. 58–60) and three variables, γ, s_-, s_+, gives it the additional capability of dealing with operation in the single-phase regions. Note that the basic flash model that is already in place, is still used. In the following subsection, we extend this equation-based model to the three-phase problem.

Three-phase formulation

The formulation for the three-phase problem analogous to Eq. 42–52 for the two-phase case is given by Eqs. 64–81:

$$F - L^{\mathrm{I}} - L^{\mathrm{II}} - V = 0 \tag{64}$$

$$Fz_i - L^{\mathrm{I}} x_i^{\mathrm{I}} - L^{\mathrm{II}} x_i^{\mathrm{II}} - Vy_i = 0 \qquad i = 1,n \tag{65}$$

$$y_i - \gamma^{\mathrm{I}} K_i^{\mathrm{I}}(P, T, x)\, x_i^{\mathrm{I}} = 0 \qquad i = 1,n \tag{66}$$

$$y_i - \gamma^{\mathrm{II}} K_i^{\mathrm{II}}(P, T, x)\, x_i^{\mathrm{II}} = 0 \qquad i = 1,n \tag{67}$$

$$\sum_i y_i - \sum_i x_i^{\mathrm{I}} = 0 \tag{68}$$

$$\sum_i y_i - \sum_i x_i^{\mathrm{II}} = 0 \tag{69}$$

$$\gamma^I - 1 = s_-^{\mathrm{I}} - s_+^{\mathrm{I}} \tag{70}$$

$$\gamma^{\mathrm{II}} - 1 = s_-^{\mathrm{II}} - s_+^{\mathrm{II}} \tag{71}$$

$$s_-^{\mathrm{I}} - s_-^{\mathrm{II}} + \theta^{\mathrm{I}} - \theta^{\mathrm{II}} = 0 \tag{72}$$

$$\left(s_+^{\mathrm{I}} + \theta^{\mathrm{I}}\right) L^{\mathrm{I}} = 0 \tag{73}$$

$$\left(s_+^{\mathrm{II}} + \theta^{\mathrm{II}}\right) L^{\mathrm{II}} = 0 \tag{74}$$

$$\left(s_-^{\mathrm{I}} + s_-^{\mathrm{II}}\right) V = 0 \tag{75}$$

$$s_-^{\mathrm{I}}\, s_+^{\mathrm{I}} = 0 \tag{76}$$

$$s_-^{\mathrm{II}}\, s_+^{\mathrm{II}} = 0 \tag{77}$$

$$\theta^{\mathrm{I}} \theta^{\mathrm{II}} = 0 \tag{78}$$

$$\delta^k, s_+^k, s_-^k, \theta^k \geq 0 \tag{79}$$

$$0 \leq x_i, \qquad y_i \leq 1 \tag{80}$$

$$0 \leq L^{\mathrm{I}}, L^{\mathrm{II}}, V \leq F. \tag{81}$$

In Appendix B we show that the preceding formulation is equivalent to the conditions derived for the existence of different phases in Gopal and Biegler (1997) for the optimization formulation.

Examples

In this section, we first consider three flash examples in increasing order of difficulty. The first example is an ideal binary system, while the second is a nonideal five-component system with at most two phases. For both examples we present a family of solutions as a function of flash temperature. In the third example, up to three phases can exist and several solutions are plotted as a function of pressure.

Finally, we consider two distillation systems that arise from the first two flash problems. In a two-phase distillation column, there could exist operating conditions that result in dry or vaporless trays. In the following examples, we consider such cases. The equation-based formulations presented in the previous section are used to model phase equilibrium for each tray. The complementarity conditions are smoothed using the interior-point smoothing function (Eq. 18). The distillation column models are formulated in GAMS (Brooke et al., 1992) and solved using CONOPT (Drud, 1985) using the modified framework described in implementation subsections. Applied to systems of nonlinear equations, CONOPT is equivalent to a general-purpose Newton method without sophisticated damping or modification for ill-conditioning. Also, no attempt is made to exploit the specific structure of the nonlinear equations in these examples.

The modified framework was chosen because of its ease of implementation within GAMS and ready extension to commercial distillation codes. However, it should be noted that a specialized implementation of Algorithm 1 along with a more efficient nonlinear equation solver is expected to decrease the number of iterations reported in this section. The computational times reported for the following examples are for a DEC Alphastation 500/400. Except where noted, all examples were solved to a tolerance of 10^{-9}.

Example 1: ideal Binary Flash. First, we consider a benzene–toluene system with a 50% mole fraction of each component in the feed (at 100 mol/s). The flash calculations were done at a pressure of 1 bar and at temperatures ranging from

Table 1. Solution of Example 1: Ideal Binary Flash with Smoothing Methods

T (K)	Iterations	Time(s)	Liquid Flow	x_B
378	2	0.035	0	0.295
376	2	0.035	0	0.294
374	2	0.036	0	0.292
372	3	0.038	0	0.291
370	5	0.038	23.46	0.333
368	6	0.038	52.58	0.395
366	5	0.037	81.47	0.459
364	10	0.044	100	0.5
362	2	0.037	100	0.5
360	2	0.037	100	0.5
358	2	0.039	100	0.5

358 K to 378 K. The two-phase formulation (Eqs. 42–47) was used to solve the problem with ideal liquid- and vapor-phase models. The problem is initialized at a solution with $T = 378$ K, and a value of 10^{-4} was used for β. The problem was solved in a descending temperature sequence starting from 378 K to 358 K, and the results are shown in Table 1. Also shown are the liquid flow rates and liquid mole fraction for benzene for each case. Note that for $L = 0$, the liquid mole fractions are fictitious.

Example 2: Nonideal Five-Component Flash. Next, we consider a five-component system of methanol, acetone, methyl acetate, benzene, and chloroform with the following mole fractions for each component [0.15, 0.40, 0.05, 0.20, 0.20] in the feed (at 100 mol/s). The flash calculations were done at a pressure of 1 bar and at temperatures ranging from 330 K to 340 K. The two-phase formulation (Eqs. 42–47) was used to solve the problem with a liquid-phase UNIQUAC model and virial equations for the vapor phase. The problem is initialized at a solution with $T = 330$ K, and a value of 10^{-4} was used for β. The problem was solved in an ascending temperature sequence starting from 331 K to 340 K, and the results are shown in Table 2. To show robustness of this approach we also solve the last case (at 331.5 K) starting from the solution at 340 K. Also shown are the liquid flow rates for each case. The liquid mole fractions for the first four components are shown in Figure 3 as a function of temperature.

Example 3: Three-Phase Flash. Here we consider the water–acrylonitrile–acetonitrile system originally described by Wu and Bishnoi (1986). The flash calculations were done at a temperature of 333 K and a feed composition of 0.6, 0.35, and 0.05 for water, acrylonitrile and acetonitrile, respectively. The three-phase formulation (Eqs. 64–81) was used to solve the problem with the liquid phases modeled using a UNI-

Table 2. Solution of Example 2: Nonideal Five Component Flash with Smoothing Methods

T (K)	Iterations	Time(s)	Liquid Flow
331	4	0.042	100
332	7	0.049	68.86
333	18	0.044	37.23
334	14	0.043	9.345
335	8	0.043	0
337	2	0.040	0
340	2	0.040	0
331.5	7	0.056	88.366

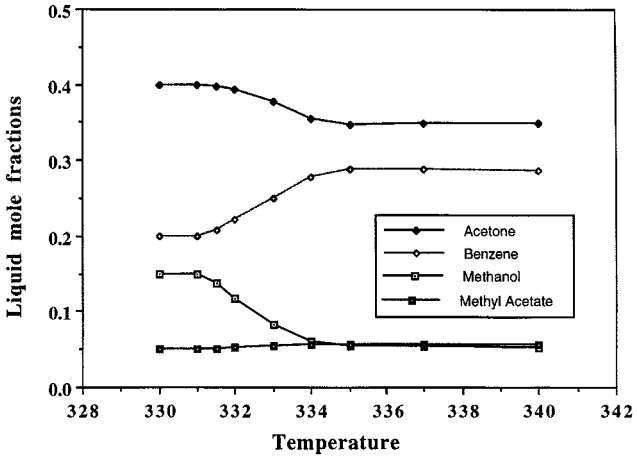

Figure 3. Flash compositions for Example 2.

QUAC model. The problem was initialized with $L_1 = 0.49$, $L_2 = 0.18$, $V = 0.33$, $x_0^1 = [0.95,\ 0.034,\ 0.017]$, $x_0^2 = [0.223,\ 0.668,\ 0.108]$, and $y_0 = [0.285,\ 0.647,\ 0.067]$. The problems were solved in ascending sequence of pressure as shown below.

Three different phase combinations were observed for a pressure range of 0.64 bar to 1.0 bar, as seen in Table 3. Sufficiently accurate solutions were obtained to capture these multiple-phase phenomena successfully with the interior-point smoothing equation (Eq. 18) and with β values ranging from 10^{-2} to 10^{-6}.

Example 4: Binary Two-Phase Ideal Column. In this example we consider a 25-tray distillation column with a saturated liquid feed of 70% benzene–30% toluene to tray 7 (numbered from the bottom), as described in Bullard and Biegler (1993). Ideal thermodynamics are used to model phase equilibrium. The column runs at a condenser pressure of 1.05 bars and a reboiler pressure of 1.2 bars, with linear interpolation between these two for the column trays. The column is initialized with linear interpolations between 0.9 and 0.5 for the liquid mole fractions for benzene, between 0.99 and 0.8 for the vapor mole fractions for benzene, and between 355 and 380 K for the tray temperatures. The tray flow rates are specified as constant based on the feed and distillate flows and the reflux ratio. All other quantities (mole fractions, en-

Table 3. Solution of Example 3: Three-Phase Flash with Smoothing Methods

P (bar)	L_1	L_2	Iterations	Time(s)	β
0.64	0.46	0	24	0.084	0.01
	0.461	0	3	0.043	10^{-4}
	0.461	0	1	0.041	10^{-6}
0.65	0.466	0	8	0.051	10^{-6}
0.66	0.471	0	23	0.066	10^{-6}
0.67	0.476	0	14	0.051	10^{-6}
0.675	0.495	0.216	58	0.13	10^{-6}
0.68	0.523	0.477	47	0.083	10^{-6}
0.70	0.523	0.477	7	0.048	10^{-6}
0.75	0.523	0.477	3	0.044	10^{-6}
0.80	0.523	0.477	3	0.043	10^{-6}
0.90	0.523	0.477	3	0.045	10^{-6}
1.0	0.523	0.477	3	0.046	10^{-6}

Table 4. Solution of Ideal Distillation Column with Decreasing Reflux Ratio

Reflux Ratio	Dry Tray Location	Iterations	Time(s)	β
10	—	13	0.171	0.01
	—	1	0.094	0.0001
	—	1	0.095	10^{-6}
5	—	14	0.113	10^{-6}
2	—	19	0.123	10^{-6}
1	—	7	0.110	10^{-6}
0.1	—	6	0.213	10^{-6}
0.01	—	6	0.096	10^{-6}
0.005	—	3	0.082	10^{-6}
0.001	—	34	0.596	0.1
	—	12	0.238	0.01
	8–25	4	0.108	10^{-4}
	8–25	1	0.075	10^{-6}

Table 5. Solution of Ideal Distillation Column with Decreasing Boilup Rate

Boilup Rate, V_1/B	Vaporless Trays	Iterations	Time(s)	β
10	—	53	0.58	0.01
	—	1	0.079	0.0001
	—	1	0.076	10^{-6}
5	—	6	0.115	10^{-6}
2	—	16	0.107	10^{-6}
1	—	11	0.096	10^{-6}
0.1	—	22	0.205	10^{-6}
0.01	—	6	0.085	10^{-6}
0.005	—	3	0.082	10^{-6}
0.001	—	10	0.122	0.1
	—	8	0.155	0.01
	1–6	4	0.105	10^{-4}
	1–6	1	0.075	10^{-6}

thalpies, etc.) are initialized based on these values.

The overhead recovery of the total feed is specified as 50%, and the column is solved in a descending sequence of reflux ratios from 10 to 10^{-3}. The smoothing parameter β is varied between 0.1 and 10^{-6} for these simulations. Table 4 lists the solution times and problem characteristics for these cases. Figure 4 also shows the liquid flow-rate profiles for this column at various reflux ratios.

Next we consider a saturated vapor feed at its dew point that is also introduced at tray 7, and we consider changes in the boilup rate, V_1/B, where B is the bottoms flow rate. The bottoms recovery of the total feed is specified as 50%, and the column is solved in a descending sequence of the boilup parameter from 10 to 10^{-3}. The smoothing parameter β is varied between 0.1 and 10^{-6} for these simulations. Otherwise, the column is initialized in the same way as in the previous case. Table 5 lists the solution times and problem characteristics for these cases. Figure 5 also shows the vapor flow-rate profiles for this column at various boilup rates.

Example 5: Five-Component Nonideal Column with Decreasing Reflux. The last example, from Bullard and Biegler (1993), is a 17-tray nonideal distillation column with a saturated liquid feed of 15% methanol–40% acetone–5% methacrylate–20% benzene–20% chloroform fed to tray 12 (numbered from the bottom). The liquid phase is modeled with UNIQUAC, and virial equations are used to model the vapor phase. The total overhead recovery of the feed is specified at 0.30. In Table 6, we show the number of iterations for solving the column with different reflux ratios. In this highly nonlinear example, we initialized the column at a reflux ratio of 10 and $\beta = 10^{-3}$, and solved this column with a decreasing sequence of reflux ratios from 10 to 0.00003 and with values of β between 0.1 and 10^{-6}. For this problem, the modified framework with a continuation of β was especially necessary. Between reflux ratios of 0.0005 and 0.0001 the problem was solved with large β values and relaxed tolerances, as described in the implementation subsection. Nevertheless, despite the nonideality of this problem, the solutions cover a wide span of reflux ratios and show the appearance of dry trays above the feed tray for reflux ratios below 0.0005. Figure 6 also shows the liquid flow-rate profiles for various reflux ratios.

Conclusions

This study considers recent developments in the application of smoothing methods to solve nondifferentiable nonlinear equations and nonlinear complementarity problems in

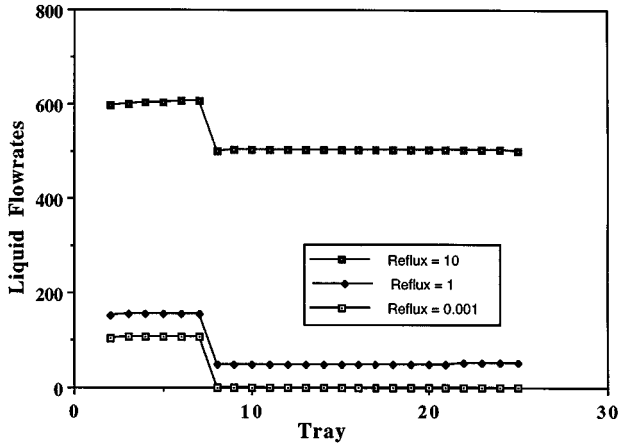

Figure 4. Liquid flow rate profiles for Example 4.

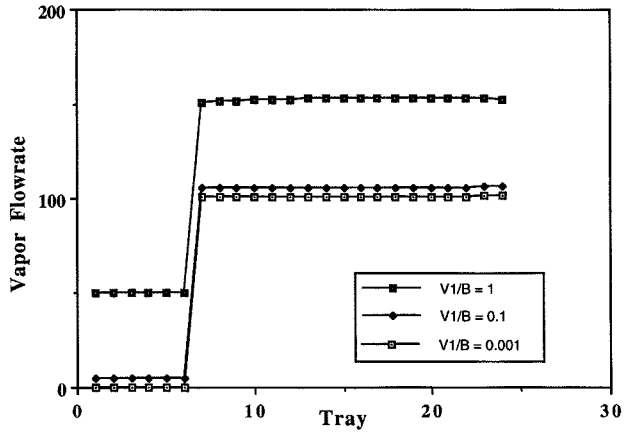

Figure 5. Vapor flow rate profiles for Example 4.

Table 6. Solution of Nonideal Distillation Column with Decreasing Reflux Ratio

Reflux Ratio	Iterations	Time(s)	Dry Trays	β	Tolerance
10	1	0.378	—	10^{-4}	10^{-9}
	4	0.648	—	10^{-5}	10^{-9}
	2	0.529	—	10^{-6}	10^{-9}
5	2	0.715	—	10^{-6}	10^{-9}
2	3	1.065	—	10^{-6}	10^{-9}
1	2	0.871	—	10^{-6}	10^{-9}
0.1	4	1.244	—	10^{-6}	10^{-9}
0.01	2	0.686	—	10^{-6}	10^{-9}
0.005	2	0.538	—	10^{-6}	10^{-9}
0.001	2	0.526	—	10^{-6}	10^{-9}
0.0005	2	0.523	—	10^{-6}	10^{-9}
0.0001	47	2.733	—	10^{-1}	1.48
	35	2.681	—	10^{-2}	0.1458
	1	0.372	13–16	10^{-4}	5.8×10^{-9}
	3	0.530	13–16	10^{-6}	10^{-9}
0.00005	2	0.465	13–16	10^{-6}	10^{-9}
0.00003	4	0.609	13–16	10^{-6}	10^{-9}

process engineering. Here we describe the properties of two well-known smoothing functions, the sigmoidal and interior-point functions, and show how they can be applied directly to solve nondifferentiable nonlinear equations. In particular, simple closed-form expressions were derived for nested derivative discontinuities, using only a single smoothing parameter. Combined with continuation methods, or a modified framework suitable for equation-based systems, smoothing functions can solve nonlinear, nondifferentiable systems of equations to arbitrary accuracy. This was demonstrated on a pipeline network that includes nondifferentiable valve equations.

Moreover, using an equivalence from Chen and Mangasarian (1996), complementarity conditions, $\xi\eta = 0,\ \xi \geq 0,\ \eta \geq 0$ can be written as

$$\xi = \max(0, \xi - \eta),$$

and therefore smoothing functions can be applied directly to nonlinear complementarity problems. In this study an equation-based formulation was derived for phase-equilibrium problem, which uses complementarity conditions to model the appearance and disappearance of phases. By using smoothing methods that are a straightforward extension of existing formulations, this approach is used to model limiting cases of flash and distillation problems. It should be noted, however, that this formulation leads only to local minima of the Gibbs free-energy function and cannot replace global methods for difficult nonideal problems.

Nevertheless, using a general-purpose nonlinear solver in GAMS, the results in this study are very encouraging and show one-, two-, and even three-phase solutions in flash and distillation processes. Even better computational performance can be expected with a more specialized implementation of the ideas described in this article. This is the goal of our future work.

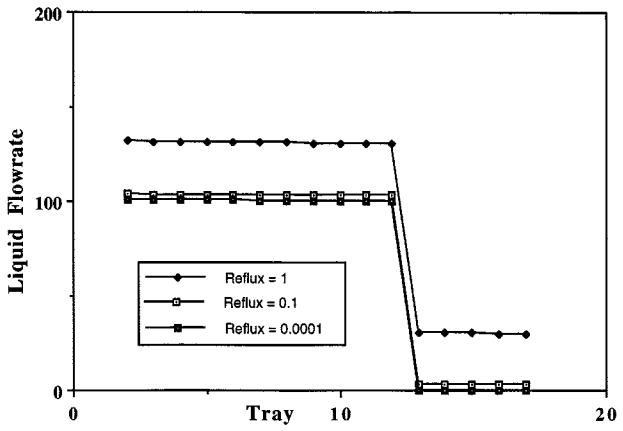

Figure 6. Liquid flow rate profiles for Example 5.

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Appendix A: Proof of Proposition 5

The relation:

$$\max(f_1, f_2, \ldots, f_k, \ldots, f_n) \approx f_k + \frac{1}{\alpha}\ln\left(1+\sum_{i=1, i\neq k}^{n} e^{-\alpha(f_k-f_i)}\right) \quad (82)$$

can be shown by induction, but first we show a supporting result.

Lemma A.1. For any $k \in \{1, \ldots, n\}$ and $\bar{k} \in \{1, \ldots, n\}$ with $k \neq \bar{k}$, we have

$$f_k = \frac{1}{\alpha}\ln\left(1+\sum_{i=1, i\neq k}^{n} e^{-\alpha(f_k-f_i)}\right) = f_{\bar{k}} + \frac{1}{\alpha}\ln\left(1+\sum_{i=1, i\neq \bar{k}}^{n} e^{-\alpha(f_{\bar{k}}-f_i)}\right). \quad (A1)$$

Proof. Subtracting the righthand side of Eq. A1 from the lefthand side leads to

$$f_k - f_{\bar{k}} + \frac{1}{\alpha}\ln\left[\left(1+\sum_{i=1, i\neq k}^{n} e^{-\alpha(f_k-f_i)}\right)\Big/\left(1+\sum_{i=1, i\neq \bar{k}}^{n} e^{-\alpha(f_{\bar{k}}-f_i)}\right)\right], \quad (A2)$$

and since

$$1+\sum_{i=1, i\neq k}^{n} e^{-\alpha(f_k-f_i)} = \sum_{i=1}^{n} e^{-\alpha(f_k-f_i)} = e^{-\alpha(f_k-f_{\bar{k}})}\sum_{i=1}^{n} e^{-\alpha(f_{\bar{k}}-f_i)} = e^{-\alpha(f_k-f_{\bar{k}})}\left(1+\sum_{i=1, i\neq \bar{k}}^{n} e^{-\alpha(f_{\bar{k}}-f_i)}\right). \quad (A3)$$

Substituting Eq. A3 into Eq. A2 leads to

$$f_k - f_{\bar{k}} + \frac{1}{\alpha}\ln(e^{-\alpha(f_k-f_{\bar{k}})}) = (f_k - f_{\bar{k}}) - (f_k - f_{\bar{k}}) \quad (A4)$$

$$= 0. \quad (A5)$$

To continue the proof we consider the induction:

- Max(f_1, f_2)

$$\max(f_1, f_2) = f_1 + \max(0, f_2 - f_1) \overset{\text{(Eq. 15)}}{\approx} f_1 + (f_2 - f_1) + \frac{1}{\alpha}\ln(1+e^{-\alpha(1+\exp(-\alpha(f_2-f_1)))}) = f_2 + \frac{1}{\alpha}\ln(1+e^{-\alpha(f_2-f_1)}). \quad (A6)$$

- Max(f_1, f_2, f_3)

$$\max(f_1, f_2, f_3) = f_1 + \max[0, f_2 - f_1, f_3 - f_1] = f_1 + \max[\max(0, f_2 - f_1), f_3 - f_1] \overset{\text{(Eq. 15)}}{\approx} f_1 + \max\left[f_2 - f_1 + \frac{1}{\alpha}\ln(1+e^{-\alpha(f_2-f_1)}), f_3 - f_1\right] \overset{\text{Eq. A6}}{\approx} f_1 + (f_3 - f_1) + \frac{1}{\alpha}\ln\left[1+e^{-\alpha(f_3-f_2-\frac{1}{\alpha}\ln(1+e^{-\alpha(f_2-f_1)}))}\right] = f_3 + \frac{1}{\alpha}\ln\left[1+e^{-\alpha(f_3-f_2)}(1+e^{-\alpha(f_2-f_1)})\right] = f_3 + \frac{1}{\alpha}\ln[1+e^{-\alpha(f_3-f_2)}+e^{-\alpha(f_3-f_1)}]. \quad (A7)$$

- Now assume that for some n:

$$\max(f_1, f_2, \ldots, f_k, \ldots, f_n) = f_k + \frac{1}{\alpha}\ln\left(1+\sum_{i=1, i\neq k}^{n} e^{-\alpha(f_k-f_i)}\right) \quad (A8)$$

and we need to show that:

$$\max(f_1, f_2, \ldots, f_k, \ldots, f_{n+1}) = f_k + \frac{1}{\alpha}\ln\left(1+\sum_{i=1, i\neq k}^{n+1} e^{-\alpha(f_k-f_i)}\right). \quad (A9)$$

From (Eq. A6) we have that

$$\max(f_1, f_2, \ldots, f_k, \ldots, f_{n+1}) = \max(f_1, f_2, \ldots, f_k, \ldots, f_n) + \max[0, f_{n+1} - \max(f_1, f_2, \ldots, f_k, \ldots, f_n)] \overset{\text{(Eq. 15)}}{\approx} \max(f_1, f_2, \ldots, f_k, \ldots, f_n) + f_{n+1} - \max(f_1, f_2, \ldots, f_k, \ldots, f_n) + \frac{1}{\alpha}\ln[1+e^{-\alpha(f_{n+1}-\max(f_1, f_2, \ldots, f_k, \ldots, f_n))}] \overset{\text{(Eq. A8)}}{\approx} f_{n+1} + \frac{1}{\alpha}\ln\left[1+e^{-\alpha[f_{n+1}-f_k-\frac{1}{\alpha}\ln[1+\sum_{i=1, i\neq k}^{n} e^{-\alpha(f_k-f_i)}]}\right] = f_{n+1} + \frac{1}{\alpha}\ln\left[1+(e^{-\alpha(f_{n+1}-f_k)})\left(\sum_{i=1}^{n} e^{-\alpha(f_k-f_i)}\right)\right] = f_{n+1} + \frac{1}{\alpha}\ln\left(1+\sum_{i=1}^{n} e^{-\alpha(f_{n+1}-f_i)}\right). \quad (A10)$$

Now by Lemma A.1 we can interchange the ordering of f_{n+1} with f_k in order to obtain

$$\max(f_1, f_2, \ldots, f_k, \ldots, f_{n+1}) = f_k + \frac{1}{\alpha}\ln\left(1 + \sum_{i=1, i\neq k}^{n+1} e^{-\alpha(f_k - f_i)}\right). \quad \text{(A11)}$$

Appendix B: Three Phase Problem

From Gopal and Biegler (1997) the following conditions can be derived for the existence of phases for the three-phase problem:

- $\gamma^{\mathrm{I}} > 1$ or $\gamma^{\mathrm{II}} > 1 \Rightarrow \mathrm{V} = 0$.
- $\gamma^{\mathrm{I}} < 1$ or $\gamma^{\mathrm{I}} < \gamma^{\mathrm{II}} \Rightarrow \mathrm{L}^{\mathrm{I}} = 0$.
- $\gamma^{\mathrm{II}} < 1$ or $\gamma^{\mathrm{II}} < \gamma^{\mathrm{I}} \Rightarrow \mathrm{L}^{\mathrm{II}} = 0$.

We will show that the equation-based formulation (Eqs. 64–81) will give identical results.

- $\mathrm{V} = 0$ case

$$\gamma^{\mathrm{I}} > 1 \overset{\text{(Eq. 70)}}{\Rightarrow} s_-^{\mathrm{I}} > 0. \quad \text{(B1)}$$

$$\gamma^{\mathrm{II}} > 1 \overset{\text{(Eq. 71)}}{\Rightarrow} s_-^{\mathrm{II}} > 0. \quad \text{(B2)}$$

Hence the complementarity condition

$$\left(s_-^{\mathrm{I}} + s_-^{\mathrm{II}}\right)V = 0 \quad \text{(B3)}$$

implies $V = 0$ when $\gamma^{\mathrm{I}} > 1$ or $\gamma^{\mathrm{II}} > 1$.

- $L^{\mathrm{I}} = 0$ case

$$\gamma^{\mathrm{I}} < 1 \overset{\text{(Eq. 70)}}{\Rightarrow} s_+^{\mathrm{I}} > 0. \quad \text{(B4)}$$

Now consider the case $1 \le \gamma^{\mathrm{I}} < \gamma^{\mathrm{II}}$. ($\gamma^{\mathrm{I}} < 1$ was covered in the previous condition.) Here $s_+^{\mathrm{I}} = 0$, $s_+^{\mathrm{II}} = 0$ and

$$1 \le \gamma^{\mathrm{I}} < \gamma^{\mathrm{II}} \overset{(70,71)}{\Rightarrow} s_-^{\mathrm{I}} < s_-^{\mathrm{II}} \overset{(72)}{\Rightarrow} \theta^{\mathrm{I}} > 0. \quad \text{(B5)}$$

The complementarity condition

$$\left(s_+^{\mathrm{I}} + \theta^{\mathrm{I}}\right)L^{\mathrm{I}} = 0 \Rightarrow L^{\mathrm{I}} = 0 \quad \text{for} \quad s_+^{\mathrm{I}} > 0 \text{ or } \theta^{\mathrm{I}} > 0. \quad \text{(B6)}$$

- $\mathrm{L}^{\mathrm{II}} = 0$ case

As for the $L^{\mathrm{I}} = 0$ case, it can be shown that the complementarity condition (Eq. 74) gives $L^{\mathrm{II}} = 0$ when $\gamma^{\mathrm{II}} < 1$ or $\gamma^{\mathrm{II}} < \gamma^{\mathrm{I}}$.

Summarizing, the following are the values of γ for different phase combinations in the three-phase problem:

$L^{\mathrm{I}}L^{\mathrm{II}}V$	$\gamma^{\mathrm{I}}, \gamma^{\mathrm{II}} = 1$
$L^{\mathrm{I}}L^{\mathrm{II}}$	$\gamma^{\mathrm{I}} = \gamma^{\mathrm{II}} > 1$
$L^{\mathrm{I}}V$	$\gamma^{\mathrm{I}} = 1, \gamma^{\mathrm{II}} < 1$
$L^{\mathrm{II}}V$	$\gamma^{\mathrm{I}} < 1, \gamma^{\mathrm{II}} = 1$
L^{I}	$\gamma^{\mathrm{I}} > 1, \gamma^{\mathrm{I}} > \gamma^{\mathrm{II}}$
L^{II}	$\gamma^{\mathrm{II}} > 1, \gamma^{\mathrm{II}} > \gamma^{\mathrm{I}}$
V	$\gamma^{\mathrm{I}}, \gamma^{\mathrm{II}} < 1$.

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