Reliable Computation of Phase Stability Using Interval Analysis: Cubic Equation of State Models

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Abstract

The reliable prediction of phase stability is a challenging computational problem in chemical process simulation, optimization and design. The phase stability problem can be formulated either as a minimization problem or as an equivalent nonlinear equation solving problem. Conventional solution methods are initialization dependent, and may fail by converging to trivial or non-physical solutions or to a point that is a local but not global minimum. Thus there has been considerable recent interest in developing more reliable techniques for stability analysis. In this paper we demonstrate, using cubic equation of state models, a technique that can solve the phase stability problem with complete reliability. The technique, which is based on interval analysis, is initialization independent, and if properly implemented provides a mathematical guarantee that the correct solution to the phase stability problem has been found.

1 Introduction

The determination of phase stability, i.e., whether or not a given mixture can split into multiple phases, is a key step in phase equilibrium calculations, and thus in the simulation and design of a wide variety of processes, especially those involving separation operations such as distillation and extraction. The phase stability problem is frequently formulated in terms of the tangent plane condition (Baker *et al.*, 1982). Minima in the tangent plane distance are sought, usually by solving a system of nonlinear equations for the stationary points (Michelsen, 1982). If any of these yield a negative tangent plane distance, indicating that the tangent plane intersects (or lies above) the Gibbs energy of mixing surface, the phase is unstable and can split (in this context, unstable refers to both the metastable and classically unstable cases). The difficulty lies in that, in general, given any arbitrary equation of state or activity coefficient model, most computational methods cannot find with complete certainty all the stationary points, and thus there is no guarantee that the phase stability problem has been correctly solved.

Standard methods (e.g., Michelsen, 1982) for solving the phase stability problem typically rely on the use of multiple initial guesses, carefully chosen in an attempt to locate all stationary points in the tangent plane distance function. However, these methods offer no guarantee that the global minimum in the tangent plane distance has been found. Because of the difficulties that thus arise, there has been significant recent interest in the development of more reliable methods for solving the phase stability problem (e.g., Nagarajan *et al.*, 1991; Sun and Seider, 1995; Eubank *et al.*, 1992; Wasylkiewicz *et al.*, 1996; McDonald and Floudas, 1995a,b,c,1997). For example, Sun and Seider (1995) apply a homotopy-continuation method, which will often find all the stationary points, and is easier to initialize than Michelsen's approach. However, their technique is still initialization dependent and provides no theoretical guarantees that all stationary points have been found. The "area" method of Eubank *et al.* (1992), which is based on exhaustive search over a grid, can also be very reliable. They suggest that a course grid be used first to find the approximate location of solutions. Then, regions appearing not to contain a solution are arbitrarily eliminated from consideration and the search continues with a finer grid in the remaining regions. However, there is no mathematical guarantee provided that the regions eliminated do not contain solutions. McDonald and Floudas (1995a,b,c,1997) show that for certain activity coefficient models, the phase stability problem can be reformulated to make it amenable to solution by powerful global optimization techniques, which do guarantee that the correct answer is found. However, in general there appears to remain a need for an efficient *general-purpose* method that can perform phase stability calculations with *mathematical certainty* for any arbitrary equation of state (EOS) or activity coefficient model.

An alternative approach, based on interval analysis, that satisfies these needs was originally suggested by Stadtherr *et al.* (1995), who applied it in connection with activity coefficient models, as later done also by McKinnon *et al.* (1996). This technique, in particular the use of an interval Newton/generalized bisection algorithm, is initialization independent and can solve the phase stability problem with mathematical certainty. Recently Hua *et al.* (1996a) extended this method to problems modeled using a simple cubic EOS (Van der Waals equation). In this paper we seek to extend the application of this technique to cubic EOS models in general. Though the technique developed is general-purpose, the applications presented focus on the Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) models with standard mixing rules.

2 Phase Stability Analysis

The determination of phase stability is often done using tangent plane analysis (Baker *et al.*, 1982; Michelsen, 1982). A phase at specified T, P, and feed mole fraction $\mathbf{z}$ is unstable if the molar Gibbs energy of mixing surface $m(\mathbf{x}, v) = \Delta g_{mix} = \Delta \hat{G}_{mix}/RT$ ever falls below a plane tangent to the surface at $\mathbf{z}$. That is, if the tangent plane distance

$$D(\mathbf{x}, v) = m(\mathbf{x}, v) - m_0 - \sum_{i=1}^{n} \left(\frac{\partial m}{\partial x_i} \right)_0 (x_i - z_i) \tag{1}$$

is negative for any composition $\mathbf{x}$, the phase is unstable. The subscript zero indicates evaluation at $\mathbf{x} = \mathbf{z}$, n is the number of components, and v is the molar volume of the mixture. A common approach for determining if D is ever negative is to minimize D subject to the mole fractions summing to one and subject to the equation of state relating $\mathbf{x}$ and v. It is readily shown that the stationary points in this optimization problem can be found by solving the system of nonlinear equations:

$$\left[\left(\frac{\partial m}{\partial x_i} \right) - \left(\frac{\partial m}{\partial x_n} \right) \right] - \left[\left(\frac{\partial m}{\partial x_i} \right) - \left(\frac{\partial m}{\partial x_n} \right) \right]_0 = 0, \qquad i = 1, \ldots, n-1 \tag{2}$$

$$1 - \sum_{i=1}^{n} x_i = 0 \tag{3}$$

$$P - \frac{RT}{v - b} + \frac{a}{v^2 + ubv + wb^2} = 0 \tag{4}$$

Equation (4) is the generalized cubic EOS given by Reid *et al.* (1987). With the appropriate choice of u and w, common models such as PR ($u = 2$, $w = -1$) and SRK ($u = 1$, $w = 0$) may be obtained. For all the example problems considered here, standard mixing rules, namely $b = \sum_{i=1}^{n} x_i b_i$ and $a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij}$, are used, with $a_{ij} = (1 - k_{ij})\sqrt{a_{ii} a_{jj}}$. The $a_{ii}(T)$ and b_i are pure component properties determined from the system temperature T, the critical temperatures T_{ci}, the critical pressures P_{ci} and acentric factors ω_i.

For this EOS the reduced molar Gibbs energy of mixing is given by:

$$m(\mathbf{x},v) = \frac{Pv}{RT} + \ln\left(\frac{RT}{v-b}\right) + \frac{a}{RTb\Delta}\ln\left(\frac{2v+ub-b\Delta}{2v+ub+b\Delta}\right) + \sum_{i=1}^{n} x_i \ln x_i - \sum_{i=1}^{n} x_i g_i^o \tag{5}$$

where the g_i^o represent the pure component reduced molar Gibbs energies and $\Delta = \sqrt{u^2-4w}$. Substituting into equation (2) yields

$$s_i(\mathbf{x},v) - s_i(\mathbf{z},v_0) = 0 \quad i = 1,\ldots,n-1 \tag{6}$$

where

$$\begin{aligned} s_i &= \frac{\partial m}{\partial x_i} - \frac{\partial m}{\partial x_n} \\ &= \frac{b_i - b_n}{b}\left(\frac{Pv}{RT} - 1\right) + \frac{a}{bRT\Delta}\left(\frac{2(\bar{a}_i - \bar{a}_n)}{a} - \frac{b_i - b_n}{b}\right)\ln\left(\frac{2v+ub-b\Delta}{2v+ub+b\Delta}\right) \\ &\quad + \ln\frac{x_i}{x_n} - (g_i^o - g_n^o) \end{aligned}$$

and $\bar{a}_i = \sum_{k=1}^{n} x_k a_{ik}$. If there are multiple real volume roots at the feed composition, then in equation (6) the molar volume v_0 at the feed composition must be the root yielding the minimum value of $m(\mathbf{z},v_0)$, the reduced molar Gibbs energy of mixing at the feed.

The $(n+1) \times (n+1)$ system given by equations (3), (4) and (6) above has a trivial root at $\mathbf{x} = \mathbf{z}$ and $v = v_0$ and frequently has multiple nontrivial roots as well. Thus conventional equation solving techniques may fail by converging to the trivial root or give an incorrect answer to the phase stability problem by converging to a stationary point that is not the global minimum of D. This is aptly demonstrated by the experiments of Green *et al.* (1993), who show that the pattern of convergence from different initial guesses demonstrates a complex fractal-like behavior for even very simple models. We demonstrate here the use of an interval Newton/generalized bisection method for solving the system of equations (3), (4) and (6). The method requires no initial guess, and will find with certainty all the stationary points of the tangent plane distance D.

3 Interval Computations

A real *interval*, X, is defined as the continuum of real numbers lying between (and including) given upper and lower bounds; i.e., $X = [a, b] = \{x \in \Re \mid a \leq x \leq b\}$, where $a, b \in \Re$ and $a \leq b$. A real interval vector $\mathbf{X} = (X_1, X_2, ..., X_n)^T$ has n real interval components and since it can be interpreted geometrically as an n-dimensional rectangle, is frequently referred to as a *box*. Note that in this section lower case quantities are real numbers and upper case quantities are intervals. Several good introductions to computation with intervals are available, including monographs by Neumaier (1990), Hansen (1992), and Kearfott (1996).

Of particular interest here are interval Newton/generalized bisection (IN/GB) methods. These techniques provide the power to find with confidence all solutions of a system of nonlinear equations (Neumaier, 1990; Kearfott and Novoa, 1990), and to find with total reliability the global minimum of a nonlinear objective function (Hansen, 1992), provided only that upper and lower bounds are available for all variables. Efficient techniques for implementing IN/GB are a relatively recent development, and thus such methods have not yet been widely applied. Schnepper and Stadtherr (1990) have suggested the use of this method for solving chemical process modeling problems, and recently described an implementation (Schnepper and Stadtherr, 1996). Balaji and Seader (1995) have also successfully applied the method to chemical engineering problems.

Consider the solution of the system of real nonlinear equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$, where it is desired to find all solutions in an specified initial interval $\mathbf{X}^{(0)}$. The basic iteration step in interval Newton methods is, given an interval $\mathbf{X}^{(k)}$, to solve the linear interval equation system

$$F'(\mathbf{X}^{(k)})(\mathbf{N}^{(k)} - \mathbf{x}^{(k)}) = -\mathbf{f}(\mathbf{x}^{(k)}) \tag{7}$$

for a new interval $\mathbf{N}^{(k)}$, where k is an iteration counter, $F'(\mathbf{X}^{(k)})$ is an interval extension of the real Jacobian $f'(\mathbf{x})$ of $f(\mathbf{x})$ over the current interval $\mathbf{X}^{(k)}$, and $\mathbf{x}^{(k)}$ is a point in the interior of $\mathbf{X}^{(k)}$, usually taken to be the midpoint. One way to evaluate the interval extension $F'(\mathbf{X}^{(k)})$ of the Jacobian is to substitute the interval $\mathbf{X}^{(k)}$ for $\mathbf{x}$ in the expression $f'(\mathbf{x})$ for the real Jacobian, and perform interval operations in place of real operations. It can be shown (Moore, 1966) that any root $\mathbf{x}^*$ of the set of equations that is within the current interval, i.e. $\mathbf{x}^* \in \mathbf{X}^{(k)}$, is also contained in the newly computed interval $\mathbf{N}^{(k)}$. This suggests that the next iteration for $\mathbf{X}$ should be the intersection of $\mathbf{X}^{(k)}$ with $\mathbf{N}^{(k)}$, i.e. $\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} \cap \mathbf{N}^{(k)}$. There are various interval Newton methods, which differ in how they determine $\mathbf{N}^{(k)}$ from equation (7) and thus in the tightness with which $\mathbf{N}^{(k)}$ encloses the solution set of (7).

While the iteration scheme discussed above can be used to tightly enclose a solution, what is of most significance here is the power of equation (7) to provide a test of whether a solution exists within a given interval and whether it is a unique solution. For several techniques for finding $\mathbf{N}^{(k)}$ from equation (7), it can be proven (e.g., Neumaier, 1990) that if $\mathbf{N}^{(k)}$ is totally contained within $\mathbf{X}^{(k)}$, i.e. $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then there is a *unique* zero of the set of nonlinear equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ in $\mathbf{X}^{(k)}$, and furthermore that Newton's method with real arithmetic will converge to that solution starting from any point in $\mathbf{X}^{(k)}$. Thus, if $\mathbf{N}^{(k)}$ is determined using one of these techniques, the computation can be used as a *root inclusion test* for any interval $\mathbf{X}^{(k)}$:

1. If $\mathbf{X}^{(k)}$ and $\mathbf{N}^{(k)}$ do not intersect, i.e., $\mathbf{X}^{(k)} \cap \mathbf{N}^{(k)} = \emptyset$, then there is no root in $\mathbf{X}^{(k)}$.
2. If $\mathbf{N}^{(k)}$ is totally contained in $\mathbf{X}^{(k)}$, then there is exactly one root in $\mathbf{X}^{(k)}$ and Newton's method with real arithmetic will find it.
3. If neither of the above is true, then no conclusion can be drawn.

In the last case, one could then repeat the root inclusion test on the next interval Newton iterate

$\mathbf{X}^{(k+1)}$, assuming it is sufficiently smaller than $\mathbf{X}^{(k)}$, or one could bisect $\mathbf{X}^{(k+1)}$ and repeat the root inclusion test on the resulting intervals. This is the basic idea of IN/GB methods. If $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ has a finite number of real solutions in the specified initial box, a properly implemented IN/GB method can find *with mathematical certainty* any and all solutions to a specified tolerance, or can determine *with mathematical certainty* that there are no solutions in the given box (Kearfott and Novoa, 1990; Kearfott, 1990). The technique used here for computing $\mathbf{N}^{(k)}$ from equation (7) is the preconditioned Gauss-Seidel-like technique developed by Hansen and Sengupta (1981). A detailed step-by-step description of the IN/GB algorithm used here is given by Schnepper and Stadtherr (1996).

The system of equations (3), (4) and (6) that must be solved here involves $n+1$ variables, the n component mole fractions $\mathbf{x}$ and the molar volume v. For the mole fraction variables, initial intervals of [0,1] are suitable. In practice the initial lower bound is set to an arbitrarily small positive number ε (10^{-10} was used) to avoid taking the logarithm of zero in subsequent calculations. This can be done without the loss of reliability providing a sufficiently small value of ε is used. The lower limit on the molar volume was taken to be the smallest pure component size parameter b_i, and the upper bound was taken to be the ideal gas molar volume for the T and P under investigation. Although it is possible to have compressibility factors greater than one at very high reduced pressure, this was deemed satisfactory for the range of reduced temperature and pressure explored below. Our implementation of the IN/GB method for the phase stability problem is based on appropriately modified routines from the packages INTBIS (Kearfott and Novoa, 1990) and INTLIB (Kearfott *et al.*, 1994).

4 Results

To test this initial implementation of IN/GB to solve phase stability problems for cubic equations of state, several different mixtures have been used. Results for mixtures modeled using either the SRK or PR EOS are presented here. In order to demonstrate the power of the method, in these studies we have found *all* the stationary points. However, it should be emphasized that, for making a determination of phase stability or instability, finding *all* the stationary points is not always necessary, as discussed in more detail below.

4.1 Problem 1

This is a mixture of hydrogen sulfide (1) and methane (2) at 190 K and 40.53 bar (40 atm.). The SRK model was used with parameters calculated from T_{c1} = 373.2 K, P_{c1} = 89.4 bar, $\omega_1 = 0.1$, T_{c2} = 190.6 K, P_{c2} = 46.0 bar, $\omega_2 = 0.008$, and a binary interaction parameter $k_{12} = 0.08$. A plot of the reduced Gibbs energy of mixing m vs. x_1 for this system is shown in Figure 1.

Several feeds were considered, as shown in Table 1, which also shows the roots (stationary points) found, and the value of the tangent plane distance D at each root. For the $z_1 = 0.5$ case, our results are consistent with those given by Sun and Seider (1995) for this problem. For the $z_1 = 0.0187$ case, a plot of the tangent plane distance D vs. x_1 is shown in Figures 2 and 3. For feeds near this point, this is known to be a difficult problem to solve (e.g., Michelsen, 1982; Sun and Seider, 1995). As noted by Michelsen and others, if one uses a locally convergent solver, with nearly pure CH_4 as the initial guess, convergence will likely be to the trivial solution at $x_1 = z_1 = 0.0187$. And if nearly pure H_2S is the initial guess, convergence will likely be to the local, but not global, minimum at $x_1 = 0.8848$. Using only these initial guesses would lead to the incorrect conclusion that the mixture is stable. This is indicative of the importance of the initialization strategy when conventional methods are used. An important advantage of the IN/GB approach described here is that it eliminates the initialization problem, since it is initialization independent. In this case, it finds all the stationary points, including the global minimum at $x_1 = 0.0767$, correctly predicting, since $D < 0$ at this point, that a mixture with this feed composition is unstable. Michelsen's algorithm, as implemented in LNGFLASH from the IVC-SEP package (Hytoft and Gani, 1996), a code that in general we have found to be extremely reliable, incorrectly predicts that this mixture is stable. As indicated in Table 1, several other feed compostions were tested using the IN/GB approach, with correct results obtained in each case. Note that the presence of multiple real volume roots does not present any difficulty, since the solver simply finds all roots for the given system.

Also included in Table 1 are the number of root inclusion tests performed in the computation and the total CPU time on a Sun Ultra 1/170 workstation. We would expect standard approaches to the phase stability problem to be faster (the run times for LNGFLASH on these problems is on the order of several milliseconds for each feed), but these methods do not reliably solve the problem in all cases. Thus, as one might expect, to obtain guaranteed reliability some premium must be paid in terms of computation time. It should be noted that earlier experience (Stadtherr *et al.*, 1995) in applying the IN/GB approach to liquid/liquid phase stability problems using the NRTL equation, indicated that the computational efficiency of IN/GB compared favorably with the model-specific technique of McDonald and Floudas (1995), which also offers guaranteed reliability on the NRTL problem. It should also be noted that this is an initial implementation of IN/GB for the phase stability problem with the generalized cubic equation of state, and we anticipate that significant improvements can be made in its computational efficiency (Hua et al., 1996b)

4.2 Problem 2

This is a mixture of methane (1) and propane (2) at 277.6 K; pressures of 50 bar and 100 bar were considered. The SRK model was used with parameters calculated from the methane data given above, $T_{c2} = 369.8$ K, $P_{c2} = 42.5$ bar, $\omega_2 = 0.152$, and a binary interaction parameter $k_{12} = 0.029$.

For $P = 50$ bar, a plot of the reduced Gibbs energy of mixing is shown in Figure 4. Feeds of $z_1 = 0.1$, 0.4, 0.6 and 0.9 were considered, with results shown in Table 2. The first and last feeds are stable and the others unstable, which is consistent with the plot in Figure 4.

For $P = 100$ bar, a plot of the reduced Gibbs energy of mixing is shown in Figure 5. Feeds of $z_1 = 0.4$, 0.68, 0.73 and 0.9 were considered, with results shown in Table 3. The first and last feeds are stable and the others unstable, which is consistent with the plot in Figure 5. The feeds of $z_1 = 0.68$ and 0.73 represent particularly difficult problems because they are in a near critical region. Several other values of T, P, and z_1 have also been tried for this system and correct results obtained.

4.3 Problem 3

This is a mixture of nitrogen (1) and ethane (2) at 270 K and 76 bar. The PR model was used with parameters calculated from $T_{c1} = 126.2$ K, $P_{c1} = 33.9$ bar, $\omega_1 = 0.04$, $T_{c2} = 305.4$ K, $P_{c2} = 48.8$ bar, $\omega_2 = 0.098$, and a binary interaction parameter $k_{12} = 0.08$. A plot of the reduced Gibbs energy of mixing is given in Figure 6. Feeds of $z_1 = 0.1$, 0.18, 0.3, 0.44 and 0.65 were considered, with results shown in Table 4. The first and last feeds are stable and the other three unstable, which is consistent with the plot in Figure 6. Several other values of T, P, and z_1 have also been tried and correct results obtained for this system.

4.4 Problem 4

This is a mixture of carbon dioxide (1) and methane (2) at 220 K and 60.8 bar. The PR model was used with parameters calculated from $T_{c1} = 304.2$ K, $P_{c1} = 73.8$ bar, $\omega_1 = 0.225$, the methane parameters given above, and a binary interaction parameter $k_{12} = 0.095$. A plot of the reduced Gibbs energy of mixing is given in Figure 7. Feeds of $z_1 = 0.1$, 0.2, 0.3, 0.43 and 0.6 were considered, with results shown in Table 5. The first and last feeds are stable and the other three unstable, which is consistent with the plot in Figure 7. Several other values of T, P, and z_1 have also been tried and correct results obtained for this system. While this problem and those above involve binary mixtures, the method is applicable to problems with any number of components, and tests involving ternary and larger systems are under way.

4.5 Discussion

In the problems above we used IN/GB to find *all* the stationary points. However, for making a determination of phase stability or instability, finding *all* the stationary points is not always necessary. For example if an interval is encountered over which the interval evaluation of D has a negative upper bound, this guarantees that there is a point at which $D < 0$, and so one can immediately conclude that the mixture is unstable without determining all the stationary points. It is also possible to make use of the underlying global minimization problem. Since the objective function D has a known value of zero at the mixture feed composition, any interval over which the interval value of D has a lower bound greater than zero cannot contain the global minimum and can be discarded, even though it may contain a stationary point (at which D will be positive and thus not of interest).

Finally it should be noted that the method described here can easily be combined with existing local methods for determining phase stability. First, the (fast) local method is used. If it indicates instability then this is the correct answer as it means a point at which $D < 0$ has been found. If the local method indicates stability, however, this may not be the correct answer since the local method may have missed the global minimum in D. Applying the new method described here can then be used to confirm that the mixture is stable if that is the case, or to correctly determine that it is really unstable if that is the case.

5 Conclusions and Significance

Results demonstrate that the interval Newton/generalized bisection algorithm can solve phase stability problems for a generalized cubic equation of state model efficiently and with complete reliability. This work represents an entirely new method for solving these problems, a method that can guarantee with mathematical certainty that the correct solutions are found, thus eliminating computational problems that are frequently encountered with currently available techniques. The method is initialization independent; it is also model independent, straightforward to use, and can be applied in connection with other equations of state or with activity coefficient models.

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References

Baker, L. E., A. C. Pierce, and K. D. Luks, Gibbs energy analysis of phase equilibria. *Soc. Petrol. Engrs. J.*, **22**, 731–742 (1982).

Balaji, G. V. and J. D. Seader, Application of interval-newton method to chemical engineering problems. *AIChE Symp. Ser*, **91**(304), 364–367 (1995).

Eubank, A. C., A. E. Elhassan, M. A. Barrufet, and W. B. Whiting, Area method for prediction of fluid-phase equilibria. *Ind. Eng. Chem. Res.*, **31**, 942–949 (1992).

Green, K. A., S. Zhou, and K. D. Luks, The fractal response of robust solution techniques to the stationary point problem. *Fluid Phase Equilibria*, **84**, 49–78 (1993).

Hansen, E. R., *Global Optimization Using Interval Analysis.* Marcel Dekkar, Inc., New York (1992).

Hansen, E. R. and R. I. Sengupta, Bounding solutions of systems of equations using interval analysis. *BIT*, **21**, 203–211 (1981).

Hua, J. Z., J. F. Brennecke, and M. A. Stadtherr, Reliable prediction of phase stability using an interval-Newton method. *Fluid Phase Equilibria*, **116**, 52–59 (1996a).

Hua, J. Z., S. R. Tessier, W. C. Rooney, J. F. Brennecke, and M. A. Stadtherr, Enhanced interval techniques for reliable computation of phase equilibrium. Presented at AIChE Annual Meeting, Chicago, November, 1996b.

Hytoft, G. and R. Gani, IVC-SEP Program Package. Technical Report SEP 8623, Institut for Kemiteknik, Danmarks Tekniske Universitet, Lyngby, Denmark (1996).

Kearfott, R. B., Interval arithmetic techniques in the computational solution of nonlinear systems of equations: Introduction, examples, and comparisons. *Lectures in Applied Mathematics*, **26**, 337–357 (1990).

Kearfott, R. B., *Rigorous Global Search: Continuous Problems.* Kluwer Academic Publishers, Dordrecht (1996).

Kearfott, R. B., M. Dawande, K.-S. Du, and C.-Y. Hu, Algorithm 737: INTLIB, a portable FORTRAN 77 interval standard function library. *ACM Trans. Math. Software*, **20**, 447–459 (1994).

Kearfott, R. B. and M. Novoa, Algorithm 681: INTBIS, a portable interval Newton/bisection package. *ACM Trans. Math. Software*, **16**, 152–157 (1990).

McDonald, C. M. and C. A. Floudas, Global optimization for the phase stability problem. *AIChE J.*, **41**, 1798–1814 (1995a).

McDonald, C. M. and C. A. Floudas, Global optimization for the phase and chemical equilibrium problem: Application to the NRTL equation. *Comput. Chem. Eng.*, **19**, 1111–1139 (1995b).

McDonald, C. M. and C. A. Floudas, Global optimization and analysis for the Gibbs free energy function using the UNIFAC, Wilson, and ASOG equations. *Ind. Eng. Chem. Res.*, **34**, 1674–1687 (1995c).

McDonald, C. M. and C. A. Floudas, GLOPEQ: A new computational tool for the phase and chemical equilibrium problem. *Comput. Chem. Eng.*, **21**, 1–23 (1997).

McKinnon, K. I. M., C. G. Millar, and M. Mongeau, Global optimization for the chemical and phase equilibrium problem using interval analysis. In Floudas, C. A. and P. M. Pardalos, editors, *State of the Art in Global Optimization: Computational Methods and Applications.* Kluwer Academic Publishers (1996).

Michelsen, M. L., The isothermal flash problem. Part I: Stability. *Fluid Phase Equilibria*, **9**, 1–19 (1982).

Moore, R. E., *Interval Analysis.* Prentice-Hall, Englewood Cliffs (1966).

Nagarajan, N. R., A. S. Cullick, and A. Griewank, New strategy for phase equilibrium and critical point calculations by thermodynamic energy analysis. Part I. Stability analysis and flash. *Fluid Phase Equilibria*, **62**, 191–210 (1991).

Neumaier, A., *Interval Methods for Systems of Equations.* Cambridge University Press, Cambridge, England (1990).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids.* McGraw-Hill (1987).

Schnepper, C. A. and M. A. Stadtherr, On using parallel processing techniques in chemical process design. Presented at AIChE Annual Meeting, Chicago, November, 1990.

Schnepper, C. A. and M. A. Stadtherr, Robust process simulation using interval methods. *Comput. Chem. Eng.*, **20**, 187–199 (1996).

Stadtherr, M. A., C. A. Schnepper, and J. F. Brennecke, Robust phase stability analysis using interval methods. *AIChE Symp. Ser.*, **91**(304), 356–359 (1995).

Sun, A. C. and W. D. Seider, Homotopy-continuation method for stability analysis in the global minimization of the Gibbs free energy. *Fluid Phase Equilibria*, **103**, 213–249 (1995).

Wasylkiewicz, S. K., L. N. Sridhar, M. F. Malone, and M. F. Doherty, Global stability analysis and calculation of liquid-liquid equilibrium in multicomponent mixtures. *Ind. Eng. Chem. Res.*, **35**, 1395–1408 (1996).

Figure Captions

Figure 1. Reduced Gibbs energy of mixing m vs. x_1 for Problem 1: Hydrogen sulfide (1) and methane (2) at $P = 40.53$ bar and $T = 190$ K, modeled using SRK.

Figure 2. Tangent plane distance D vs. x_1 for Problem 1 with feed composition $z_1 = 0.0187$. See Figure 3 for enlargement of area near the origin.

Figure 3. Enlargement of part of Figure 2, showing area near the origin.

Figure 4. Reduced Gibbs energy of mixing m vs. x_1 for Problem 2: Methane (1) and propane (2) at $P = 50$ bar and $T = 277.6$ K, modeled using SRK.

Figure 5. Reduced Gibbs energy of mixing m vs. x_1 for Problem 2: Methane (1) and propane (2) at $P = 100$ bar and $T = 277.6$ K, modeled using SRK.

Figure 6. Reduced Gibbs energy of mixing m vs. x_1 for Problem 3: Nitrogen (1) and ethane (2) at $P = 76$ bar and $T = 270$ K, modeled using PR.

Figure 7. Reduced Gibbs energy of mixing m vs. x_1 for Problem 4: Carbon dioxide (1) and methane (2) at $P = 60.8$ bar and $T = 220$ K, modeled using PR.

Table 1: Results for Problem 1: Hydrogen sulfide (1) and methane (2) at $P = 40.53$ bar and $T = 190$ K, modeled using SRK.

Feed (z_1, z_2)	**Roots** (x_1, x_2, v)	**D**	**Number of Root Inclusion Tests**	**CPU Time (sec) Sun Ultra 1/170**
(0.0115, 0.9885)	(0.0115, 0.9885, 212.8)	0.0	5424	1.024
	(0.0237, 0.9763, 97.82)	0.0137		
	(0.0326, 0.9674, 78.02)	0.0130		
(0.0187, 0.9813)	(0.8848, 0.1152, 36.58)	0.0109	8438	1.671
	(0.0187, 0.9813, 207.3)	0.0		
	(0.0313, 0.9687, 115.4)	0.0079		
	(0.0767, 0.9233, 64.06)	-0.004		
	(0.4905, 0.5095, 41.50)	0.0729		
(0.07, 0.93)	(0.8743, 0.1257, 36.65)	0.0512	8504	1.690
	(0.5228, 0.4772, 40.89)	0.0965		
	(0.0178, 0.9822, 208.0)	0.0015		
	(0.0304, 0.9696, 113.7)	0.0100		
	(0.07 , 0.93 , 65.35)	0.0		
(0.50, 0.50)	(0.8819, 0.1181, 36.60)	-0.057	8406	1.660
	(0.0184, 0.9816, 207.5)	-0.079		
	(0.0311, 0.9689, 114.9)	-0.071		
	(0.0746, 0.9254, 64.44)	-0.082		
	(0.50 , 0.50 , 41.32)	0.0		
(0.888, 0.112)	(0.888 , 0.112 , 36.55)	0.0	8396	1.671
	(0.0190, 0.9810, 207.1)	0.0026		
	(0.0316, 0.9684, 116.0)	0.0103		
	(0.0792, 0.9208, 63.60)	-0.002		
	(0.4795, 0.5205, 41.72)	0.0683		
(0.89, 0.11)	(0.89 , 0.11 , 36.54)	0.0	8410	1.673
	(0.0192, 0.9808, 206.9)	0.0113		
	(0.0319, 0.9681, 116.4)	0.0189		
	(0.0809, 0.9191, 63.31)	0.0058		
	(0.4725, 0.5275, 41.87)	0.0724		

Table 2: Results for Problem 2: Methane (1) and propane (2) at $P = 50$ bar and $T = 277.6$ K, modeled using SRK.

Feed (z_1, z_2)	**Roots (x_1, x_2, v)**	**D**	**Number of Root Inclusion Tests**	**CPU Time (sec) Sun Ultra 1/170**
(0.10, 0.90)	(0.10 , 0.90 , 86.71)	0.0	1969	0.413
(0.40, 0.60)	(0.8654, 0.1346, 378.4)	-0.153	4345	0.905
	(0.5515, 0.4485, 115.3)	0.0106		
	(0.40 , 0.60 , 89.46)	0.0		
(0.60, 0.40)	(0.7058, 0.2942, 313.0)	-0.007	3706	0.782
	(0.60 , 0.40 , 216.5)	0.0		
	(0.1928, 0.8072, 86.07)	-0.223		
(0.90, 0.10)	(0.90 , 0.10 , 388.5)	0.0	3290	0.640

Table 3: Results for Problem 2: Methane (1) and propane (2) at $P = 100$ bar and $T = 277.6$ K, modeled using SRK.

Feed (z_1, z_2)	**Roots (x_1, x_2, v)**	**D**	**Number of Root Inclusion Tests**	**CPU Time (sec) Sun Ultra 1/170**
(0.40, 0.60)	(0.40 , 0.60, 82.22)	0.0	2518	0.5220
(0.68, 0.32)	(0.7721, 0.2279, 126.0)	-3.3×10^{-4}	19986	3.966
	(0.6881, 0.3119, 103.0)	4.10×10^{-7}		
	(0.68, 0.32, 101.4)	0.0		
(0.73, 0.27)	(0.7567, 0.2433, 121.1)	-2.0×10^{-5}	14768	2.967
	(0.73, 0.27, 113.2)	0.0		
	(0.6506, 0.3494, 96.38)	-2.9×10^{-4}		
(0.90, 0.10)	(0.90, 0.10, 165.2)	0.0	2485	0.5136

Table 4: Results for Problem 3: Nitrogen (1) and ethane (2) at $P = 76$ bar and $T = 270$ K, modeled using PR.

Feed (z_1, z_2)	**Roots (x_1, x_2, v)**	**D**	**Number of Root Inclusion Tests**	**CPU Time (sec) Sun Ultra 1/170**
(0.10, 0.90)	(0.10 , 0.90 , 71.11)	0.0	1881	0.4004
(0.18, 0.82)	(0.4943, 0.5057, 198.3)	-0.010	4560	0.9791
	(0.2961, 0.7039, 110.4)	0.0058		
	(0.18 , 0.82 , 78.61)	0.0		
(0.30, 0.70)	(0.4893, 0.5107, 198.3)	-0.0138	4586	0.9804
	(0.30, 0.70, 112.3)	0.0		
	(0.1767, 0.8233, 78.18)	-0.007		
(0.44, 0.56)	(0.44, 0.56, 181.2)	0.0	4649	0.9914
	(0.3353, 0.6647, 131.5)	0.0026		
	(0.1547, 0.8453, 75.64)	-0.016		
(0.60, 0.40)	(0.60, 0.40, 227.8)	0.0	3312	0.6506

Table 5: Results for Problem 4: Carbon dioxide (1) and methane (2) at $P = 60.8$ bar and $T = 220$ K, modeled using PR.

Feed (z_1, z_2)	**Roots (x_1, x_2, v)**	**D**	**Number of Root Inclusion Tests**	**CPU Time (sec) Sun Ultra 1/170**
(0.10, 0.90)	(0.10, 0.90, 168.5)	0.0	4162	0.8393
(0.20, 0.80)	(0.20, 0.80, 141.6) (0.2589, 0.7411, 88.51) (0.4972, 0.5028, 47.98)	0.0 0.0022 -0.007	13630	2.8266
(0.30, 0.70)	(0.1848, 0.8152, 141.6) (0.30, 0.70, 69.79) (0.3579, 0.6421, 59.13)	-0.007 0.0 -1.9×10^{-4}	19664	4.078
(0.43, 0.57)	(0.1911, 0.8088, 138.7) (0.2732, 0.7268, 79.62) (0.43 , 0.57 , 52.14)	-0.001 0.0032 0.0	15454	3.1781
(0.60, 0.40)	(0.60, 0.40, 43.69)	0.0	10764	2.239

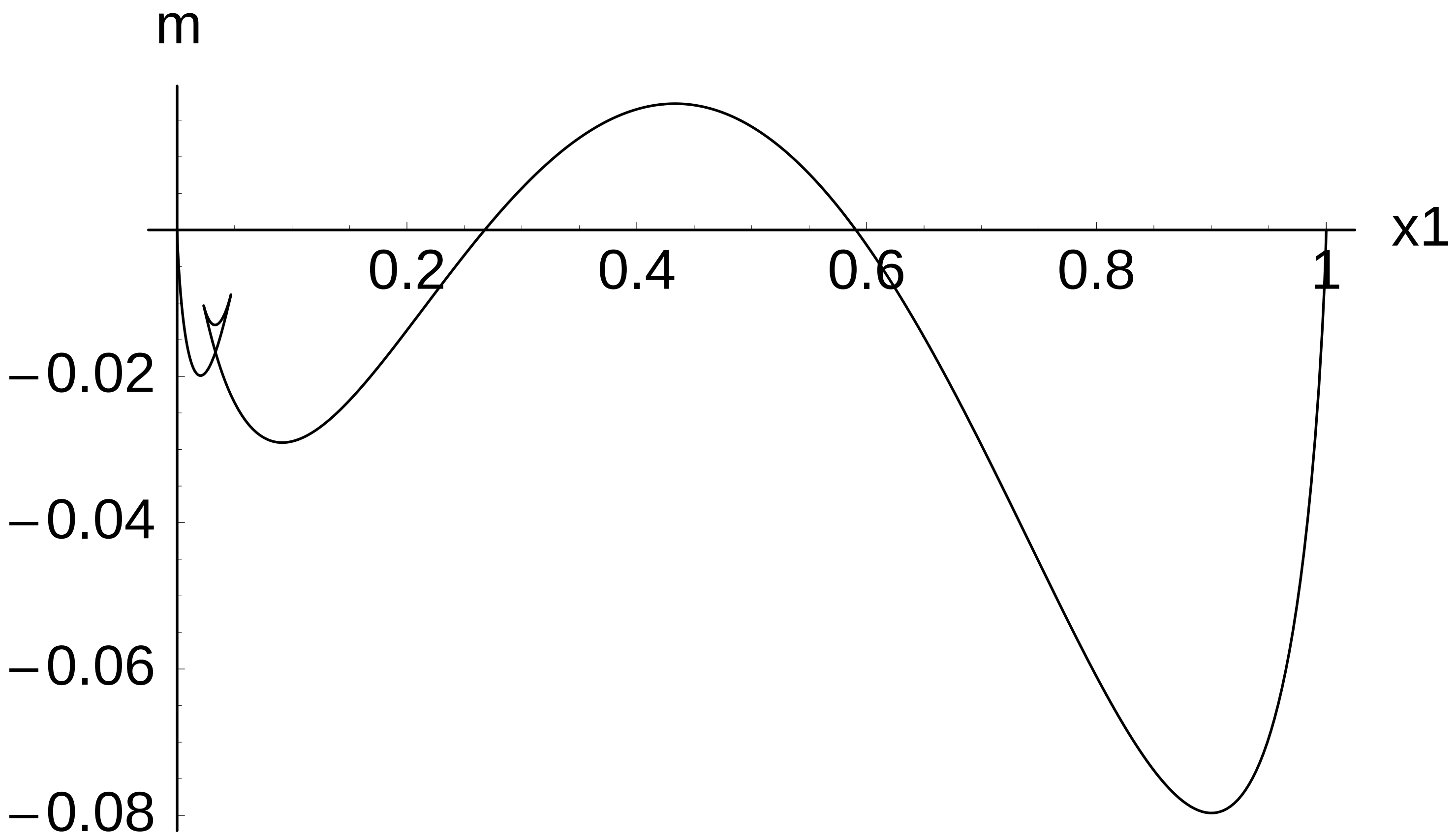

Figure 1: Reduced Gibbs energy of mixing m vs. x_1 for Problem 1: Hydrogen sulfide (1) and methane (2) at $P = 40.53$ bar and $T = 190$ K, modeled using SRK.

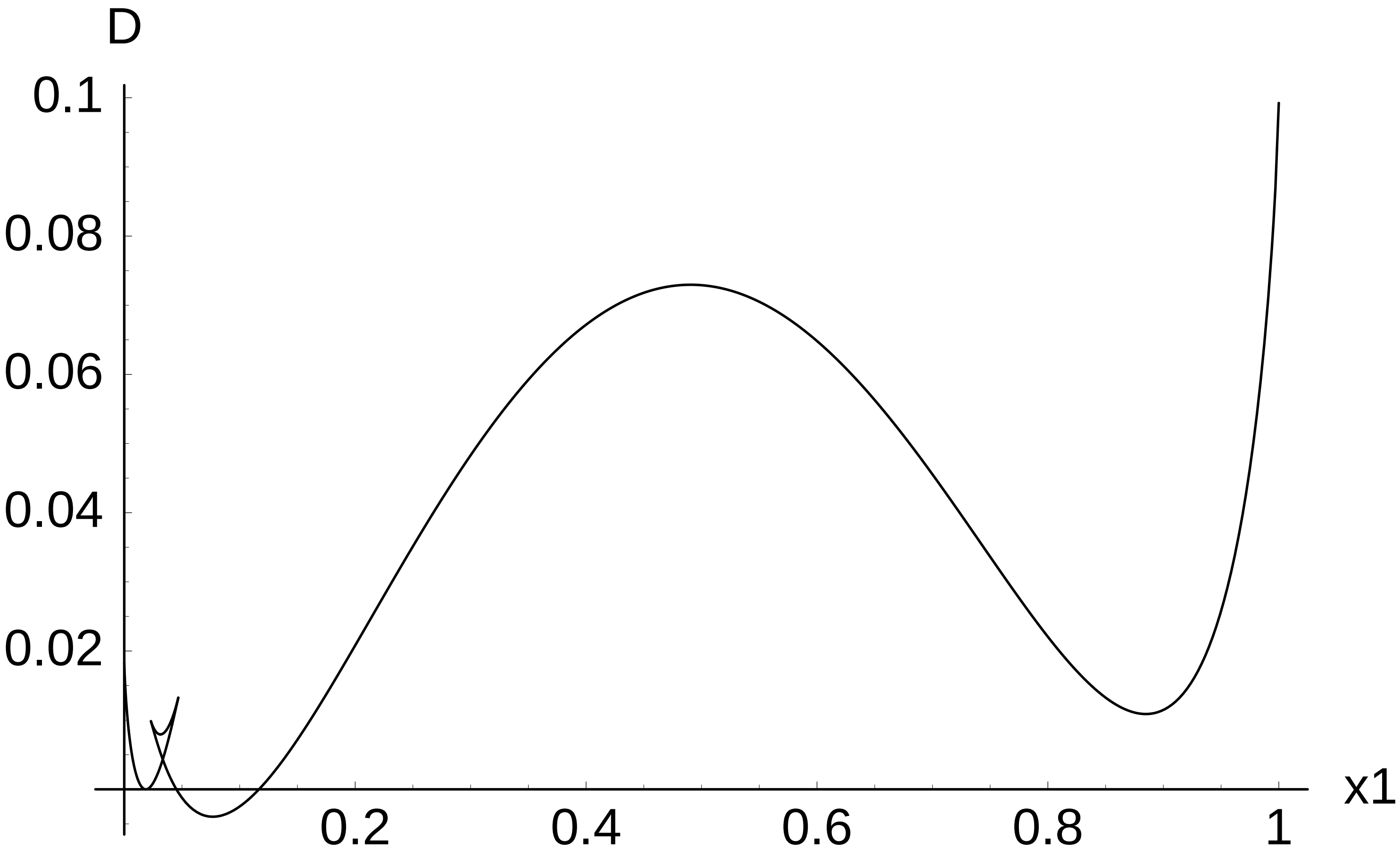

Figure 2: Tangent plane distance D vs. x_1 for Problem 1 with feed composition $z_1 = 0.0187$. See Figure 3 for enlargement of area near the origin.

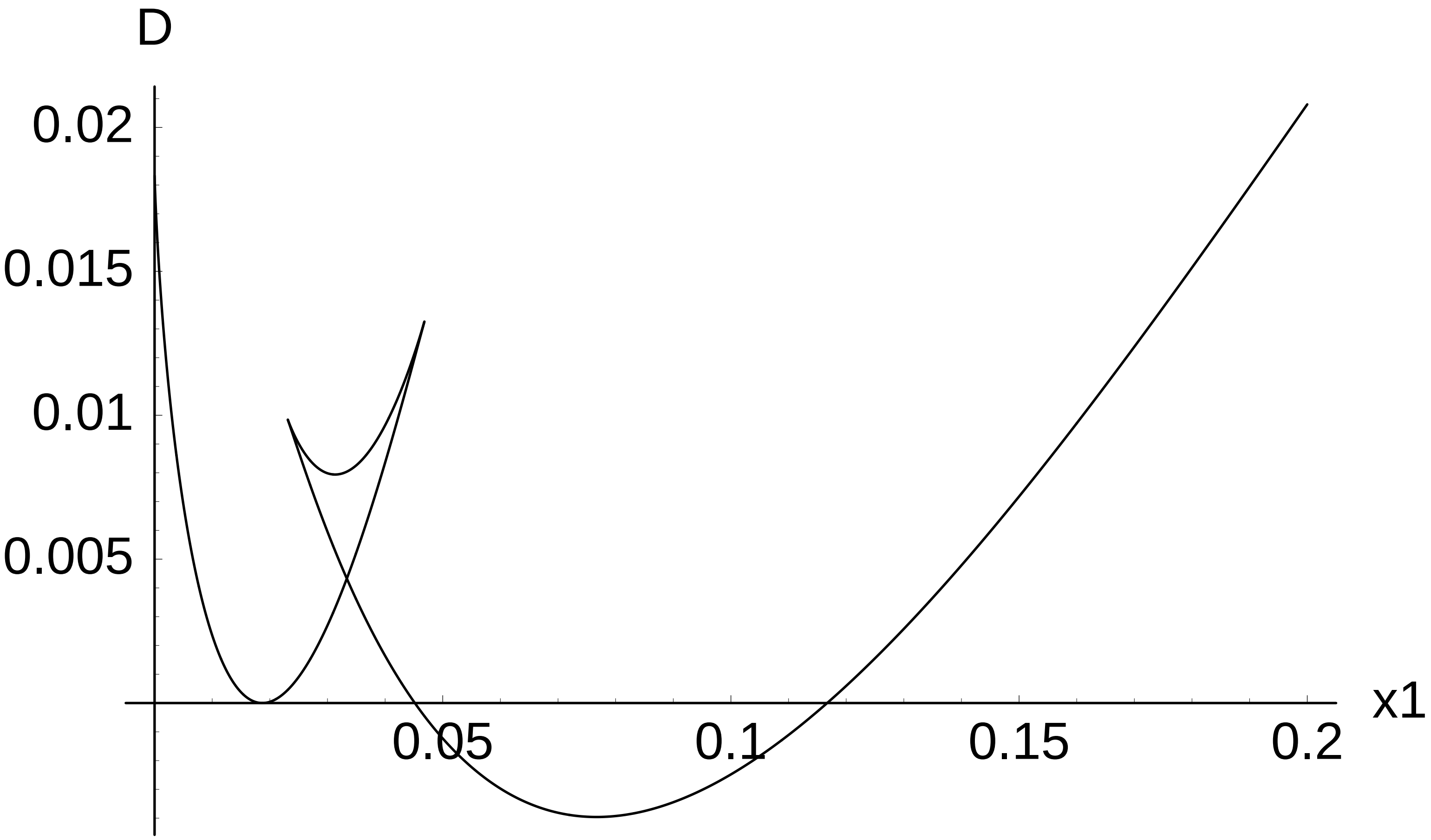

Figure 3: Enlargement of part of Figure 2, showing area near the origin.

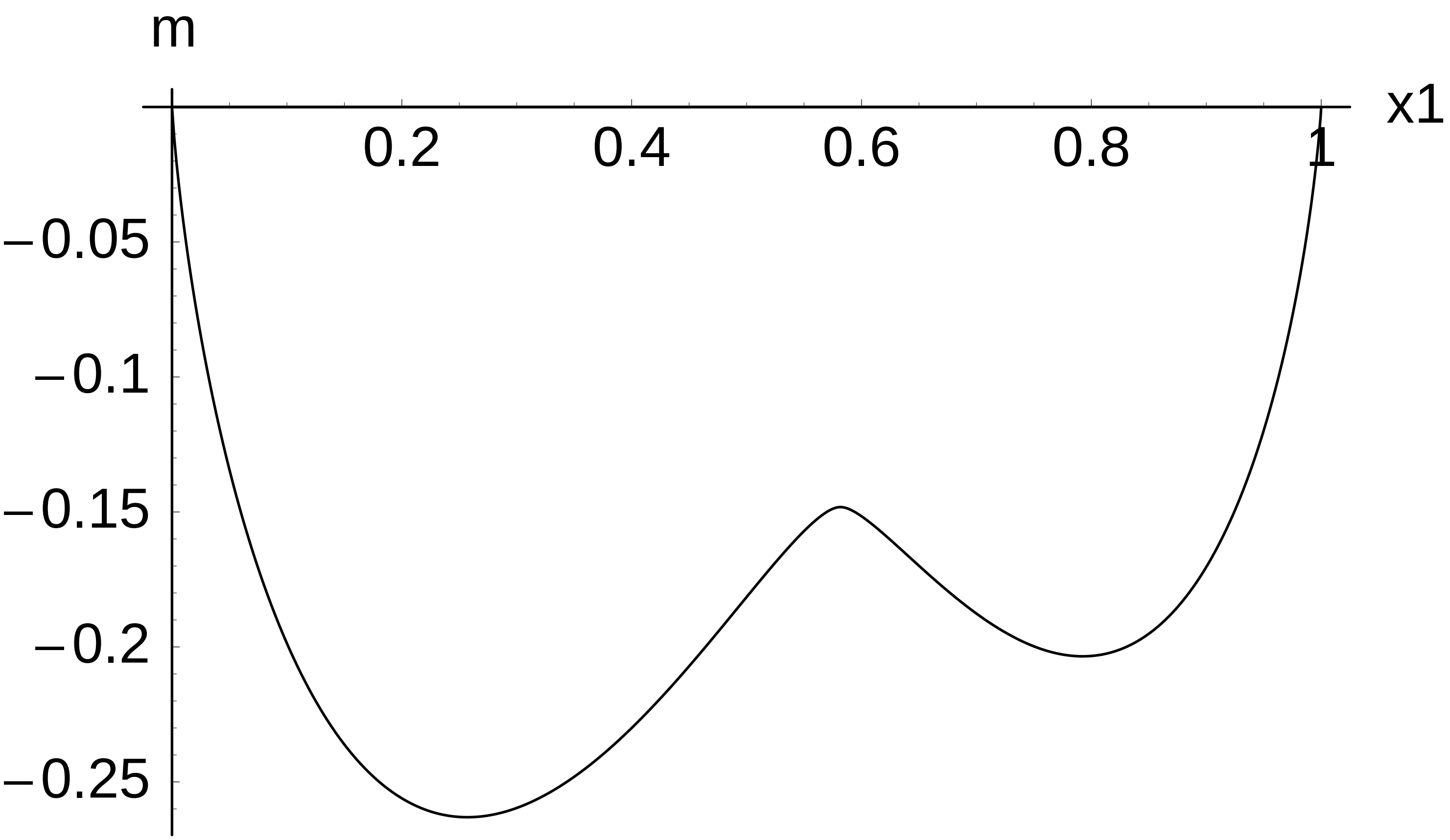

Figure 4: Reduced Gibbs energy of mixing m vs. x_1 for Problem 2: Methane (1) and propane (2) at $P = 50$ bar and $T = 277.6$ K, modeled using SRK.

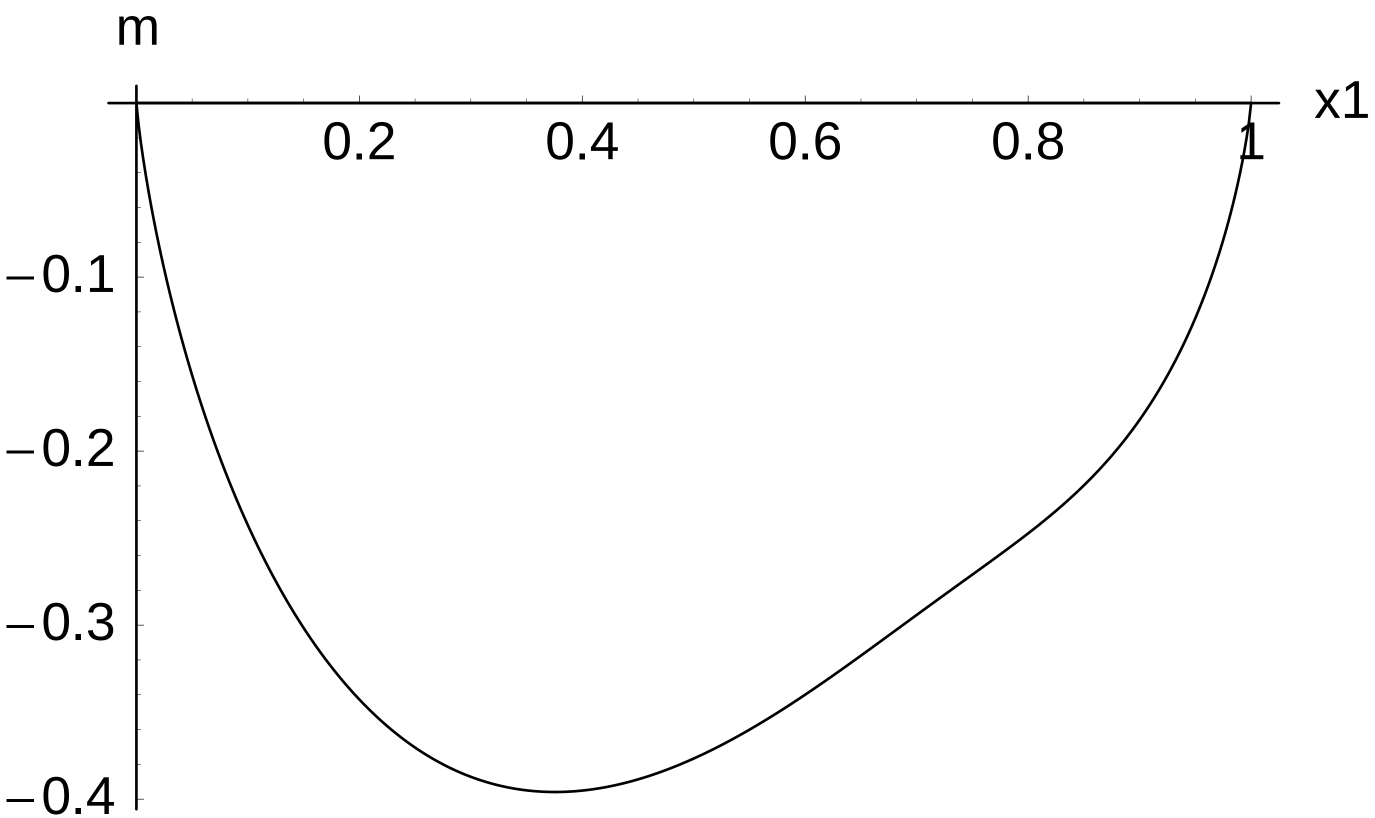

Figure 5: Reduced Gibbs energy of mixing m vs. x_1 for Problem 2: Methane (1) and propane (2) at $P = 100$ bar and $T = 277.6$ K, modeled using SRK.

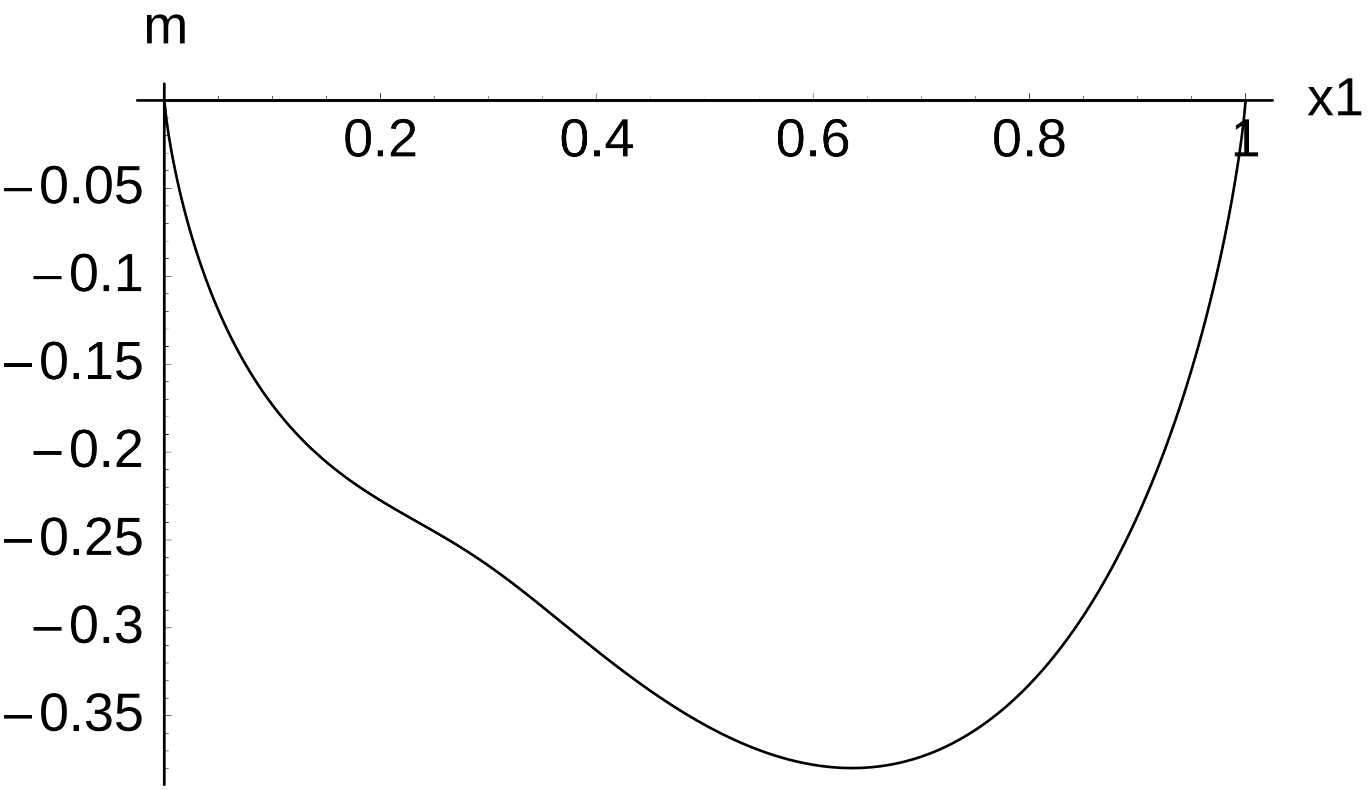

Figure 6: Reduced Gibbs energy of mixing m vs. x_1 for Problem 3: Nitrogen (1) and ethane (2) at $P = 76$ bar and $T = 270$ K, modeled using PR.

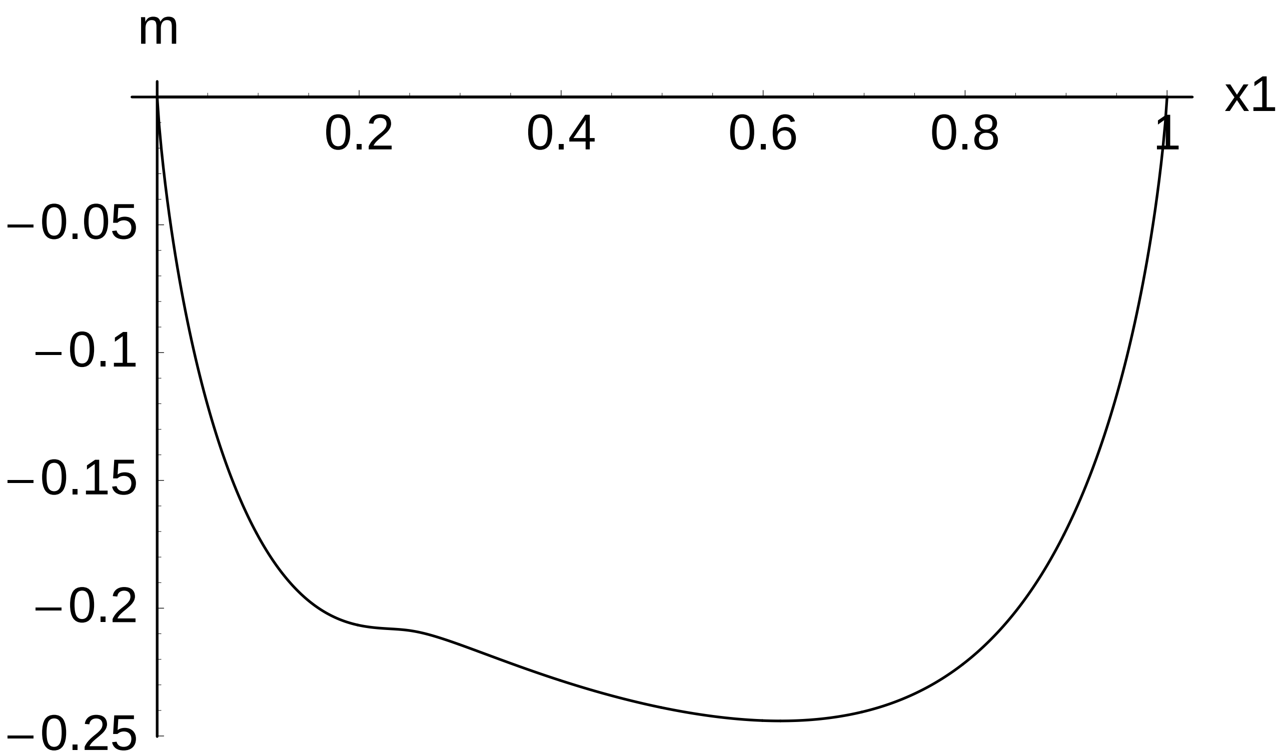

Figure 7: Reduced Gibbs energy of mixing m vs. x_1 for Problem 4: Carbon dioxide (1) and methane (2) at $P = 60.8$ bar and $T = 220$ K, modeled using PR.