Phase Stability with Cubic Equations of State: A Global Optimization Approach

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Abstract

Calculation of phase and chemical equilibria is of fundamental importance for the design and simulation of chemical processes. Methods that minimize the Gibbs free energy provide equilibrium solutions that are only candidates for the true equilibrium solution. This is because the number and type of phases must be assumed before the Gibbs energy minimization problem can be formulated. The tangent plane stability criterion is a means of determining the stability of a candidate equilibrium solution. The Gibbs energy minimization problem and the tangent plane stability problem are very challenging due to the highly nonlinear thermodynamic functions that are used. In this work the goal is to develop a global optimization approach for the tangent plane stability problem that (i) provides a theoretical guarantee about the stability of the candidate equilibrium solution and (ii) is computationally efficient. Cubic equations of state are used in this approach due to their ability to accurately predict the behavior of nonideal vapor and liquid phases across a broad range of pressures. The mathematical form of the stability problem is analyzed and nonlinear functions with special structure are identified. These special structures are exploited to achieve faster convergence of the algorithm. The proposed approach has been applied to the SRK, Peng-Robinson, and van der Waals cubic equations of state and can address a variety of mixing rules. Results for several example problems, including an eight component problem, are presented.

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1 Introduction

Calculation of phase and chemical equilibria is of fundamental importance for the design and simulation of chemical processes. The thermodynamic function most widely used is the Gibbs free energy, since it can be used to determine the equilibrium state at constant temperature and pressure. The global minimum of the Gibbs free energy corresponds to the true equilibrium configuration of the system. Optimization methods have received much attention, because minimization of the Gibbs free energy is a natural course for calculating the equilibrium state of a system. However, the most commonly used approaches employ local optimization methods that can provide no theoretical guarantee that the equilibrium solution will be obtained in all cases.

White *et al.* (1958) developed the RAND algorithm for minimizing the Gibbs free energy. A review of the early contributions in this area can be found in Seider *et al.* (1980). In addition, Ohanomah and Thompson (1984a), (1984b), (1984c) conducted a computational evaluation of several algorithms. The three-phase flash problem was addressed by Soares *et al.* (1982) using a Newton-Raphson method. Lantagne *et al.* (1988) developed a mixed-penalty function method for equilibrium calculations. Paules and Floudas (1989) applied the Global Optimal Search method of Floudas *et al.* (1989) for minimization of the Gibbs free energy. However, all of these methods can converge to local equilibrium solutions, since there is no guarantee that the true equilibrium solution can be located.

The difficulty of locating the global minimum of the Gibbs free energy is due to two main points: 1) there is no method to determine *a priori* the number and type of phases present in the true equilibrium state, and 2) for nonideal systems the Gibbs energy surface may contain multiple local minima. A phase combination, such as two liquid phases, must be postulated before the problem of minimizing the Gibbs free energy can be formulated. If the true equilibrium state contains a vapor phase, or three liquid phases, then even though the optimization method may locate the global minimum Gibbs free energy for two liquid phases, the solution will not correspond to the true equilibrium state. In this case, one or more of the liquid phases will be unstable. Baker *et al.* (1982) formalized the concept of phase stability for a multicomponent mixture, based on the principles first identified by Gibbs (1873). They proved that a necessary and sufficient condition for the stability of a phase is that the tangent plane to the Gibbs free energy surface, constructed at the composition of the candidate phase, lie on or below the Gibbs energy surface for all possible composition values. Therefore, the stability of a phase can be determined by identifying the global minimum of the tangent plane distance function, defined as the difference between the Gibbs free energy surface and the tangent plane. If the global minimum is nonnegative, then the candidate phase is stable, otherwise the phase is metastable or unstable.

Several methods have been developed recently for implementing the tangent plane stability test. Michelsen (1982a) (1982b) used a two stage approach in which local solutions of the stability problem are used as starting points in the search for an equilibrium solution with a lower value of the Gibbs free energy. Swank and Mullins (1986) reported that these methods are more reliable than direct minimization of the Gibbs free energy. Nagarajan *et al.* (1991a) (1991b) proposed a reformulation of Michelsen's approach in terms of molar densities in order to improve its reliability. Gupta *et al.* (1991) developed an approach that solves the flash calculation and the stability problem simultaneously. Eubank *et al.* (1992) developed an area calculation method for the stability problem. In their approach the Gibbs energy surface is integrated, searching for endpoints that maximize the area. A homotopy continuation algorithm was used by Sun and Seider (1995) to locate all of the stationary points of the tangent plane distance function. The stationary points are then used to search for a lower value of the Gibbs free energy. These methods for the stability problem are substantial improvements over the direct minimization of the Gibbs free energy, both in the computational effort and in reliability. However, none of the methods described above can provide a theoretical guarantee that the equilibrium solution will be obtained in all cases.

McDonald and Floudas (1995a), (1995b) developed deterministic global optimization methods for solving the stability problem for systems where the nonideal liquid phases are represented by activity coefficient equations. These methods *guarantee* that the global minimum of the tangent plane distance function can be identified regardless of the starting point chosen. In addition, they applied the same global optimization approach for the minimization of the Gibbs free energy (see McDonald and Floudas (1994), (1995c)). These two contributions have been combined into the GLOPEQ algorithm that generates equilibrium solutions by minimizing the Gibbs free energy, and verifies the stability of the solution by finding the global minimum of the tangent plane distance function (see McDonald and Floudas (1997)).

Hua et al., (1996, 1998a, 1998b) proposed an interval Newton method to locate all stationary points and applied it to the phase stability problem for systems containing two and three components. It should be pointed out that it is not possible to *exactly* locate all finite stationary points, as it was proven by Hansen *et al.* (1992) (see also Maranas and Floudas (1995)). Instead, it is possible to *enclose* all stationary points, that is, construct tight intervals around the stationary points. The approach of Hua et al. encloses all stationary points of the tangent plane distance function within intervals of some tolerance ϵ. An important theoretical and computational issue that arises is whether within an interval there exist one or multiple stationary points, that is, the uniqueness issue. Several key contributions appeared attempting to address this uniqueness issue and it is instructive to point out the theoretical and computational issues/results that are currently available. A theoretical condition for uniqueness that needs to be met in the interval Newton methods is that the interval Jacobian matrix is a *regular* Lipschitz matrix. The fact that the interval matrix is Lipschitz is well known (see Neumaier (1990), page 175). As a result, the key issue becomes whether it is possible to (i) state *a priori* whether the interval Jacobian matrix is regular (i.e., consider necessary and sufficient conditions for regularity), or (ii) check *a posteriori* whether within an interval there exists a unique solution (i.e., consider sufficient conditions for regularity). It is interesting to note that Poljak and Rohn (1993) proved that checking regularity of interval matrices is an NP-Hard problem, and hence it is regarded as a very difficult problem (see also Neumaier (1990), page 76). In regard to (i), necessary and sufficient conditions for regularity of the interval jacobian matrix are available (see for instance section 6.2, page 223 of Neumaier (1990)). These conditions exhibit exponential behavior and they are not a part of any of the existing interval analysis implementations (the recent work of Jansson and Rohn (1999) is a step in this direction). In regard to (ii), sufficient conditions for regularity of the interval jacobian matrix are available (see for instance Chapter 4.1 of Neumaier (1990) and the recent work by Rex and Rohn (1999)). These sufficient conditions are based on the class of *strongly regular* interval matrices for which there exist rigorous criteria of testing in order (n^3) operations. If a matrix is not found strongly regular, then the box is split and the test is repeated. As the diameter of the interval matrix becomes smaller, the likelihood of having a strongly regular matrix increases except when near singular solutions are approached. In this case, the verification cannot be done rigorously and the implementations introduce ad hoc heuristics. The most common test used involves the preconditioning by the midpoint inverse matrix and the check whether the resulting matrix is an H matrix (see Neumaier (1990), Rex and Rohn (1999)). If the midpoint matrix is nearly singular, then this test becomes ineffective. Other tests based on the calculation of eigenvalues and positive definiteness have been proposed, but these require squaring of the condition number.

As is pointed out by Hua *et al.* (1998b), in the context of the phase stability test, all stationary points need not be located if the candidate phase is unstable, since a function evaluation, interval bounds test, or local minimization of the tangent plane distance function can be performed during the interval computations. If the result of the evaluation is a negative tangent plane distance, then the procedure can be terminated. In the more difficult case where the candidate phase is stable, all stationary points must either be zero or positive. In this case all stationary points must be located, or it must be verified that no negative stationary points exist. The method of Hua *et al.* (1998b) avoids locating all stationary points by setting an upper bound on the tangent plane distance function of zero. Therefore, only stationary points that have a zero tangent plane distance must be located when the candidate phase is stable.

The minimization of the tangent plane distance function offers an advantage over an approach based on enclosing all stationary points. In the minimization approach, the solver explicitly searches for the lowest possible value of the tangent plane distance function. Since regions that have the lowest solution of the lower bounding problem are chosen to investigate first, negative tangent plane distance solutions, if they exist, are usually encountered in the first few iterations. An approach based on enclosing all stationary points, since it does not focus exclusively on regions likely to contain minimum values of the tangent plane distance function is likely to, on average, require more iterations to locate a negative tangent plane distance.

In this work, a deterministic global optimization method is presented for the solution of the stability problem by minimization of the tangent plane distance function. This approach extends the work of McDonald and Floudas (1995a), (1995b), and addresses the problem using cubic equations of state to model the vapor and liquid phases. Equations of state are increasingly being used to model the thermodynamic behavior of complex mixtures. The attractive features of equations of state are that they can be used to model the behavior of both the vapor and liquid phases, and they are not limited to low pressure systems, like activity coefficient methods. These advantages come at a cost, however, since equations of state add a highly nonlinear equality constraint to the formulation of the stability problem. The Gibbs energy function, the cubic equations of state, and the mixing rules have been analyzed to identify the special structure of the nonlinear expressions. For bilinear terms and univariate concave terms the tightest possible convex underestimators are used. The α-underestimation approach, (Adjiman *et al.* (1998a), (1998b)), is used to generate tight convex underestimators for terms that do not possess special structure. The proposed method has been tested through several challenging examples using the Soave-Redlich-Kwong, the Peng-Robinson, and the van der Waals cubic equations of state. In the next section, the formulation of the stability problem is presented. Then the structure of the mathematical formulation is discussed in detail and the solution algorithm is presented. Several computational studies are discussed, including a very challenging system containing eight components.

2 Problem Statement

The motivation for using the tangent plane stability criterion arises from an assumption that must be made in order to formulate the Gibbs free energy minimization problem. That is, the number and type of phases that are present in the true equilibrium state must be specified. However, for a given number and type of phases, the global minimum of the Gibbs free energy is not a sufficient condition for the true equilibrium solution. This is because a different set of phases may contain a solution that has a lower value for the Gibbs energy. Given a candidate equilibrium solution, the advantage of the tangent plane criterion is that it provides an unambiguous means of determining if the proposed solution is stable or unstable.

The tangent plane distance function is defined as the distance between the Gibbs free energy surface for the new phase and the tangent plane to the Gibbs energy surface constructed at the point x^F. The expression for the tangent plane distance function is:

$$\mathcal{F}(\mathbf{x}) = \sum_{i \in C} x_i \left\{ \mu_i(\mathbf{x}) - \mu_i^F(\mathbf{x}^F) \right\} \tag{1}$$

Note that the tangent plane distance criterion does not provide candidate equilibrium solutions, nor does it provide a method for determining where the tangent plane touches the Gibbs energy surface so that it always lies below it. Therefore, the tangent plane criterion cannot be used by itself to determine the true equilibrium solution.

Recent developments in global optimization, (see Visweswaran and Floudas (1990), (1993), Adjiman and Floudas (1996), and Adjiman *et al.* (1998a)), can provide theoretical guarantees that an ϵ-global minimum can be obtained for very broad classes of nonlinear functions, such as twice-differentiable ones. Based on these developments, the global minimization of the tangent plane distance function is a promising approach. McDonald and Floudas (1995a), (1995b) proposed the first methods for activity coefficient equations that provide theoretical guarantees that the global minimum of the tangent plane distance function is obtained.

As part of every iteration in the optimization procedure, a function evaluation or a local minimization of the tangent plane distance function must be performed. If *at any point* the value of the tangent plane distance is negative, then the optimization procedure can be terminated, since the candidate phase is unstable. Therefore, in cases where the candidate solution is unstable, the problem need not be solved to global optimality and, as is shown in the computational studies, Section 7, often the problem can be terminated in the first few iterations.

2.1 Problem Formulation

The formulation of the tangent plane distance minimization problem begins with the following assumptions. We are given a system of $|C|$ components at constant temperature, T, and pressure, P. In addition, the composition of a candidate phase is provided, $\mathbf{x}^F$. When an equation of state is chosen as the thermodynamic model for the system, we can calculate the compressibility, z^F, and the chemical potential of every component, μ_i^F, of the candidate phase. The objective is to minimize the tangent plane distance function, which is a nonlinear function of the composition and the compressibility of the new phase. The problem is constrained by the bounds on the mole fractions, the restriction that the mole fractions must sum to one. In addition, the equation of state of the new phase must be satisfied. The optimization formulation for the tangent plane distance minimization problem, (S), is given as:

$$\left.\begin{array}{ll}\min\limits_{\mathbf{x},z} & \mathcal{F} = \sum\limits_{i\in C} x_i\mu_i(\mathbf{x},z) - \sum\limits_{i\in C} x_i\mu_i^F \\ \text{s.t.} & EOS(\mathbf{x},z) = 0 \\ & \sum\limits_{i\in C} x_i = 1 \\ & 0 \le x_i \le 1 \ \forall\, i \in C \\ & z \ge 0 \\ & \mathbf{x} \in \Re^{|C|}, z \in \Re \end{array}\right\} (S)$$

where $EOS(\mathbf{x}, z)$ represents the equation of state for the new phase, and is a nonlinear function of composition and compressibility. The objective function has been written as the difference of two terms. The first term represents the molar Gibbs energy surface and is a nonlinear function of composition and compressibility. The second term represents the tangent plane to the Gibbs energy surface and is a linear function of composition. Therefore, formulation (S) is a nonlinear programming problem (NLP). If a nonnegative global minimum is obtained, then the postulated phase is stable. However, obtaining the global minimum solution for (S) is difficult due to the highly nonlinear nature of the equation of state models for $\mu_i(\mathbf{x}, z)$ and $EOS(\mathbf{x}, z)$. In this work, the application of cubic equations of state to (S) will be analyzed.

2.2 Application to Cubic Equations of State

The application of equations of state to the phase stability problem results in a more difficult formulation than when activity coefficient equations are used. This is because the equation of state is an additional nonlinear equality constraint that must be satisfied. As a result, the feasible region for the problem is nonconvex.

As an illustration of the complexity of the equation of state, consider the van der Waals equation, one of the simplest cubic equations of state:

$$z^3 - (B^{mix} + 1)z^2 + A^{mix}z - A^{mix}B^{mix} = 0.$$

The equation is cubic in terms of the compressibility factor, z, and also depends on the values of the mixing parameters, A^{mix} and B^{mix}. The mixing parameters are not simply fixed values, but are *functions of composition.* Many different "mixing rules" have been proposed for every equation of state. The original Van der Waals mixing rules:

$$
\begin{aligned}
A^{mix} &= \sum_{i\in C}\sum_{j\in C} A_{ij}x_ix_j \\
B^{mix} &= \sum_{i\in C} B_ix_i
\end{aligned}
\tag{2}
$$

are very widely used. The binary interaction parameter, A_{ij}, is obtained from the pure component parameters, A_i. The parameter, B_i, is also a pure component parameter. The equations used to calculate the pure component parameters are different for each equation of state. In all of the examples in this work the van der Waals mixing rules have been used. The equation for A^{mix} is a nonlinear equation that contains a sum of bilinear terms, and the equation for B^{mix} is linear. The dependence of the mixing parameters on the composition means that the equation of state is not a simple polynomial, but a much more difficult signomial equation. By applying Eqn. 2 to (S), we obtain:

$$
\left.
\begin{array}{rl}
\min\limits_{\mathbf{x},z,A^{mix},B^{mix}} & \mathcal{F} = \sum\limits_{i\in C} x_i\mu_i(\mathbf{x},z,A^{mix},B^{mix}) - \sum\limits_{i\in C} x_i\mu_i^F \\
\text{s.t.} & EOS(\mathbf{x},z,A^{mix},B^{mix}) \le 0 \\
& -EOS(\mathbf{x},z,A^{mix},B^{mix}) \le 0 \\
& A^{mix} - \sum\limits_{i\in C} x_i\bar{a}_i = 0 \\
& B^{mix} - \sum\limits_{i\in C} B_ix_i = 0 \\
& \bar{a}_i - \sum\limits_{j\in C} A_{ij}x_j = 0 \ \forall\ i\in C \\
& \sum\limits_{i\in C} x_i = 1 \\
& 0 \le x_i \le 1 \ \forall\ i \in C \\
& z \ge 0 \\
& \mathbf{x} \ \in\ \Re^{|C|}, z \ \in\ \Re
\end{array}
\right\} (\hat{S})
$$

In formulation $(\hat{S})$, the mixing parameters, A^{mix} and B^{mix}, are treated as variables rather than substituting their definitions into the expressions for the equation of state and the chemical potential. This simplifies the nonlinear terms at the cost of introducing new constraints into the problem. Note that the nonlinear equality constraint for EOS has been written as two inequality constraints. The addition of the substitution variable, $\bar{a}_i$, reduces the number of bilinear terms in the problem from $|C|^2$ to $|C|$, at the expense of adding $|C|$ variables and $|C|$ linear constraints.

The chemical potential, μ_i, also depends on the equation of state. By using the definitions of the chemical potential and the fugacity coefficient,

$$\mu_i = \Delta G_i^f + RT \ln \frac{\hat{f}_i}{f_i^0}$$
$$\phi_i = \frac{f_i^0}{P}$$
$$\hat{\phi}_i = \frac{\hat{f}_i}{x_i P}$$

the tangent plane distance function can be transformed through the following steps:

$$\begin{aligned}
\frac{\mathcal{F}}{RT} &= \sum_{i \in C} x_i \frac{\mu_i(\mathbf{x}, z, A^{mix}, B^{mix})}{RT} - \sum_{i \in C} x_i \frac{\mu_i^F}{RT} \\
&= \sum_{i \in C} x_i \left(\frac{\Delta G_i^f(T, \Pi_{new})}{RT} + \ln \hat{f}_i - \ln f_i^0 \right) - \sum_{i \in C} x_i \left(\frac{\Delta G_i^f(T, \Pi_{candidate})}{RT} + \ln \hat{f}_i^F - \ln f_i^0 \right) \\
&= \sum_{i \in C} x_i \left(\frac{\Delta G_i^{f,n}}{RT} + \ln x_i \hat{\phi}_i P - \ln \phi_i P \right) - \sum_{i \in C} x_i \left(\frac{\Delta G_i^{f,c}}{RT} + \ln x_i^F \hat{\phi}_i^F P - \ln \phi_i P \right)
\end{aligned}$$

where $\Delta G_i^f(T, \Pi_{new})$ is the Gibbs free energy of formation of component i which is calculated at the system temperature in the new phase, Π_{new}, and $\Delta G_i^f(T, \Pi_{candidate})$ is the corresponding Gibbs free energy of formation for the candidate phase, $\Pi_{candidate}$. For notational simplicity, these symbols are shortened to $\Delta G_i^{f,n}$ and $\Delta G_i^{f,c}$ respectively. Combining the terms in the last equation results in the general form of the tangent plane distance function for equations of state:

$$\frac{\mathcal{F}}{RT} = \sum_{i \in C} x_i \left(\frac{\Delta G_i^{f,n}}{RT} - \frac{\Delta G_i^{f,c}}{RT} - \ln x_i^F \hat{\phi}_i^F \right) + \sum_{i \in C} x_i \ln x_i + \sum_{i \in C} x_i \ln \hat{\phi}_i. \tag{3}$$

The terms in the first summation are linear since the quantities inside the parentheses are constant, the terms in the second summation are convex, and the terms in the third summation are nonconvex. The fugacity coefficient for component i in the mixture, $\hat{\phi}_i$, is derived from the equation of state. For instance, when the equation of state is given in pressure-explicit form, the mixture fugacity coefficient is derived by

$$RT \ln \hat{\phi}_i = \int_V^{\infty} \left[\frac{\partial P}{\partial n_i} - \frac{RT}{V} \right] dV - RT \ln z.$$

When the stability of a liquid phase is tested with respect to another liquid phase, the Gibbs energies of formation will cancel and can be removed from the objective function. However, when the stability of a liquid phase is tested with respect to a vapor phase, these terms cannot be discarded. In many cases, the need to locate Gibbs energies of formation for both liquid and vapor phases can be eliminated by using the following approximation:

$$\frac{\Delta G_i^{L,f}}{RT} = \frac{\Delta G_i^{V,f}}{RT} + \ln \frac{P_i^{sat}}{P_i^0}.$$

The parameters needed to calculate the saturated vapor pressure are more readily available than Gibbs energies of formation.

In the following sections, the properties of the cubic equations of state and the fugacity coefficient of a component in the mixture will be examined for three common cubic equations of state. In sections 3, 4, and 5, the SRK equation, the Peng-Robinson, and the Van der Waals equation are addressed, respectively.

3 Analysis for the SRK equation

3.1 Formulation of the Phase Stability Problem

Redlich and Kwong (1949) introduced a cubic equation of state that was a substantial improvement over the equations of state used at that time. Soave (1972) modified the temperature dependence of the a parameter. The polynomial form of the Soave-modified Redlich-Kwong equation of state for mixtures is:

$$z^3 - z^2 + (A^{mix} - B^{mix} - {B^{mix}}^2)z - A^{mix}B^{mix} = 0. \tag{4}$$

The pressure explicit form of the SRK equation is:

$$P = \frac{RT}{V - b^{mix}} - \frac{a^{mix}}{V(V + b^{mix})}$$

from which the fugacity coefficient of a component in the mixture can be derived,

$$\begin{aligned} \ln \hat{\phi}_i = & \tfrac{B_i}{B^{mix}}(z-1) - \ln(z - B^{mix}) \\ & + \tfrac{A^{mix}}{B^{mix}} \left[\tfrac{B_i}{B^{mix}} - \tfrac{2}{A^{mix}} \sum_{j \in C} A_{ij} x_j \right] \ln\left(1 + \tfrac{B^{mix}}{z}\right). \end{aligned} \tag{5}$$

In the tangent plane distance function, Eqn. 3, the mixture fugacity coefficients participate in the term:

$$\sum_{i \in C} x_i \ln \hat{\phi}_i.$$

Some simplifications of this term can be made based on the following properties:

$$\begin{aligned}
\sum_{i \in C} x_i \tfrac{B_i}{B^{mix}}(z-1) &= z-1 \\
\sum_{i \in C} x_i \ln(z - B^{mix}) &= \ln(z - B^{mix}) \\
\sum_{i \in C} x_i \tfrac{A^{mix}}{B^{mix}} \left[\tfrac{B_i}{B^{mix}} - \tfrac{2}{A^{mix}} \sum_{j \in C} A_{ij} x_j \right] \ln\left(1 + \tfrac{B^{mix}}{z}\right) &= -\tfrac{A^{mix}}{B^{mix}} \ln\left(1 + \tfrac{B^{mix}}{z}\right).
\end{aligned}$$

When Eqn. 4 and the simplified mixture fugacity coefficient equation are applied to the tangent plane distance minimization problem $(\hat{S})$, the following formulation is obtained:

$$\left.\begin{aligned}
\min \ \tfrac{\mathcal{F}}{RT} = \quad & \sum_{i \in C} x_i \left(\tfrac{\Delta G_i^{f,n}}{RT} - \tfrac{\Delta G_i^{f,c}}{RT} - \ln x_i^F \hat{\phi}_i^F \right) \\
& + \sum_{i \in C} x_i \ln x_i \\
& + z - 1 - \ln w \\
& - \tfrac{A^{mix}}{B^{mix}} \ln\left(1 + \tfrac{B^{mix}}{z}\right) \\
\text{s.t.} \quad & z^3 - z^2 + (A^{mix} - B^{mix} - {B^{mix}}^2) z - A^{mix} B^{mix} \leq 0 \\
& -z^3 + z^2 - (A^{mix} - B^{mix} - {B^{mix}}^2) z + A^{mix} B^{mix} \leq 0 \\
& A^{mix} - \sum_{i \in C} x_i \bar{a}_i = 0 \\
& B^{mix} - \sum_{i \in C} B_i x_i = 0 \\
& \bar{a}_i - \sum_{j \in C} A_{ij} x_j = 0 \ \forall \ i \in C \\
& \sum_{i \in C} x_i = 1 \\
& w = z - B^{mix} \\
& 0 \leq x_i \leq 1 \ \forall \ i \in C \\
& z \geq 0 \\
& w > 0
\end{aligned}\right\} (\hat{S}^{SRK})$$

Note that a new variable, w, has been introduced to remove the possibility that the logarithm of a negative number will be taken during the solution of the problem. Formulation $(\hat{S}^{SRK})$ contains $|C| + 2$ variables and seven constraints. The size of the problem is relatively small, even for systems with a large number of components. However, the number of bilinear terms, $x_i x_j$, in the A-mixing rule grows quickly as the number of components increases.

3.2 Classification and Convex Underestimation of Nonconvex Terms

Formulation ($\hat{S}^{SRK}$) is a nonlinear optimization problem with nonconvex terms in the objective function and in the constraints. Due to the presence of nonconvexities, a "local" optimization technique may converge to a suboptimal solution. The proposed methodology, discussed in section 6, provides a theoretical guarantee of convergence to the global minimum solution. This guarantee relies on generating valid convex underestimating functions for every nonconvex term in formulation ($\hat{S}^{SRK}$). A convex lower bounding problem is formulated by replacing every nonconvex term in ($\hat{S}^{SRK}$) with a convex underestimating function. At every iteration, the lower bounding problem can be solved to global optimality since it is a convex NLP. The speed of convergence can be enhanced by identifying nonconvex terms with special structure. In many cases, these special structures can be exploited to find the tightest possible convex underestimating function.

3.2.1 Univariate Concave Terms

Two univariate concave terms occur in the equation of state constraints in formulation ($\hat{S}^{SRK}$). These are the following:

$$-z^2 \text{ and } -z^3, \text{ with } z \geq 0.$$

The tightest possible convex underestimator for a univariate concave function is the convex envelope of the function. This is simply the line segment between the function values at the boundary of the current domain, $f(x^L)$ and $f(x^U)$. Therefore, in the lower bounding problem, every univariate concave term is replaced by the following expression:

$$f(x^L) + \frac{f(x^U) - f(x^L)}{x^U - x^L}\left(x - x^L\right).$$

For example, the term $-z^3$ is replaced by:

$$-(z^L)^3 - \frac{(z^U)^3 - (z^L)^3}{z^U - z^L}\left(z - z^L\right).$$

3.2.2 Bilinear Terms

Formulation ($\hat{S}^{SRK}$) also contains several bilinear terms. These are the following:

- In the equation of state constraints:

$$\pm A^{mix}z, \;\pm B^{mix}z, \text{ and } \pm A^{mix}B^{mix}.$$

- In the A-mixing rule constraints:

$$\sum_{i\in C} x_i \bar{a}_i.$$

The tightest convex lower bound of a bilinear term, xy, over the domain, $\left[x^L, x^U\right] \times \left[y^L, y^U\right]$ was identified by Al-Khayyal and Falk (1983). For every bilinear term, xy, a new variable is introduced, s_B, which replaces every occurence of xy in the problem. The new variable must satisfy:

$$s_B = \max\left\{x^L y + x y^L - x^L y^L; x^U y + x y^U - x^U y^U\right\}.$$

This relationship is included in the lower bounding problem through two linear inequality constraints,

$$\begin{aligned} -s_B + x^L y + x y^L - x^L y^L &\leq 0 \\ -s_B + x^U y + x y^U - x^U y^U &\leq 0 \end{aligned}$$

which serve as a convex lower bound on the original bilinear term xy. An upper bound on the substituted variable can also be applied through two additional linear constraints, (McCormick (1976)),

$$\begin{aligned} s_B - x^U y - x y^L + x^U y^L &\leq 0 \\ s_B - x^L y - x y^U + x^L y^U &\leq 0. \end{aligned}$$

Based on this approach, every bilinear term requires the addition of one new variable and four linear inequality constraints to the lower bounding problem. For the SRK equation, this is equal to $\frac{|C|(|C|-1)}{2} + 3$ variables and $2|C|(|C|-1) + 12$ constraints.

3.2.3 General Nonconvex Terms

Certain nonconvex terms do not appear to possess a special structure that can be exploited in generating a convex underestimating function. In formulation ($\hat{S}^{SRK}$) the following terms are classified as general nonconvex terms:

- In the objective function:

$$-\frac{A^{mix}}{B^{mix}} \ln\left(1 + \frac{B^{mix}}{z}\right)$$

- In the equation of state constraints:

$$\pm (B^{mix})^2 z$$

For terms of this sort, we use the α-based underestimators developed by Maranas and Floudas (1994), Adjiman and Floudas (1996), and Adjiman *et al.* (1998a), (1998b). In this approach, a C^2-continuous real-valued nonconvex function, $f(\mathbf{x}), x \in \Re^n$ is underestimated over the domain $\left[\mathbf{x}^L, \mathbf{x}^U\right]$ by the following function, $\mathcal{L}$,

$$\mathcal{L}(\mathbf{x}) = f(\mathbf{x}) + \sum_{i=1}^{n} \alpha_i (x_i^L - x)(x_i^U - x) \tag{6}$$

where the α_i's are positive scalars. All of the terms in the summation are negative, therefore $\mathcal{L}$ is always an underestimator of f. The α parameters must satisfy the following criterion in order for $\mathcal{L}$ to be a convex function.

$$\alpha \geq \max\left\{0, -\frac{1}{2} \min_i \min_{\mathbf{x}^L \leq \mathbf{x} \leq \mathbf{x}^U} \lambda_i(\mathbf{x})\right\} \tag{7}$$

The λ_i's are the eigenvalues of the Hessian matrix of $f(\mathbf{x})$. The exact solution of the right-hand side of Eqn. 7 provides the smallest possible value of α that convexifies $f(\mathbf{x})$. However, the minimization problem in Eqn. 7 is, in general, a nonconvex optimization problem. It is often much easier to obtain a valid lower bound on α through the use of interval Hessian methods, (see Adjiman *et al.* (1998a), 1998b).

In a few cases it is possible to derive an exact expression that satisfies Eqn. 7. For example, the minimum eigenvalue of the term $(B^{mix})^2 z$ is,

$$\lambda^{min} = z^U \left(1 - \sqrt{1 + \frac{4({B^{mix}}^U)^2}{(z^U)^2}}\right).$$

Therefore, for the region $\left[{B^{mix}}^L, {B^{mix}}^U\right] \times \left[z^L, z^U\right]$, the exact smallest value of α that convexifies $(B^{mix})^2 z$ is,

$$\alpha = \frac{z^U}{2}\left(\sqrt{1 + \frac{4({B^{mix}}^U)^2}{(z^U)^2}} - 1\right).$$

For the nonconvex term in the objective function there is no simple expression for the exact value of α, and hence an interval Hessian method is used to obtain a valid upper bound on α.

In section 7.2 the phase stability problem for several systems is solved using the SRK cubic equation of state.

4 Analysis for the Peng-Robinson equation

4.1 Formulation of the Phase Stability Problem

Another cubic equation of state was developed by Peng and Robinson (1976). The Peng-Robinson equation of state is very similar to the SRK equation, but is able to predict liquid compressibilities more accurately. The polynomial form of the Peng-Robinson equation of state for mixtures is:

$$z^3 - (1 - B^{mix})z^2 + (A^{mix} - 2B^{mix} - 3{B^{mix}}^2)z - A^{mix}B^{mix} + {B^{mix}}^2 + {B^{mix}}^3 = 0. \tag{8}$$

The pressure explicit form of the Peng-Robinson equation is:

$$P = \frac{RT}{V - b^{mix}} - \frac{a^{mix}}{V^2 + 2b^{mix}V - {B^{mix}}^2}$$

from which the fugacity coefficient for a component in the mixture can be derived,

$$\begin{aligned}\ln \hat{\phi}_i = \; & \tfrac{B_i}{B^{mix}}(z-1) - \ln(z - B^{mix}) \\ & + \tfrac{A^{mix}}{2\sqrt{2}B^{mix}}\left[\tfrac{B_i}{B^{mix}} - \tfrac{2}{A^{mix}}\sum_{j\in C} A_{ij}x_j\right]\ln\left(\tfrac{z+(1+\sqrt{2})B^{mix}}{z+(1-\sqrt{2})B^{mix}}\right).\end{aligned} \tag{9}$$

In the tangent plane distance function, Eqn. 3, the mixture fugacity coefficients participate in the term:

$$\sum_{i \in C} x_i \ln \hat{\phi}_i.$$

Some simplifications of this term can be made based on the following properties:

$$\begin{aligned}
\sum_{i \in C} x_i \frac{B_i}{B^{mix}}(z-1) &= z - 1 \\
\sum_{i \in C} x_i \ln(z - B^{mix}) &= \ln(z - B^{mix}) \\
\sum_{i \in C} x_i \frac{A^{mix}}{2\sqrt{2}B^{mix}} \left[\frac{B_i}{B^{mix}} - \frac{2}{A^{mix}} \sum_{j \in C} A_{ij} x_j \right] \ln\left(\frac{z+(1+\sqrt{2})B^{mix}}{z+(1-\sqrt{2})B^{mix}} \right) &= -\frac{A^{mix}}{2\sqrt{2}B^{mix}} \ln\left(\frac{z+(1+\sqrt{2})B^{mix}}{z+(1-\sqrt{2})B^{mix}} \right).
\end{aligned}$$

When Eqn. 8 and the simplified mixture fugacity coefficient equation are applied to the tangent plane distance minimization problem $(\hat{S})$, the following formulation is obtained:

$$\left.\begin{aligned}
\min\ \frac{\mathcal{F}}{RT} = \quad & \sum_{i \in C} x_i \left(\frac{\Delta G_i^{f,n}}{RT} - \frac{\Delta G_i^{f,c}}{RT} - \ln x_i^F \hat{\phi}_i^F \right) \\
& + \sum_{i \in C} x_i \ln x_i \\
& + z - 1 - \ln w \\
& - \frac{A^{mix}}{2\sqrt{2}B^{mix}} \ln\left(\frac{z+(1+\sqrt{2})B^{mix}}{w+(2-\sqrt{2})B^{mix}} \right) \\
\text{s.t.}\quad & z^3 - (1 - B^{mix})z^2 + (A^{mix} - 2B^{mix} - 3{B^{mix}}^2)z - A^{mix}B^{mix} + {B^{mix}}^2 + {B^{mix}}^3 \leq 0 \\
& -z^3 + (1 - B^{mix})z^2 - (A^{mix} - 2B^{mix} - 3{B^{mix}}^2)z + A^{mix}B^{mix} - {B^{mix}}^2 - {B^{mix}}^3 \leq 0 \\
& A^{mix} - \sum_{i \in C} x_i \bar{a}_i = 0 \\
& B^{mix} - \sum_{i \in C} B_i x_i = 0 \\
& \bar{a}_i - \sum_{j \in C} A_{ij} x_j = 0 \ \forall\ i \in C \\
& \sum_{i \in C} x_i = 1 \\
& w = z - B^{mix} \\
& 0 \leq x_i \leq 1 \ \forall\ i \in C \\
& z \geq 0 \\
& w > 0
\end{aligned}\right\} (\hat{S}^{PR})$$

A new variable, w, has been introduced to remove the possibility that the logarithm of a negative number will be taken during the solution of the problem. Formulation $(\hat{S}^{PR})$ contains $|C| + 2$ variables and seven constraints.

4.2 Classification of Nonconvex Terms for Formulation ($\hat{S}^{PR}$)

As explained in section 3.2, the guarantee of convergence to the global minimum solution depends on the construction of valid convex underestimating functions for every nonconvex term in ($\hat{S}^{PR}$). In sections 4.2.1, 4.2.2, and 4.2.3, the nonconvex terms present in formulation ($\hat{S}^{PR}$) are identified. Convex underestimating functions for these terms are generated in the same manner as described in section 3.2.

4.2.1 Univariate Concave Terms

Several univariate concave terms occur in the equation of state constraints in formulation ($\hat{S}^{PR}$). These are the following:

$$-z^2,\ -z^3,\ \text{with } z \geq 0$$
$$-(B^{mix})^2,\ -(B^{mix})^3 \text{ with } B^{mix} \geq 0.$$

4.2.2 Bilinear Terms

Formulation ($\hat{S}^{PR}$) also contains several bilinear terms. These are the following:

- In the equation of state constraints:

$$\pm A^{mix} z,\ \pm 2B^{mix} z,\ \text{and}\ \pm A^{mix} B^{mix}.$$

- In the A-mixing rule constraints:

$$\sum_{i \in C} x_i \bar{a}_i.$$

4.2.3 General Nonconvex Terms

In formulation ($\hat{S}^{PR}$) the following terms are classified as general nonconvex terms:

- In the objective function:

$$-\frac{A^{mix}}{2\sqrt{2}B^{mix}} \ln\left(\frac{z + (1+\sqrt{2})B^{mix}}{w + (2-\sqrt{2})B^{mix}}\right)$$

- In the equation of state constraints:

$$\pm B^{mix} z^2 \text{ and } \pm 3(B^{mix})^2 z$$

5 Analysis for the van der Waals equation

5.1 Formulation of the Phase Stability Problem

The van der Waals equation 1873 is a two-parameter cubic equation of state. The polynomial form for mixtures is:

$$z^3 - (B^{mix} + 1)z^2 + A^{mix}z - A^{mix}B^{mix} = 0. \tag{10}$$

The pressure explicit form of the Van der Waals equation is:

$$P = \frac{RT}{V\left(V - b^{mix}\right)} - \frac{a^{mix}}{V^2}$$

from which the fugacity coefficient for a component in the mixture can be derived,

$$\ln\hat{\phi}_i = \frac{B_i}{z - B^{mix}} - \ln(z - B^{mix}) - \frac{2\sum\limits_{j\in C} A_{ij}x_j}{z}. \tag{11}$$

In the tangent plane distance function, equation 3, the mixture fugacity coefficients participate in the term:

$$\sum_{i\in C} x_i \ln\hat{\phi}_i.$$

Some simplifications of this term can be made based on the following properties:

$$\begin{aligned}
\sum_{i\in C} x_i \tfrac{B_i}{z-B^{mix}} &= \tfrac{B^{mix}}{z-B^{mix}} \\
\sum_{i\in C} x_i \ln(z - B^{mix}) &= \ln(z - B^{mix}) \\
\sum_{i\in C} x_i \frac{2\sum\limits_{j\in C} A_{ij}x_j}{z} &= \tfrac{2A^{mix}}{z}.
\end{aligned}$$

When Eqn. 10 and the simplified mixture fugacity coefficient equation are applied to the tangent plane distance minimization problem $(\hat{S})$, the following formulation is obtained:

$$
\left.
\begin{aligned}
\min\ \frac{\mathcal{F}}{RT} = \quad & \sum_{i \in C} x_i \left(\frac{\Delta G_i^{f,n}}{RT} - \frac{\Delta G_i^{f,c}}{RT} - \ln x_i^F \hat{\phi}_i^F \right) \\
& + \sum_{i \in C} x_i \ln x_i \\
& + \frac{B^{mix}}{w} - \ln w \\
& - \frac{2A^{mix}}{z} \\
\text{s.t.} \quad & z^3 - (B^{mix} + 1) z^2 + A^{mix} z - A^{mix} B^{mix} \leq 0 \\
& -z^3 + (B^{mix} + 1) z^2 - A^{mix} z + A^{mix} B^{mix} \leq 0 \\
& A^{mix} - \sum_{i \in C} x_i \bar{a}_i = 0 \\
& B^{mix} - \sum_{i \in C} B_i x_i = 0 \\
& \bar{a}_i - \sum_{j \in C} A_{ij} x_j = 0 \ \forall \ i \in C \\
& \sum_{i \in C} x_i = 1 \\
& w = z - B^{mix} \\
& 0 \leq x_i \leq 1 \ \forall \ i \in C \\
& z \geq 0 \\
& w > 0
\end{aligned}
\right\} (\hat{S}^{VDW})
$$

A new variable, w, has been introduced to remove the possibility that the logarithm of a negative number or division by zero will take place during the solution of the problem. Formulation $(\hat{S}^{VDW})$ contains $|C| + 2$ variables and seven constraints.

5.2 Classification of Nonconvex Terms for Formulation $(\hat{S}^{VDW})$

As explained in section 3.2, the guarantee of convergence to the global minimum solution depends on the construction of valid convex underestimating functions for every nonconvex term in $(\hat{S}^{VDW})$. In sections 5.2.1, 5.2.2, 5.2.3, and 5.2.4, the nonconvex terms present in formulation $(\hat{S}^{VDW})$ are identified. Convex underestimating functions for these terms are generated in the same manner as described in section 3.2.

5.2.1 Univariate Concave Terms

The van der Waals equation of state contains two univariate concave terms in the formulation of the tangent plane distance minimization problem, $(\hat{S}^{VDW})$. These are the following:

$$-z^2, \text{ and } -z^3, \text{ with } z \geq 0.$$

5.2.2 Bilinear Terms

Formulation ($\hat{S}^{VDW}$) also contains several bilinear terms. These are the following:

- In the equation of state constraints:

$$\pm A^{mix} z \text{ and } \pm A^{mix} B^{mix}.$$

- In the A-mixing rule constraints:

$$\sum_{i \in C} x_i \bar{a}_i.$$

5.2.3 Fractional Bilinear Terms

Formulation ($\hat{S}^{VDW}$) contains the two bilinear fractional terms in the objective function:

$$\frac{B^{mix}}{w} \text{ and } -\frac{2A^{mix}}{z}.$$

Maranas and Floudas (1995) derived a procedure for constructing the convex envelope of products of arbitrary univariate functions. For a bilinear fractional term, $\frac{x}{y}$, this procedure requires the addition of a new variable, u_B. Two constraints are added that provide a lower bound on the new variable. The new constraints are convex and are written:

$$\begin{aligned} -u_B + \frac{x^L}{y} + \frac{x}{y^U} - \frac{x^L}{y^U} &\leq 0 \\ -u_B + \frac{x^U}{y} + \frac{x}{y^L} - \frac{x^U}{y^L} &\leq 0 \end{aligned}$$

For example, the convex underestimators for the bilinear fractional term $\frac{B^{mix}}{w}$ are:

$$\begin{aligned} -u_B + \frac{{B^{mix}}^L}{w} + \frac{B^{mix}}{w^U} - \frac{{B^{mix}}^L}{w^U} &\leq 0 \\ -u_B + \frac{{B^{mix}}^U}{w} + \frac{B^{mix}}{w^L} - \frac{{B^{mix}}^U}{w^L} &\leq 0. \end{aligned}$$

5.2.4 General Nonconvex Terms

In formulation ($\hat{S}^{VDW}$) there is only one term that is classified as a general nonconvex term. This term appears in the equation of state constraints and is $\pm B^{mix} z^2$.

6 Computational Approach

Problem $(\hat{S})$ contains nonconvex terms in both the objective function and in the constraints, so nonlinear solvers may find a local minimum, or may fail to find a feasible solution. The so-called "trivial" solution (where $\mathbf{x} = \mathbf{x}^F$ and $z = z^F$) is always a stationary point of the tangent plane distance function. In many cases, the trivial solution is a local minimum with a large basin of attraction. When the candidate phase is unstable, the trivial solution often causes a local approach to miss the negative global solution. In order to guarantee that the global minimum has not been missed, a convex lower bounding problem, $(\hat{S}^{LB})$ based on $(\hat{S})$ is solved. The solution of $(\hat{S}^{LB})$ is guaranteed to be less than or equal to the solution of $(\hat{S})$ over the same domain. In addition, since $(\hat{S}^{LB})$ is convex, its global minimum can always be obtained.

The basic idea is to bracket the global solution by generating a nonincreasing sequence of upper bounds and a nondecreasing sequence of lower bounds. This procedure is guaranteed to converge within ϵ of the global minimum solution. Upper bounds are obtained by using a "local" nonlinear solver to get a solution of $(\hat{S})$. Lower bounds are obtained by solving $(\hat{S}^{LB})$. The generation of the lower bounding problem is discussed in section 6.1. A branch and bound procedure is used to generate the sequence of upper and lower bounds. The original search domain is partitioned into smaller and smaller domains. As the size of the domains decreases, the quality of solution obtained from the lower bounding problem increases. When the solution of the lower bounding problem in a particular domain is larger than the best upper bound then the domain can be discarded. When the difference between the best upper bound and the minimum lower bound becomes less than a small number, ϵ, the algorithm terminates with the best upper bound as the ϵ-global minimum solution.

6.1 Convex Lower Bounding Problem

In order to provide a guarantee of convergence to the global solution, there are several requirements that the lower bounding problem must meet. These requirements are: 1) the objective function and the feasible domain must be convex, 2) the objective function of the lower bounding problem must be an *underestimator* of the objective function of the original problem, 3) the feasible domain of the lower bounding problem must contain the entire feasible domain of the original problem, and 4) the lower bounding problem must be a reasonable approximation of the original problem, and the quality of approximation must improve as the size of the domain decreases. Requirement 1 guarantees that the global minimum of the lower bounding problem can always be obtained. Requirements 2 and 3 guarantee that the solution of the lower bounding problem is, in fact, a lower bound on the solution of the original problem. Requirement 4 is necessary so that a nondecreasing sequence of lower bounds can be generated, and so that the sequence will converge to the global minimum of the original problem.

The first step is to find a convex underestimator of the objective function, equation 3. In order to highlight the nonconvex portion of the objective function, the equation can be written

$$\frac{\mathcal{F}}{RT} = C(\mathbf{x}) + NC(\mathbf{x}, z, A^{mix}, B^{mix})$$

where,

$$C(\mathbf{x}) = \sum_{i\in C} x_i \left(\frac{\Delta G_i^{f,n}}{RT} - \frac{\Delta G_i^{f,c}}{RT} - \ln x_i^F \hat{\phi}_i^F \right) + \sum_{i\in C} x_i \ln x_i$$
$$NC(\mathbf{x}, z, A^{mix}, B^{mix}) = \sum_{i\in C} x_i \ln \hat{\phi}_i$$

and $C(\mathbf{x})$ denotes the convex portion of $\mathcal{F}$ and $NC(\mathbf{x}, z, A^{mix}, B^{mix})$ denotes the nonconvex portion. A convex underestimating function for $\mathcal{F}$ can be generated by *replacing the nonconvex terms* in $NC(\mathbf{x}, z, A^{mix}, B^{mix})$ with *convex underestimating terms*, which are shown for the SRK, Peng-Robinson, and van der Waals equation in sections 3, 4, and 5, respectively. This results in the equation:

$$\frac{\breve{\mathcal{F}}}{RT} = C(\mathbf{x}) + \breve{NC}(\mathbf{x}, z, A^{mix}, B^{mix}) \leq \frac{\mathcal{F}}{RT}$$

where the symbol $\smile$ denotes the convex underestimating function.

The constraints of problem $(\hat{S})$ consist of nonlinear inequalities and linear equalities. In order to simplify the following analysis, the constraints are grouped:

$$\mathbf{g}(\mathbf{x}, z, A^{mix}, B^{mix}) \leq 0 \quad \equiv \begin{cases} EOS & \leq 0 \\ -EOS & \leq 0 \\ A^{mix} - \sum_{i\in C} x_i \bar{a}_i & = 0 \end{cases}$$

$$\mathbf{h}(\mathbf{x}, B^{mix}) = 0 \quad \equiv \begin{cases} B^{mix} - \sum_{i\in C} B_i x_i & = 0 \\ \bar{a}_i - \sum_{j\in C} A_{ij} x_j & = 0 \;\forall\; i \in C \\ 1 - \sum_{i\in C} x_i & = 0 \end{cases}$$

Now, let the set, $\mathcal{Y}$, define the feasible region of problem $(\hat{S})$.

$$\mathcal{Y} \equiv \{\{\mathbf{x}, z, A^{mix}, B^{mix}\}: \quad \begin{array}{l} \mathbf{g}(\mathbf{x}, z, A^{mix}, B^{mix}) \leq 0,\ \mathbf{h}(\mathbf{x}, z, A^{mix}, B^{mix}) = 0 \\ \mathbf{x}^L \leq \mathbf{x} \leq \mathbf{x}^U,\ z^L \leq z \leq z^U \Big\} \end{array}$$

In general, $\mathcal{Y}$ is a nonconvex set. By replacing every nonconvex term in the set of inequality constraints, $\mathbf{g}(\mathbf{x}, z, A^{mix}, B^{mix})$, with a convex underestimating function, we obtain a *convex relaxation* of the feasible region, $\breve{\mathcal{Y}}$. Convex relaxation refers to the fact that the new feasible region is convex, contains $\mathcal{Y}$, and is at least as large as $\mathcal{Y}$.

$$\breve{\mathcal{Y}} \equiv \{\{\mathbf{x}, z, A^{mix}, B^{mix}\}: \quad \begin{array}{l} \breve{\mathbf{g}}(\mathbf{x}, z, A^{mix}, B^{mix}) \leq 0,\ \mathbf{h}(\mathbf{x}, z, A^{mix}, B^{mix}) = 0 \\ \mathbf{x}^L \leq \mathbf{x} \leq \mathbf{x}^U,\ z^L \leq z \leq z^U \Big\} \end{array}$$

In the next section, the basic steps of the branch and bound global optimization algorithm are described. Using the notation introduced above, the upper bounding problem is,

$$\begin{array}{lll} (UB) & \min & \frac{\mathcal{F}(\mathbf{x}, z, A^{mix}, B^{mix})}{RT} \\ & \text{s.t.} & \{\mathbf{x}, z, A^{mix}, B^{mix}\} \in \mathcal{Y} \end{array}$$

and the lower bounding problem is,

$$\begin{array}{lll} (LB) & \min & \frac{\breve{\mathcal{F}}(\mathbf{x}, z, A^{mix}, B^{mix})}{RT} \\ & \text{s.t.} & \{\mathbf{x}, z, A^{mix}, B^{mix}\} \in \breve{\mathcal{Y}}. \end{array}$$

6.2 Algorithmic Description

The αBB algorithm, (Androulakis *et al.* (1995), Adjiman *et al.* (1998a) (1998b)), is employed to determine the global solution of $(\hat{S})$. Each iteration of αBB consists of a *branching* step and a *bounding* step. In the bounding step, problems (UB) and (LB) are solved. In the branching step, the current subdomain is divided into a number of smaller subdomains. The subdivision of the domains results in increasingly tight lower bounding problems, creating a nondecreasing sequence of lower bounds on the global solution.

In the αBB approach, nonconvex terms with special structure are identified and replaced with tight convex underestimating functions to formulate (LB). Nonconvex terms that do not possess special structure are replaced with an α-based underestimator, equation 6. The value of α required to convexify a term decreases as the bounds on the variables are tightened. Therefore, in each subdomain, new α values are calculated.

The basic steps of the algorithm are now described. A detailed description of the αBB algorithm can be found in Androulakis *et al.* (1995), and Adjiman *et al.* (1998b).

STEP 0 - Initialization

The relative convergence tolerance, ϵ, is specified and the iteration counter, $Iter$, is set to one. The current subdomain, $\left[\mathbf{y}^{L,Iter}, \mathbf{y}^{U,Iter}\right]$ is set to the global domain, $\left[\mathbf{y}^{LBD}, \mathbf{y}^{UBD}\right]$. Note that $\mathbf{y} = \{\mathbf{x}, z, A^{mix}, B^{mix}\}$. The lower and upper bounds, LBD and UBD, on the global minimum of $(\hat{S})$ are initialized. An initial current point, $\mathbf{y}^{c,Iter}$ is chosen.

STEP 1 - Update Upper Bound on Global Solution

The current point is used as a starting point for a local solution to problem (UB). If the solution to this problem is less than UBD, then UBD is updated to the new solution, and the variable values at the new upper bound are stored.

Important Note: If the solution of (UB) *in any iteration* is negative, then the global optimization procedure can be terminated, since the phase is unstable.

STEP 2 - Select Branching Variable and Partition Current Region

The current domain is partitioned into two subdomains, r_1 and r_2 by bisecting the edge corresponding to a chosen variable. The criterion for choosing the branching variable is discussed in Section 6.3.

STEP 3 - Solution of Bound Update Problems in r_1 and r_2

The bounds on the variables in a subdomain can be improved by solving a so-called *bound update problem.* This problem is formulated by replacing the objective function of (LB) with the variable whose bound is to be updated. For example, the bounds on the variable x_i are updated by solving the following two problems:

$$\begin{aligned} x_i^L = \ & \min \quad x_i \\ & \text{s.t.} \quad \{\mathbf{x}, z, A^{mix}, B^{mix}\} \in \breve{\mathcal{Y}} \end{aligned}$$

$$\begin{aligned} x_i^U = \ & \min \quad -x_i \\ & \text{s.t.} \quad \{\mathbf{x}, z, A^{mix}, B^{mix}\} \in \breve{\mathcal{Y}}. \end{aligned}$$

The variables whose bounds are updated by this method and the frequency of bound updates are discussed in section 6.5.

STEP 4 - Update α's in r_1 and r_2

The α parameters are updated inside both subdomains. The method for calculating the α's is discussed in section 6.4.

STEP 5 - Solve Lower Bounding Problems in r_1 and r_2

The lower bounding problem (LB) is solved in subdomains r_1 and r_2. If the solution in a subdomain is greater than the current upper bound, then this region is guaranteed not to contain the global minimum and it is fathomed. Otherwise, the solution is stored along with the variable bounds for the region and the variable values at the solution.

STEP 6 - Update iteration counter and LBD

The iteration counter is increased by one. The lower bound, LBD, is updated to be the minimum of all stored solutions. The current search region is selected as the subdomain containing the minimum of all stored lower bound solutions. The current variable bounds, $\left[\mathbf{y}^{L,Iter}, \mathbf{y}^{U,Iter}\right]$ are updated to be the bounds of the current region, and the current point $\mathbf{y}^{c,Iter}$ is updated to the solution point of the current region.

STEP 7 - Convergence Check

If $\frac{(UBD-LBD)}{UBD+1} > \epsilon$ then return to STEP 1.
Otherwise, ϵ-convergence to the global minimum solution has been achieved.

This global optimization algorithm has been extensively tested with a variety of phase stability problems. While the basic outline of the algorithm is rigid, there is significant freedom in selecting options such as the criterion used to determine the branching variable, the method for calculating the α parameters, and how often to solve variable bound update problems. Through the computational studies, the options that provide the best performance have been identified. In the next three sections, these options are briefly described.

6.3 Analysis of the Branching Criteria

Formulations ($\hat{S}^{SRK}$), ($\hat{S}^{PR}$), and ($\hat{S}^{VDW}$), each contain the same set of variables, $\{\mathbf{x}$, z, A^{mix}, B^{mix}, w $\}$. The mole fraction and compressibility variables, $\mathbf{x}$ and z, are the only independent variables in the formulation. The remaining variables, A^{mix}, B^{mix}, w, are actually functions of $\mathbf{x}$ and z. Therefore, it is natural to select only the $\mathbf{x}$ and z variables to branch on, and calculate the bounds on A^{mix}, B^{mix} and w based on the bounds of $\mathbf{x}$ and z. However, A^{mix} and B^{mix} participate in nonconvex terms in both the objective function and in the equation of state constraints. It was found that convergence is achieved faster when A^{mix} and B^{mix} are branched on in addition to $\mathbf{x}$ and z.

Many alternatives exist for selecting the branching variable at each iteration. These are briefly summarized below:

1. Variable with the least reduced axis.
2. Variable with the least reduced axis in the nonconvex term with the maximum possible separation.
3. Variable with the least reduced axis in the nonconvex term with the largest difference between the original nonconvex term and the convex underestimator at the current point.
4. Variable with largest sum of maximum possible separation over all nonconvex terms it participates in.
5. Variable with largest sum of differences over all nonconvex terms it participates in.

Least reduced axis refers to the variable whose bounds in the current domain have the largest separation. Going down the list, each option becomes more sophisticated and requires more computational effort, but provides "better" choices for branching variables. The computational studies have shown that option 5 provides the best results. The computational effort required to select the branching variables is less than one percent of the total computational effort.

6.4 Analysis of α Calculation Methods

The α parameter plays an important role in the αBB algorithm. Using the smallest possible value of α enhances the convergence of the algorithm. Therefore, when it has been possible to derive an expression for the exact smallest value of α, this expression has been used.

For some terms, it is not possible to derive a simple expression for α. In these cases some approximation of α must be used. Adjiman *et al.* (1998a) have developed a large number of alternative methods for obtaining tight lower bounds on α. The basic idea of these methods is to use obtain a lower bound on the minimum eigenvalue of the interval Hessian matrix of a nonconvex term. The computational studies have shown that a scaled Gerschgorin method provides the best α values.

We have observed that the general nonconvex terms in formulations ($\hat{S}^{SRK}$), ($\hat{S}^{PR}$), and ($\hat{S}^{VDW}$), are usually very close to convex. The α calculation methods, however must be valid over the entire domain in order to provide the guarantee of global optimality. As a result, very small α values are usually sufficient to convexify the term over most of the domain, and a larger value is needed only in a small subdomain. We have solved each of the test problems in section 7 using small fixed values of α. In each case, the global solution was obtained, and the number of iterations needed is drastically reduced.

6.5 Variable Bound Updates

The inclusion of variable bound update problems in the αBB algorithm can provide a significant reduction in the number of iterations needed to converge to the global solution. There are two issues to address for the solution of variable bound update problems. The first is that some or all of the variables may not benefit from the solution of bound update problems. Through the computational studies we have found that the bounds on the $\mathbf{x}$, z, A^{mix} and B^{mix} variables can be improved, but not the w substitution variable.

The second issue is that for every variable whose bounds are updated, two additional local optimization problems must be solved. This implies that, for a two component example where the $\mathbf{x}$, z, A^{mix} and B^{mix} variables are updated every iteration, 10 additional problems are solved per iteration. For an eight component system, the number increases to 22 additional problems. In order to make this additional effort worthwhile the improved variable bounds should result in at least a corresponding reduction in the number of iterations. In the computational studies it has been found that for problems with two or three components, it is beneficial to update all variables at every iteration. However, for problems with four or more components, five variables are selected at random every iteration, and bound update problems for only those five variables are solved.

7 Computational Studies

A number of test problems taken from the literature illustrate the proposed global optimization approach. These problems have been solved using the αBB algorithm, which has been written in C. All computations were performed on a Hewlett-Packard J-2240 workstation. The local nonlinear solver SNOPT was used for the upper bounding and lower bounding problems and for the variable bound update problems. Pure component data, such as critical constants and acentric factors, were obtained from Reid *et al.* (1987), except when noted.

For each example, the solutions have been obtained using an interval-Hessian α calculation method, and using small fixed values of α. A convergence tolerance of 1×10^{-6} is used for determining global optimality. A solution is identified as negative, thus terminating the procedure, when the objective function becomes less than -1×10^{-6}. Explicit formulations of these examples can be found in the handbook of test problems by Floudas *et al.* (1999). In all examples, the initial bounds for the mole fraction variables are 1×10^{-6} and 1.0. The convergence of the procedure is independent of any initial guess, so at every iteration, a random point can be used to initialize the solution of the upper and lower bounding problems.

It has been suggested that branch and bound algorithms are subject to errors induced by round-off error, especially in deciding whether to keep or reject a region based on the solution of the lower bounding problem. Specifically, the NLP solvers used may find a solution to the lower bounding problem that is only accurate to 1×10^{-6}. This error may cause the lower bound solution to be *greater* than the current best upper bound by some small amount, and the region will be incorrectly rejected. In our approach, a region is only rejected if the solution of the lower bounding problem obtained in that region is *greater than* $UB + \epsilon_o$. A typical value of ϵ_o is 1×10^{-7}.

7.1 Van der Waals equation

7.1.1 Example 1: Binary Type I Mixture

This is a binary mixture classified by Konynenburg and Scott (1980) as having type I behavior. This system was studied by Hua *et al.* (1998b) using interval-Newton methods to enclose all stationary points. The binary interaction parameters and the composition of the candidate phase are shown in Table 1. This system contains only one minimum in the Gibbs free energy, which is the trivial solution. Out of 100 local optimization runs from random starting points, the minimum was found every time (see Table 2). The candidate phase is stable and the proposed approach converged to the global solution in about 2 seconds (see Table 3).

7.2 SRK equation

Four examples are solved using the SRK equation of state.

For the first two examples, we have used the original Soave equations to calculate the pure-component parameters. These are:

$$
\begin{aligned}
&A_i = 0.42747\frac{PT_{c,i}^2}{P_{c,i}T^2}\left[1 + (0.480 + 1.574\omega_i - 0.176\omega_i^2)(1 - \sqrt{\tfrac{T}{T_{c,i}}})\right]^2\\
&B_i = 0.08664\frac{PT_{c,i}}{P_{c,i}T}\\
&A_{ij} = (1 - k_{ij})\sqrt{A_iA_j}.
\end{aligned}
$$

For examples 4 and 5, the Graboski-Daubert pure component equations have been used, as compiled in Walas (1985). These are:

$$A_i = 0.42747\frac{PT_{c,i}^2}{P_{c,i}T^2}\left[1 + (0.48508 + 1.55171\omega_i - 0.15613\omega_i^2)(1 - \sqrt{\tfrac{T}{T_{c,i}}})\right]^2$$
$$B_i = 0.08664\frac{PT_{c,i}}{P_{c,i}T}$$
$$A_{ij} = (1 - k_{ij})\sqrt{A_i A_j}.$$

7.2.1 Example 2: Hydrogen Sulfide and Methane

The system hydrogen sulfide-methane is a standard benchmark in the phase stability literature. It was introduced by Michelsen (1982a) to illustrate that the stability problem can be quite difficult, even in small systems. In this work, the stability of six potential solutions is analyzed (see Table 4). Multiple local minima are present in all cases (see Table 5). Candidate solution 2 appears to be especially difficult. Out of 100 trials with a local solver, stable (nonnegative) solutions were found 83 times, but the phase is actually unstable. For the six candidate phases, the locations of the local minima are identical to those reported in Hua *et al.* (1998b). The computational results for the proposed approach are shown in Table 6. The unstable cases, (2, 4, and 5) are terminated in less than 0.20 seconds. For the stable phases, (1, 3, and 6), convergence is obtained in 3 to 5 seconds when α is calculated. When a small fixed value of α is used, the computational effort is reduced by 40 to 50 percent.

7.2.2 Example 3: Water, Carbon Dioxide, Isopropanol, Ethanol

This example is a challenging four component system whose phase behavior of was examined by Kohse and Heidemann (1992). The candidate solutions in this example were obtained near the tricritical lines. Table 7 shows the compositions of the candidate phases. All of the binary interaction parameters were set to zero for this example. For each system, multiple local minima exist, and the minima with negative tangent plane distances are very hard to locate for the local solver (see Table 8). For candidate phase 1, the local solver found a stable (nonnegative) solution 86 out of 100 times. The system is actually unstable, but a negative minimum was found only 4 out of 100 times. For candidate phase 2, a stable solution was found 94 out of 100 times. This system is also unstable, but a negative minimum was found only 6 out of 100 times, and the global solution was not located by the local solver. Candidate solution 3 is also unstable, but a negative solution was found only 3 times out of 100 local solutions. Similarly, candidate solution 5 is unstable, but the local solver found a negative solution only 5 out of 100 times. Candidate phase 7 is stable, but the global minimum solution was located only 3 out of 100 times.

In examples containing two or three components, it is possible to plot the tangent plane distance function versus the $|C|-1$ independent mole fractions and identify the global minimum visually. However in systems with four or more components, it is not possible to determine the solution graphically. Hence, rigorous global optimization methods, such as the proposed approach, must be used. The computational results are shown in Table 9. Even though this is a large, difficult example, the procedure terminated with a negative tangent plane distance in about 1 second for all six candidate phases. For the stable phase, the procedure converged to the global minimum solution in around two minutes.

7.2.3 Example 4: Eight Hydrocarbons

This system of eight hydrocarbons was studied by Nagarajan *et al.* (1991a) and Sun and Seider (1995). We have used the Peng-Robinson binary interaction parameters reported by Nagarajan *et al.* (1991a) in the SRK formulation, due to the similarity of the two equations of state. The binary interaction parameters and the compositions of the three candidate phases are shown in Table 10. For the two unstable phases, two local minima were located for each, and for candidate phase 2, the local solver found the global minimum only five times out of 100, (see Table 11). This example was chosen to illustrate the application of the global optimization approach to systems containing a large number of components. For candidate phase 1, the proposed approach terminated after 23 seconds when a solution with a negative tangent plane distance was located, shown in Table 12. For candidate phase 2, a negative solution was found in 25.6 seconds with α caluculated and in 20 seconds when a small fixed value of α was used. Candidate phase 3 is stable, and the proposed approach required about 7 and a half minutes to converge to the global minimum. When a small value of alpha is used, the required time drops to just under 7 minutes.

7.3 Peng-Robinson equation

Six examples are solved using the Peng-Robinson equation of state. The original formulas are used to calculate the pure-component parameters, Peng and Robinson (1976). These are:

$$
\begin{aligned}
A_i &= 0.45724 \tfrac{PT_{c,i}^2}{P_{c,i}T^2}\left[1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2)(1 - \sqrt{\tfrac{T}{T_{c,i}}})\right]^2 \\
B_i &= 0.07780 \tfrac{PT_{c,i}}{P_{c,i}T} \\
A_{ij} &= (1 - k_{ij})\sqrt{A_i A_j}.
\end{aligned}
$$

7.3.1 Example 5: Hydrogen Sulfide and Methane

This is the same hydrogen sulfide-methane system as studied in example 2. The same binary interaction parameters used for the SRK implementation of this example have been used for the Peng-Robinson implementation. For the Peng-Robinson equation, the stability of two potential solutions is analyzed. The compositions of the candidate solutions and the binary interaction parameters are shown in Table 13. Multiple local minima are present in each case (see Table 14). For candidate phase 1, stable solutions were found in 78 out of 100 local runs, while the negative solution was found only 22 times. Table 15 shows the results of the global optimization approach. For candidate phase 1, a negative solution was found in 0.10 second. For candidate phase 2, the procedure converged to the global minimum solution in 4.95 seconds when the α parameters were calculated with and interval-Hessian method. Using a small fixed value of α reduced the CPU time to 3.03 seconds.

7.3.2 Example 6: Nitrogen, Methane and Ethane

The ternary system nitrogen-methane-ethane was studied by Hua *et al.* (1998b). The binary interaction parameters and four candidate phase compositions are shown in Table 16. For candidate phase 1, all of the 100 local runs found a negative solution (see Table 17). Therefore it is easy for the global optimization approach to determine that this system is unstable in the first iteration, as shown in Table 18. Candidate phase 2 is a more challenging example for the local solver, as the negative solution was found 34 out of 100 times. This candidate phase is also more difficult for the interval-Newton method applied by Hua *et al.* (1998b), since many more root-inclusion tests were required for this phase than any other candidate phase. This is most likely due to the presence of a stationary point in close proximity to the trivial solution. The global optimization approach quickly locates the negative solution and terminates in 0.24 seconds. These examples illustrate the advantage of using a global optimization approach for the minimization of the tangent plane distance function. The problem can be terminated at a very early stage when a negative tangent plane distance is located.

Candidate phases 3 and 4 are both stable, with the trivial solution as the only minimum. The global optimization approach converged to the solution in 12.8 seconds for phase 3 and 10 seconds for phase 4. Using a small fixed value of α results in a reduction of the computational effort by 60 to 70 percent for candidate phases 3 and 4.

7.3.3 Example 7: Methane, Hexane and Hydrogen Sulfide

The ternary system methane-hexane-hydrogen sulfide was studied by Kohse and Heidemann (1992). This system has a complicated phase diagram containing regions where the equilibrium state consists of three and four phases. The binary interaction parameters and candidate phase compositions are shown in Table 19. Both candidate solutions in this example are stable (see Table 20). The computational results for this system are shown in Table 21. For candidate phase 1, the procedure converges to the global minimum solution in 7.7 seconds when α is calculated, and in about 7 seconds when a small fixed value of α is used. Similar results are seen for candidate phase 2, with CPU times of 8.5 seconds and 7.9 seconds for the α-calculated and α-fixed runs, respectively.

7.3.4 Example 8: Eight Hydrocarbons

This is the same 8-hydrocarbon example addressed in example 4 for the SRK equation. In this case, the Peng-Robinson equation is used, as was done by Nagarajan *et al.* (1991a) and Sun and Seider (1995). The binary interaction parameters and candidate phase composition are provided in Table 22. We have used the compositions of the global minimum solution reported by Sun and Seider (1995) and shown in Table 22 as the candidate phases. However, as Table 23 shows, we found both phases to be unstable, with small negative solutions for the tangent plane distance. This is most likely due to the fact that different binary interaction parameters were used. For both candidate phases, the proposed procedure was able to terminate quickly when a negative tangent plane distance was found (see Table 24). Despite the large number of components in this system, the computational effort was around 12 seconds. We also generated a stable candidate phase to test the computational effort for solving such a large problem to global optimality. Candidate phase 3 required 8.5 minutes for α-calculated underestimators, and about 8 minutes for small, fixed values of α. This effort is very reasonable, given the size of the problem.

8 Conclusions

It has been shown that the phase stability problem can be formulated as an optimization problem using equations of state to model both liquid and vapor phase behavior. The optimization approach has the benefit that it can be terminated at a very early stage if a negative tangent plane distance value is found. This work presents a global optimization approach that provides a theoretical guarantee that the global minimum tangent plane distance can be determined. Three cubic equations of state, SRK, Peng-Robinson, and van der Waals, have been studied in this work. It should be noted that the proposed method can be applied to any equation of state, and to any mixing rule. Special structures that arise from using these three equations of state have been identified and exploited in the global optimization approach. The solution of several test problems involving up to eight components has shown that this method is computationally efficient and can handle large problems.

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Example 1: T = 608.40 K; P = 239.112 bar		
k_{ij}	1	2
1	0.0	-0.212463
2	-0.212463	0.0
Trial	$\mathbf{x}^F; z^F$	
1	(0.40,0.60); 0.320336	

Table 1: Data for Example 1

Postulated Phase	Solutions		Times Located out of 100 Local Optimization Trials
	Solution ($\mathbf{x}$) z	TPD	
1	(0.40,0.60) 0.32034	0.0	100

Table 2: Local and global minima for Example 1

Postulated Phase	Global Solution		α-Calculated	α=0.001
	Solution ($\mathbf{x}$) z	TPD	CPU	CPU
1	(0.40,0.60) 0.32034	0.0	2.31	1.91

Table 3: Computational results for Example 1

Example 2: $T = 190$ K; $P = 40.53$ bar		
k_{ij}	1	2
1	0.0	0.08
2	0.08	0.0
Trial	$\mathbf{x}^F; z^F$	
1	(0.0115,0.9885); 0.545951	
2	(0.0187,0.9813); 0.53198	
3	(0.0700,0.9300); 0.167687	
4	(0.5000,0.5000); 0.10601	
5	(0.8880,0.1120); 0.0937813	
6	(0.8900,0.1100); 0.0937415	

Table 4: Data for Example 2

Postulated Phase	Solutions: Solution ($\mathbf{x}$) z	Solutions: TPD	Times Located out of 100 Local Optimization Trials
1	(0.02369,0.97631) 0.25088	0.013753	40
	(0.03257,0.96743) 0.20024	0.013061	25
	(0.01150,0.98850) 0.54595	0.0	35
2	(0.88477,0.11523) 0.09385	0.01098	4
	(0.03133,0.96867) 0.29605	0.00795	15
	(0.01870,0.98130) 0.53198	0.0	65
	(0.07668,0.92332) 0.16382	-0.00393	16
3	(0.87426,0.12574) 0.09406	0.05128	6
	(0.03043,0.96957) 0.29176	0.00997	30
	(0.01784,0.98216) 0.53375	0.00145	36
	(0.07000,0.93000) 0.16769	0.0	28
4	(0.88186,0.11814) 0.09390	-0.05689	4
	(0.03107,0.96893) 0.29478	-0.07122	16
	(0.01844,0.98156) 0.53251	-0.07934	67
	(0.07462,0.92538) 0.16536	-0.08252	13
5	(0.03165,0.96835) 0.29754	0.01016	15
	(0.01901,0.98099) 0.53135	0.00240	66
	(0.88800,0.11200) 0.09378	0.0	5
	(0.07918,0.92082) 0.16323	-0.00244	14
6	(0.03185,0.96815) 0.29851	0.01871	30
	(0.01921,0.98079) 0.53093	0.01108	40
	(0.08087,0.91913) 0.16247	0.00563	24
	(0.89000,0.11000) 0.09374	0.0	6

Table 5: Local and global minima for Example 2

Postulated Phase	Global Solution		α-Calculated	α=0.001
	Solution ($\mathbf{x}$) z	TPD	CPU	CPU
1	(0.01150,0.98850) 0.54595	0.0	2.84	1.65
2	(0.07668,0.92332) 0.16382	-0.00393	0.18	0.08
3	(0.07000,0.93000) 0.16769	0.0	4.69	1.87
4	(0.07462,0.92538) 0.16536	-0.08252	0.15	0.04
5	(0.07918,0.92082) 0.16323	-0.00244	0.15	0.04
6	(0.89000,0.11000) 0.09374	0.0	5.00	2.95

Table 6: Computational results for Example 2

Example 3: T = 350.0 K; P = 22.5 bar	
$k_{ij} = 0 \ \forall \ (i,j)$	
Trial	$\mathbf{x}^F; z^F$
1	(0.58223,0.07232,0.18797,0.15748); 0.0372065
2	(0.03154,0.93280,0.02311,0.01255); 0.919594
3	(0.04647,0.95071,0.00167,0.00115); 0.92743
4	(0.61462,0.00105,0.21065,0.17368); 0.03789
5	(0.02981,0.96694,0.00152,0.00173); 0.92969
6	(0.99758,0.00003,0.00013,0.00226); 0.019238
7	(0.17170,0.14230,0.37430,0.31170); 0.05531

Table 7: Data for Example 3

Postulated Phase	Solutions Solution $(\mathbf{x})$ z	TPD	Times Located out of 100 Local Optimization Trials
1	(0.07332,0.67750,0.17818,0.07100) 0.12412	0.63328	3
	(0.03153,0.93280,0.02312,0.01255) 0.91959	0.0	83
	(0.31949,0.12415,0.35670,0.19966) 0.04955	-0.02291	3
	(0.99808,0.00107,0.00007,0.00078) 0.01919	-0.45086	1
2	(0.07334,0.67750,0.17814,0.07102) 0.12411	0.63333	3
	(0.03154,0.93280,0.02311,0.01255) 0.91959	0.0	91
	(0.31966,0.12411,0.35651,0.19972) 0.04954	-0.02903	6
	(0.99808,0.00106,0.00007,0.00079) 0.01919	-0.45103	0
3	(0.22541,0.72309,0.03479,0.01671) 0.06817	0.91915	4
	(0.04647,0.95071,0.00167,0.00115) 0.92743	0.0	93
	(0.99923,0.00072,0.00000,0.00005) 0.01915	-0.84346	3
4	(0.37575,0.24684,0.24280,0.13461) 0.47843	2.34180	2
	(0.33650,0.00185,0.43011,0.23154) 0.05240	-0.02837	20
	(0.99898,0.00002,0.00008,0.00092) 0.01918	-0.44128	78
5	(0.18941,0.73400,0.04167,0.03392) 0.06085	0.99176	4
	(0.02981,0.96694,0.00152,0.00173) 0.92969	0.0	91
	(0.99874,0.00114,0.00000,0.00012) 0.01916	-0.40150	5
6	(0.25572,0.30249,0.23283,0.20896) 0.47648	2.39401	39
	(0.99758,0.00003,0.00013,0.00227) 0.01924	0.0	1
	(0.18498,0.00238,0.45438,0.35825) 0.05853	-0.01286	60
7	(0.04668,0.67967,0.16562,0.10803) 0.12748	0.64643	2
	(0.02057,0.93736,0.02231,0.01976) 0.91947	0.02509	95
	(0.17170,0.14230,0.37430,0.31170) 0.05531	0.0	3

Table 8: Local and global minima for Example 3

Postulated Phase	Global Solution		α-Calculated	α=0.001
	Solution ($\mathbf{x}$) z	TPD	CPU	CPU
1	(0.99808,0.00107,0.00007,0.00078) 0.01919	-0.45086	0.94	0.13
2	(0.99808,0.00106,0.00007,0.00079) 0.01919	-0.45103	0.87	0.64
3	(0.99923,0.00072,0.00000,0.00005) 0.01915	-0.84346	0.83	0.66
4	(0.99898,0.00002,0.00008,0.00092) 0.01918	-0.44128	0.78	0.70
5	(0.99874,0.00114,0.00000,0.00012) 0.01916	-0.40150	0.84	0.25
6	(0.18498,0.00238,0.45438,0.35825) 0.05853	-0.01286	1.00	0.67
7	(0.17170,0.14230,0.37430,0.31170) 0.05531	0.0	129.1	72.2

Table 9: Computational results for Example 3

Example 4: $T = 353.0$ K; $P = 385.0$ bar								
k_{ij}	1	2	3	4	5	6	7	8
1	0.0	0.002	0.017	0.015	0.02	0.039	0.05	0.09
2	0.002	0.0	0.0	0.025	0.01	0.056	0.04	0.055
3	0.017	0.0	0.0	0.0	0.0	0.0	0.01	0.01
4	0.015	0.025	0.0	0.0	0.0	0.0	0.0	0.0
5	0.02	0.01	0.0	0.0	0.0	0.0	0.0	0.0
6	0.039	0.056	0.0	0.0	0.0	0.0	0.0	0.0
7	0.05	0.04	0.01	0.0	0.0	0.0	0.0	0.0
8	0.09	0.055	0.01	0.0	0.0	0.0	0.0	0.0
Trial	$\mathbf{x}^F; z^F$							
1	(0.7212,0.09205,0.04455,0.03123,0.01273,0.01361,0.07215,0.01248); 1.13452							
2	(0.6598,0.09084,0.04726,0.03509,0.01492,0.01657,0.1047,0.03082); 1.24278							
3	(0.5854,0.1951,0.0488,0.0488,0.0244,0.02435,0.0488,0.02435); 1.055057							

Table 10: Data for Example 4

Postulated Phase	Solutions		Times Located out of 100 Local Optimization Trials
	Solution ($\mathbf{x}$) z	TPD	
1	(0.74890,0.09158,0.04253,0.02884, 0.01144,0.01185,0.05768,0.00718) 1.10392	-0.00005	4
	(0.59569,0.08715,0.04848,0.03772, 0.01658,0.01953,0.13415,0.06070) 1.41401	-0.00260	95
2	(0.64343,0.09010,0.04770,0.03588, 0.01539,0.01730,0.11285,0.03735) 1.28096	-0.000008	95
	(0.76967,0.09070,0.04055,0.02668, 0.01030,0.01022,0.04753,0.00435) 1.08800	-0.00165	5
3	(0.5854,0.1951,0.0488,0.0488, 0.0244,0.02435,0.0488,0.02435) 1.055057	0.0	90

Table 11: Local and global minima for Example 4

Postulated Phase	Global Solution		α-Calculated	α=0.001
	Solution ($\mathbf{x}$) z	TPD	CPU	CPU
1	(0.59569,0.08715,0.04848,0.03772, 0.01658,0.01953,0.13415,0.06070) 1.41401	-0.00260	10.01	9.44
2	(0.76967,0.09070,0.04055,0.02668, 0.01030,0.01022,0.04753,0.00435) 1.08800	-0.00165	9.64	9.29
3	(0.5854,0.1951,0.0488,0.0488, 0.0244,0.02435,0.0488,0.02435) 1.055057	0.0	455.2	403.6

Table 12: Computational results for Example 4

Example 5: $T = 190.0$ K; $P = 40.53$ bar		
k_{ij}	1	2
1	0.0	0.08
2	0.08	0.0
Trial	$\mathbf{x}^F; z^F$	
1	(0.0384,0.9616); 0.45055	
2	(0.8802,0.1198); 0.08339	

Table 13: Data for Example 5

Postulated Phase	Solutions		Times Located out of 100 Local Optimization Trials
	Solution ($\mathbf{x}$) z	TPD	
1	(0.04573,0.95427) 0.36089	0.00048	3
	(0.03840,0.96160) 0.45055	0.0	75
	(0.94563,0.05437) 0.08233	-0.49698	22
2	(0.03335,0.06665) 0.28442	0.02775	3
	(0.02102,0.97898) 0.49948	0.02139	79
	(0.09275,0.90725) 0.14048	0.01072	10
	(0.88021,0.11979) 0.08339	0.0	8

Table 14: Local and global minima for Example 5

Postulated Phase	Global Solution		α-Calculated	α=0.001
	Solution ($\mathbf{x}$) z	TPD	CPU	CPU
1	(0.94563,0.05437) 0.08233	-0.49698	0.11	0.05
2	(0.88021,0.11979) 0.08339	0.0	4.95	3.03

Table 15: Computational results for Example 5

Example 6: $T = 270.0$ K; $P = 76.0$ bar			
k_{ij}	1	2	3
1	0.0	0.038	0.08
2	0.038	0.0	0.021
3	0.08	0.021	0.0
Trial	$\mathbf{x}^F; z^F$		
1	(0.30, 0.10, 0.60); 0.496366		
2	(0.15, 0.30, 0.55); 0.448135		
3	(0.08, 0.38, 0.54); 0.405804		
4	(0.05, 0.05, 0.90); 0.235641		

Table 16: Data for Example 6

Postulated Phase	Solutions		Times Located out of 100 Local Optimization Trials
	Solution ($\mathbf{x}$) z	TPD	
1	(0.31158,0.10161,0.58681) 0.51850	-0.00001	53
	(0.13306,0.06780,0.79914) 0.26222	-0.01481	47
2	(0.15000,0.30000,0.55000) 0.44813	0.0	65
	(0.09681,0.24513,0.65806) 0.30553	-0.00117	34
3	(0.08000,0.38000,0.54000) 0.40580	0.0	99
4	(0.05000,0.05000,0.90000) 0.23564	0.0	99

Table 17: Local and global minima for Example 6

Postulated Phase	Global Solution		α-Calculated	α=0.001
	Solution $(\mathbf{x})$ z	TPD	CPU	CPU
1	(0.13306,0.06780,0.79914) 0.26222	-0.01481	0.31	0.28
2	(0.09681,0.24513,0.65806) 0.30553	-0.00117	0.24	0.20
3	(0.08000,0.38000,0.54000) 0.40580	0.0	12.80	4.11
4	(0.05000,0.05000,0.90000) 0.23564	0.0	10.41	4.06

Table 18: Computational results for Example 6

Example 7: $T = 180.0$ K; $P = 80.0$ bar			
k_{ij}	1	2	3
1	0.0	0.0	0.08
2	0.0	0.0	0.0
3	0.08	0.0	0.0
Trial	$\mathbf{x}^F; z^F$		
1	(0.7440,0.0379,0.2181); 0.22477		
2	(0.1591,0.0173,0.8236); 0.18066		

Table 19: Data for Example 7

Postulated Phase	Solutions		Times Located out of 100 Local Optimization Trials
	Solution ($\mathbf{x}$) z	TPD	
1	(0.37876,0.05317,0.56807) 0.20647	0.00581	1
	(0.74402,0.03793,0.21805) 0.22477	0.0	99
2	(0.15913,0.01732,0.82355) 0.10866	0.0	100

Table 20: Local and global minima for Example 7

Postulated	Global Solution		α-Calculated	α=0.001
Phase	Solution $(\mathbf{x})$ z	TPD	CPU	CPU
1	(0.74402,0.03793,0.21805) 0.22477	0.0	7.70	6.94
2	(0.15913,0.01732,0.82355) 0.10866	0.0	8.54	7.95

Table 21: Computational results for Example 7

Example 8: $T = 353.0$ K; $P = 385.0$ bar								
k_{ij}	1	2	3	4	5	6	7	8
1	0.0	0.002	0.017	0.015	0.02	0.039	0.05	0.09
2	0.002	0.0	0.0	0.025	0.01	0.056	0.04	0.055
3	0.017	0.0	0.0	0.0	0.0	0.0	0.01	0.01
4	0.015	0.025	0.0	0.0	0.0	0.0	0.0	0.0
5	0.02	0.01	0.0	0.0	0.0	0.0	0.0	0.0
6	0.039	0.056	0.0	0.0	0.0	0.0	0.0	0.0
7	0.05	0.04	0.01	0.0	0.0	0.0	0.0	0.0
8	0.09	0.055	0.01	0.0	0.0	0.0	0.0	0.0
Trial	$\mathbf{x}^F$; z^F							
1	(0.7212,0.09205,0.04455,0.03123,0.01273,0.01361,0.07215,0.01248); 1.02995							
2	(0.6598,0.09084,0.04726,0.03509,0.01492,0.01657,0.1047,0.03082); 1.12486							
3	(0.7112,0.0985,0.0474,0.0461,0.0225,0.0218,0.0398,0.0127); 1.019531							

Table 22: Data for Example 8

Postulated Phase	Solutions		Times Located out of 100 Local Optimization Trials
	Solution ($\mathbf{x}$) z	TPD	
1	(0.75799,0.09130,0.04173,0.02794, 0.01096,0.01122,0.05294,0.00592) 1.00311	-0.00065	99
2	(0.65972,0.09084,0.04726,0.03509, 0.01492,0.01657,0.10473,0.03087) 1.12500	0.000001	1
	(0.6598,0.09084,0.04726,0.03509, 0.01492,0.01657,0.1047,0.03082) 1.12486	0.0	63
	(0.74039,0.09196,0.04304,0.02947, 0.01176,0.01210,0.06250,0.00878) 1.01589	-0.00026	34
3	(0.60583,0.09513,0.05233,0.05617, 0.02951,0.03143,0.07307,0.05651) 1.20773	0.0	80
	(0.71078, 0.09851,0.04743,0.04616, 0.02254,0.02185,0.03994,0.01281) 1.01990	0.0	20

Table 23: Local and global minima for Example 8

Postulated Phase	Global Solution		α-Calculated	α=0.001
	Solution ($\mathbf{x}$) z	TPD	CPU	CPU
1	(0.75799,0.09130,0.04173,0.02794, 0.01096,0.01122,0.05294,0.00592) 1.00311	-0.00065	11.17	10.58
2	(0.74039,0.09196,0.04304,0.02947, 0.01176,0.01210,0.06250,0.00878) 1.01589	-0.00026	12.93	9.05
3	(0.60583,0.09513,0.05233,0.05617, 0.02951,0.03143,0.07307,0.05651) 1.20773	0.0	521.1	496.0

Table 24: Computational results for Example 8