GLOPEQ: A NEW COMPUTATIONAL TOOL FOR THE PHASE AND CHEMICAL EQUILIBRIUM PROBLEM

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Abstract

Calculation of phase and chemical equilibrium represents a crucial phase in the modeling of many separation processes. For conditions of constant temperature and pressure, a necessary and sufficient condition for the true equilibrium solution is that (i) the total Gibbs free energy of the system be at its global minimum, or (ii) the minimum of the tangent plane distance function be nonnegative for all phase models used to represent the system. In this work, the goal is to obtain equilibrium solutions corresponding to a global minimum of the Gibbs free energy as efficiently as possible, for cases where the liquid phase or phases can be modeled by the NRTL, UNIQUAC, UNIFAC, Wilson, modified Wilson and ASOG equations. Vapor phases whose behavior can be described as ideal can also be handled. In achieving this goal, there are two distinct problems of relevance: (i) the minimization of the Gibbs free energy, denoted (G), and (ii) the minimization of the tangent plane distance function, or the tangent plane stability criterion, denoted (S). For all these activity coefficient models, GLOPEQ (Global OPtimization for the Phase and chemical EQuilibrium problem) can guarantee global solutions for problems (G) and (S), but a combined algorithm employs them in tandem, using (G) to generate candidate equilibrium solutions which can then be verified for thermodynamic stability by solving (S). Two key features of the combined algorithm are that (i) as much information as is possible is obtained from local searches, and (ii) it is preferable to verify a globally stable equilibrium solution using the tangent plane criterion, as this problem contains fewer

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variables than the minimization of the Gibbs free energy. Results for several examples are presented, and all but one of them are for the case of phase equilibrium, due to the paucity of examples for reacting systems that employ excess Gibbs free energy models.

1 Introduction

The phase and chemical equilibrium problem is extremely important for predicting fluid phase behavior for a very large number of separation process applications. The ubiquity of the flash calculation in chemical engineering is just one example of its prevalence. Process simulators need to be able to reliably and efficiently predict the correct number of phases that will exist at equilibrium, and the distribution of components within those phases. However, the local optimization approaches which are in common use can provide no theoretical guarantee that the equilibrium solution will be obtained in all cases.

For chemical engineering applications, the thermodynamic function of foremost interest is the Gibbs free energy as it can be used to describe equilibrium at conditions of constant temperature and pressure. A global minimum of the Gibbs free energy corresponds to the true equilibrium solution. Optimization methods have become increasingly popular since White *et al.* (1958) minimized the Gibbs free energy for ideal systems, using what came to be known as the RAND algorithm. Gautam and Seider (1979a) used Wolfe's Quadratic Programming algorithm and compared its performance to some other methods for the minimization of the Gibbs free energy. For these calculations, phases could be eliminated as the algorithm progressed but this could lead to incorrect prediction of the number of phases present at equilibrium. Castillo and Grossmann (1981) used a variable metric projection method to minimize the Gibbs free energy function. They proposed solving one problem for the maximum possible number of phases that could be present in the system, thus avoiding elimination of phases from consideration at an early stage of the algorithm. A review of these and other contributions can be found in Seider *et al.* (1980). In a series of papers, Ohanomah and Thompson (1984a,b,c) provide an extensive evaluation of several algorithms, including Newton–based methods, for the computation of multiphase equilibria. The study highlighted the difficulties generated when a large number of excess phases is assumed. Soares *et al.* (1982) used Newton–Raphson based methods for the calculation of the three–phase flash problem. Lantagne *et al.* (1988) presented a mixed penalty function method for the computation of complex equilibria. Paules and Floudas (1989) used the Global Optimal Search of Floudas *et al.* (1989) in an attempt to avoid convergence to local extrema of the Gibbs function. However, all these approaches could not eliminate the possibility of converging to local or constrained extrema of the Gibbs free energy function.

One of the main difficulties associated with minimizing the Gibbs free energy is the *a priori* determination of the number of phases to be considered. If too few phases are allowed, then convergence to constrained minima can occur; if too many are assumed, then numerical problems may arise (e.g. Jacobian singularities in Newton–based methods), or convergence to trivial or local extrema may occur. In this context, thermodynamic stability is a very useful criterion of determining if a given solution corresponds to a local or a global minimum of the Gibbs free energy. Gautam and Seider (1979b) incorporated a phase–splitting algorithm with the RAND method, and it was reported to show a much greater degree of reliability for systems with at least one partially miscible pair than by direct minimization of the Gibbs free energy. Walraven and van Rompay (1988) proposed an improvement in the algorithm of Gautam and Seider (1979b) for short–cut phase equilibrium calculations. Baker *et al.* (1982) formalized the concepts of thermodynamic stability for multicomponent mixtures, the fundamental principles of which had first been stated by Gibbs (1873). They proved that a necessary and sufficient for an equilibrium solution to correspond to a global minimum of the Gibbs free energy is that the tangent plane corresponding to this solution lie on or below the Gibbs free energy surface for all possible values of the composition. The metastable region is recognized as unstable. The authors did not present an implementation of the criterion. Michelsen (1982a,b) proposed a two stage approach whereby the stability problem was used to generate initial points for use in the search for an equilibrium solution with a lower value of the Gibbs free energy. These methods have been found to be more reliable and robust than minimizing the Gibbs function directly, as discussed by Swank and Mullins (1986) in their review of algorithms specifically for use in distillation columns where more than one liquid phase might form. Wu and Bishnoi (1986) used a Newton-Raphson method and employed a liquid–phase stability test for the three–phase flash calculation. Nagarajan *et al.* (1991a,b) reformulate Michelsen's analysis in terms of molar densities to improve its reliability, but with longer times. Gupta *et al.* (1991) consider the flash calculation and the stability problem simultaneously. Eubank *et al.* (1992) integrated the Gibbs energy surface in order to derive a necessary and sufficient condition for an equilibrium solution to be a global one. Sun and Seider (1995) use a homotopy continuation algorithm to solve the phase stability problem. These results are then used in the search for a lower value of the Gibbs free energy function. However, the problem with all these approaches is that even though the likelihood of failure can be reduced, there is no theoretical guarantee that the equilibrium solution will be obtained in all cases.

It is important to realize that all of the approaches discussed above lead to a local solution at best. In this sense, they are "local" techniques. Recently, global optimization has been proposed and applied for the computation of phase and chemical equilibrium. McDonald and Floudas (1995c) use the Global OPtimization algorithm of Floudas and Visweswaran (1990,1993) to obtain global solutions for the minimization of the Gibbs free energy when the liquid phase is modeled by the NRTL equation. When the nonideal liquid phases can be modeled using the UNIQUAC equation, McDonald and Floudas (1994a) show how the Gibbs function can be transformed into the difference of two convex functions, so that application of a variant of the branch and bound algorithm of (Falk and Soland, 1969) can be used. For cases where the UNIFAC, Wilson, modified Wilson and ASOG equations can be used to calculate liquid phase activity coefficients, McDonald and Floudas (1995b) show how the molar Gibbs free energy functions can be transformed so the same algorithm can also be applied to these formulations. McDonald and Floudas (1995a) show how global solutions can be obtained for the phase stability problem when the liquid phases can be modeled using the NRTL or UNIQUAC equations.

In this work, an algorithm is presented which is theoretically *guaranteed* to converge to the global equilibrium solution, no matter how poor the supplied starting point. This is the key contribution of the proposed work. In addition, an extensive array of examples is presented for some very challenging examples that have been taken from the literature. The algorithm itself is conceptually similar to the work of Gautam and Seider (1979b), and the approach of Michelsen (1982b) in that it uses the tangent plane criterion to establish if the Gibbs free energy of a current equilibrium solution can be reduced. The main difference is that global optimization is used to solve the subproblems (G) and (S) (as opposed to local techniques), thus allowing guarantees to be made at each step of the algorithm. In the next section, the two problems at the heart of the phase and chemical equilibrium problem are briefly discussed. Then the combined algorithm GLOPEQ is described in detail. Several examples are presented and sample input and output files of GLOPEQ are shown.

2 Background of GLOPEQ

In what follows, the set of components is given by the set $C \equiv \{i\}$, the set of elements is denoted by the set $E \equiv \{e\}$, the set of phases is described by $P = P_L \cup P_V \equiv \{k\}$, where P_L and P_V correspond to the liquid phases and vapor phase respectively. The variables used in the problem formulations are (i) the mol numbers $\boldsymbol{n} \equiv \{n_i^k\}$, representing the number of mols of component i present in phase k, (ii) the liquid mol fractions $\boldsymbol{x} \equiv \{x_i^k\}$ defined as $x_i^k = n_i^k / \sum_j n_j^k$, and (iii) the vapor mol fractions $\boldsymbol{y} \equiv \{y_i^k\}$, defined similarly. In addition, n^T is the total number of mols in the system, with $n^k = \sum_i n_i^k$ representing the number of mols of substance in phase k. The parameter $\phi^k = n^k / n^T$ is defined as the fraction of mass in phase k so that $\sum_k \phi^k = 1$.

There are essentially two approaches that can be taken in order to obtain or confirm that an equilibrium solution corresponds to a global minimum of the Gibbs free energy. The two optimization problems associated with these approaches are:

(i) The minimization of the Gibbs free energy, and

(ii) The tangent plane criterion (minimization of the tangent plane distance function).

A discussion of their relative advantages and disadvantages motivates an implementation of an algorithm that utilizes the relative merits of each approach to generate global solutions to the phase and chemical equilibrium problem as efficiently as possible. Equilibrium solutions can be guaranteed for liquid phases that can be adequately modeled by any of the following equations:

- NRTL (Renon and Prausnitz, 1968)
- UNIQUAC (Abrams and Prausnitz, 1975)
- UNIFAC (Fredenslund *et al.*, 1977)
- Wilson (Wilson, 1964)
- Modified Wilson (Tsuboka and Katayama, 1975)
- ASOG (Kojima and Tochigi, 1979)

Vapor phases that behave ideally or can be modeled using the B–truncated pressure explicit virial equation are easily incorporated. At present, GLOPEQ is not capable of handling phases whose fugacities are obtained using equations of state, because these quantities cannot be obtained explicitly as functions of composition. The two individual problems of relevance are now discussed.

2.1 Minimization of the Gibbs free energy

At constant temperature and pressure, the condition of equilibrium is that the Gibbs free energy function attain its global minimum:

$$\left.\begin{array}{ll} \min & G(\boldsymbol{n}) \\ s.t. & \mathbf{A}\,\boldsymbol{n} - \mathbf{b} = \mathbf{0} \\ & 0 \leq \boldsymbol{n} \leq n^T \end{array}\right\} \text{(G)}$$

where $G(\boldsymbol{n})$ is the total Gibbs free energy of a system containing C components and P phases, and the equality constraints $\mathbf{A}\ \boldsymbol{n} - \mathbf{b} = \mathbf{0}$ correspond to the mass balances. These can take either of the following two forms depending on whether reaction occurs in the system:

(i) Phase and chemical equilibrium (reacting system):

$$\sum_{i \in C} \sum_{k \in P} a_{ei} n_i^k = b_e \quad \forall \quad e \in E \tag{1}$$

where a_{ei} represents the number of gram–atoms of element e in component i and b_e the total number of gram–atoms of element e in the system.

(ii) Phase equilibrium (no reaction):

$$\sum_{k \in P} n_i^k = n_i^T \quad \forall \quad i \in C \tag{2}$$

where n_i^T represents the total number of mols of component i in the system.

The mol numbers at the global minimum of the Gibbs free energy function supply the true distribution of components and phases at equilibrium. The total number of variables N_V of Formulation (G) and the number of independent variables N_{CV} are then:

$$N_V = |C| \cdot |P| \quad \text{and} \quad N_{CV} = |C| \cdot |P| - r$$

where r is the rank of the material balance matrix $\mathbf{A}$. For the phase equilibrium problem, $r = |C|$ and r variables can always be obtained from the remaining $N_{CV} - r$ variables. Note that N_{CV} is the most important indicator of difficulty for global optimization algorithms.

One of the main difficulties in solving (G) is selection of the number of phases P. The phase rule supplies an obvious upper bound on the maximum number of phases that can be present at equilibrium. However, for systems of several components, this rule is of limited use as it can lead to a large number of *potential* phases that need be considered in the system, This characteristic is usually associated with numerical difficulties. One approach is to eliminate phases (Gautam and Seider, 1979a), but then there is the possibility of converging to a constrained minimum. On the other hand, assuming excess phases can lead to numerical difficulties (Ohanomah and Thompson, 1984a). Paules and Floudas (1989) introduced binary variables representing the existence or absence of a phase to circumvent this problem. However, none of these approaches can provide guarantees that the global solution to (G) will be obtained.

McDonald and Floudas (1995c) show how the GOP algorithm of Floudas and Visweswaran (1990,1993) Visweswaran and Floudas (1990,1993) can be used to obtain global minima when the liquid phase is modeled by the NRTL equation. For the case of the UNIQUAC equation, McDonald and Floudas (1994a) show how a branch and bound algorithm of Falk and Soland (1969) can be used to determine the global minimum of the Gibbs free energy. This same algorithm can be used for the UNIFAC, ASOG and modified Wilson equations as shown by McDonald and Floudas (1995b). Solving (G) using global optimization for these activity coefficient correlations led to the following observations:

- To *theoretically guarantee* a global minimum for (G), the formulation can contain a large number of variables, making a global optimization algorithm computationally expensive, particularly for larger systems.
- When using global optimization to solve (G), the global solution is often generated at an early stage in the procedure of the algorithm. This implies that in order to converge to the global solution may require many additional iterations of the global optimization algorithm.

For these reasons, the phase stability problem presents many advantages, which will be discussed in the next section.

2.2 Tangent Plane Stability Criterion

Any equilibrium solution to (G) must satisfy equality of chemical potentials corresponding to the first order necessary condition of equilibrium For nonideal systems, there may be multiple solutions satisfying equality of chemical potentials, corresponding to local extrema of the Gibbs free energy function and a sufficiency condition is required. This is provided by the tangent plane criterion.

Let the mol fractions of one of the phases corresponding to an equilibrium solution be represented by $\boldsymbol{z} \equiv \{z_i\}$. Then, the tangent constructed at $\boldsymbol{z}$ must lie everywhere below the Gibbs surface for the equilibrium solution to correspond to a global minimum of the Gibbs free energy, as first shown by Gibbs (1873). Baker *et al.* (1982) supply a proof of this criterion for the phase equilibrium problem when the Gibbs function can be represented as a continuous first order function. Smith *et al.* (1993) have generalized the necessary and sufficiency conditions for an equilibrium solution to correspond to a global minimum of the Gibbs free energy for the phase and chemical equilibrium problem. The tangent plane stability criterion is defined as the following problem:

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

where $\mathcal{F}(\boldsymbol{x})$ represents the tangent plane distance function calculated as the difference between the Gibbs surface, $g(\boldsymbol{x})$ and the tangent plane constructed using $\mu_i^0(\boldsymbol{z})$, the chemical potential of component i evaluated at $\boldsymbol{z}$ corresponding to the mol fractions in one of the phases of the candidate solution. Nonnegativity of the tangent plane distance function for all phase types in the system provides a necessary and sufficient condition for the equilibrium solution to correspond to a global minimum of the Gibbs free energy.

(S) is itself a difficult and challenging problem. The complexity of the expressions used for $g(\boldsymbol{x})$ mean that there may be multiple local solutions. Often, there will be a local solution with a zero value for the tangent plane distance function, when the global solution has in fact a negative value. Thus local approaches may make incorrect predictions in relation to the thermodynamic stability of candidate equilibrium solutions. McDonald and Floudas (1995a) discuss the application of global optimization to the solution of (S) when the liquid phases are modeled by the NRTL or UNIQUAC equations. McDonald and Floudas (1995b) apply the branch and bound algorithm of Falk and Soland (1969) to obtain global solutions to (S) for problems where the UNIFAC, modified Wilson or ASOG equations can be used to model the nonideal liquid phase. For the tangent plane criterion, the total number of variables and the number of independent variables are defined respectively as follows:

$$N_V = |C| \text{ and } \quad N_{CV} = |C| - 1$$

The following comments can be made in relation to Problem (S):

- No matter how many phases are present in the candidate equilibrium solution being tested for thermodynamic instability, the number of variables in (S) does not change for a particular problem.

- If a negative tangent plane distance function is found, then (S) can be terminated at once as the candidate solution is then unstable.

The second point above raises an important distinction between the approach proposed in this work, and that taken by researchers such as Sun and Seider (1995). In their work, if a negative tangent plane distance is found, these solutions are used as a starting point for a search for a new equilibrium solution which will have a lower Gibbs free energy value, the assumption being that the equilibrium mol fractions will be closely approximated by the solution of (S) (see, for example, Cairns and Furzer, 1990). However there is no guarantee that the correct equilibrium solution will be obtained using this starting point. In addition, even if an improved solution is found, then there is still no guarantee that this is the true global solution. The approach of Michelsen (1982b) uses a descent method for the Gibbs free energy minimization, which with good initial estimates from (S), is highly reliable (Swank and Mullins, 1986), although there is no theoretical guarantee that it will converge to a solution with a lower Gibbs energy. In this work, the solutions obtained from (S) are *not* used as first estimates for the subsequent search for a lower value of the Gibbs free energy. A global optimization algorithm is used to minimize the Gibbs free energy until an improved equilibrium solution is found, which will then be tested for stability. This process is repeated until an equilibrium solution is generated which leads to a nonnegative tangent plane distance function when (S) is solved, as determined by a *global* optimization algorithm. Other approaches cannot make such a claim as at best a solution satisfying the necessary condition of equilibrium can be obtained.

3 Description of GLOPEQ

As has been discussed, there are two possible methods of employing global optimization in order to obtain an equilibrium solution corresponding to a global minimum of the Gibbs free energy function. The first requires globally minimizing the Gibbs free energy function. For rigorous determination of phase and chemical equilibrium, the maximum allowable number of phases as determined by the phase rule must be considered. However, for systems of several components, this may lead to a global optimization problem with a large number of variables. Consider a five–component system where no reaction occurs. There may exist up to five liquid phases, although it is highly unlikely that this number of phases will exist at equilibrium. However, this number of phases must be considered in order to theoretically guarantee that a global solution will be obtained. This will lead to a global optimization problem with 25 variables.

The second approach involves *verifying* that an equilibrium solution corresponds to a global minimum of the Gibbs free energy, using the tangent plane criterion. No matter how many phases are present in the candidate equilibrium solution, the stability test will always contain the same number of variables, that is, the number of components in the system. It is more preferable to employ this problem than minimizing the Gibbs free energy since it contains fewer variables and thus demonstrates better lower bounding characteristics and faster convergence.

A striking illustration of the points just discussed is motivated by an example studied by McDonald and Floudas (1994a), taken from Castillo and Grossmann (1981). It involves three components (benzene, acetonitrile and water) with a potential of two liquid phases and a vapor phase at a temperature of 333 K and a pressure of 0.769 atm. Direct minimization of the Gibbs free energy using the GOP and assuming two liquid phases and a vapor phase takes approximately 6000 iterations and 770 cpu sec to converge to the global LLV solution. However, if this global solution is tested for thermodynamic stability using the tangent plane criterion, then 80 iterations are required to establish that the global solution of the tangent plane distance function is nonnegative. The time taken to verify that this is the global solution is 0.76 cpu sec. Thus, it is clear that *verifying* a globally stable solution can represent enormous computational savings. This is one of the main motivating factors behind the development of GLOPEQ. The question of how to obtain candidate equilibrium solutions remains. They can be generated using local or global searches for minima of the Gibbs free energy function. Globally solving (G) is expensive but strategies to avoid solving it to ϵ-global convergence are easily implemented. An obvious one is to employ local searches because they are computationally cheap. This provides the opportunity to find a better candidate equilibrium solution at an early stage of the search. In addition, as observed by McDonald and Floudas (1995c), the global solution of (G) will often be generated at a relatively early stage of the algorithm. If an improved equilibrium solution is found with a lower Gibbs free energy value, then the algorithm is terminated and this solution is tested for thermodynamic stability using the tangent plane criterion. The main characteristics of GLOPEQ are summarized as follows:

(i) As much information is obtained from local searches as is possible.

(ii) Global minimization of the tangent plane distance function is preferable to global minimization of the Gibbs free energy function.

The algorithm is now described in full.

3.1 The combined algorithm in GLOPEQ

In what follows, the current phase configuration is denoted as $\mathcal{P}$, and signifies how many liquid phases are present in the current configuration and if there is a vapor phase present. This is denoted as $\mathcal{P} = L_l V_v$ where l is the number of liquid phases present, and $v = 0$ or 1, depending on whether a vapor phase is present. $\mathcal{P}^*$ is the phase configuration of the equilibrium solution obtained thus far with the lowest Gibbs free energy value of G_B^* and associated mol numbers $\boldsymbol{n}_B^*$. $(\mathrm{S})_L$ and $(\mathrm{S})_V$ signifies the stability problem (S) for the case when the liquid and vapor phase is being checked for stability, respectively, with associated tangent plane distance function values $\mathcal{F}_L^*$ and $\mathcal{F}_V^*$. At this point, it will be helpful to distinguish between local and global searches: a local search means solving either (G) or (S) using a random starting point using MINOS5.4 as a nonlinear solver. This will generate an extremum solution that may of may not be the global solution to (G) or (S). Solving (G) or (S) globally implies using a global optimization algorithm as described in McDonald and Floudas (1994a; 1995a,b,c) to generate the global solution. It is important to distinguish these global solutions of problems (G) and (S) from the true equilibrium solution, which is the "global" solution that is being sought.

3.1.1 Initialization

In this phase, the best possible equilibrium solution is generated by using a number of local searches. For fixed temperature and pressure, the maximum number of liquid phases that can be present at equilibrium is C, the number of components in the system. For reacting systems this may be further reduced by the number of independent reactions occurring in the system. Thus, the initial phase configuration is chosen as $\mathcal{P} = L_C V$. The Gibbs free energy function is then minimized (i.e. (G) is solved) using local searche(s). The number of local searches is set by the user and is labelled κ_G. The best solution obtained from the κ_G local searches is then denoted G_B^*. The mol number solution associated with G_B^* is stored as n_B^*.

3.1.2 Stability Check

The stability check phase tests if the current candidate solution (which satisfies the necessary conditions of equal chemical potentials) is stable with respect to perturbations in both the liquid *and* vapor phases (if a vapor phase is postulated.) For many problems the conditions of temperature (or pressure) will be such that a vapor phase cannot exist and $(\mathrm{S})_V$ need not be solved. The first step is to calculate the tangent plane as represented by $\mu_i^0(\boldsymbol{z})$. The following procedure is undertaken for solving the stability problem:

1. Solve (S) locally κ_S times. Store the minimum of these solutions as $\mathcal{F}_B^* = \arg\min_{\kappa_S} \mathcal{F}^*$.

2a. If $\mathcal{F}_B^* \geq 0$, then solve (S) globally. If $\mathcal{F}^* < 0$ at any point in this search proceed to next phase.

2b. If $\mathcal{F}_B^* < 0$, then proceed to next phase.

The first step is to solve (S) locally κ_S times using MINOS5.4 as the local optimization solver. If at this phase, a negative TPDF is found, then this portion of the program is exited and an equilibrium solution with a lower Gibbs value must be sought. The procedure for this eventuality is described in the next section. On the other hand, if a nonnegative TPDF is obtained from the local search phase, then (S) must be solved *globally*. If the TPDF is still nonnegative, then the current solution is stable with respect to perturbations for this phase type. It is apparent that if a negative value for the tangent plane distance function is obtained at any point, then it is clear that the current best solution is unstable, and a new solution must be sought. It has been noted by McDonald and Floudas (1995a) that when solving (S) globally, if the actual global solution is negative, it is usually obtained at an early iteration which is a very useful characteristic. Both liquid and vapor phases must be checked for stability at this point. For ideal vapor phases, the stability formulations are convex and only one local search is required to establish if they are stable. If these checks yield nonnegative TPDF's then GLOPEQ can terminate as this is precisely a necessary and sufficient condition for stability of the postulated solution. Otherwise, an equilibrium solution with a lower Gibbs free energy value must be sought, as is now described.

3.1.3 Improving the value of the Gibbs energy

Phase 1: Choosing P and P_V

Before proceeding to solve (G), the phase configuration $\mathcal{P}$ for use in the current search must be selected. The procedure adopted here is simple, and other schemes are certainly possible. The basic idea is to build up the number of liquid phases present in the system. On the first pass, it is assumed two liquid phases will be present, that is $l = 2$. If the current best solution contains a vapor phase, or the stability check with respect to an incipient vapor phase gave a negative TPDF, then a vapor phase is assumed present, that is $v = 1$. It should be noted that for the local search phase, the phase configuration remains the same as $\mathcal{P} = L_C V_1$. On subsequent passes, l is incremented by 1. This strategy which builds up the liquid phases ensures that the global solution will not be missed. For example, if the global solution contains one liquid phase, then the global search with $l = 2$ will attain the single phase global minimum with a mathematical two phase solution where the mol fractions in both phases will be the same, while it actually corresponds to a physical one phase solution.

Phase 2: Minimization of the Gibbs free energy

Firstly (G) is solved locally. If no decrease in the Gibbs free energy is effected, then a global search must be initialized using the phase configuration decided upon in Phase 1. If at any point an improved solution is obtained, the global optimization algorithm is terminated, and this improved solution is tested for stability by returning to Section 3.1.2 as described above.

A diagrammatic summary of GLOPEQ is provided in Figure 1. In the best case scenario, the global equilibrium solution will be generated using local searches, so that only (S) need be solved globally. In this case, only one global optimization problem will be solved. The worst case scenario consists of GLOPEQ iterating between solving (G) and (S) globally. The latter case rarely occurs.

3.2 Summary

A summary of the combined algorithm is now given.

Step 1. Initialization:

Set $\mathcal{P} = L_C V_1$ and solve (G) locally κ_G times to obtain G_B^*. Store $\boldsymbol{n}_B^*$ and set $l = 1$.

Step 2. Stability check:

Calculate $\mu_i^0(\boldsymbol{z})$ using $\boldsymbol{n}_B^*$.

2a. Vapor phase: If $v = 0$, solve $(\mathrm{S})_V$ to yield $\mathcal{F}_V^*$.

2b. Liquid phase: Solve $(\mathrm{S})_L$ locally to yield $\mathcal{F}_L^*$. If $\mathcal{F}_L^* \geq 0$, solve $(\mathrm{S})_L$ globally to yield $\mathcal{F}_L^*$.

Check for stability:
If $\mathcal{F}_L^* \geq 0$ and $\mathcal{F}_V^* \geq 0$ then STOP.
Otherwise proceed to Step 3.

Step 3. Gibbs search:

Phase 1: Select $\mathcal{P}$
(i) If $\mathcal{F}_L^* < 0$, then set $l = l + 1$.
(ii) If $\mathcal{F}_V^* < 0$ then set $v = 1$.

Phase 2:
(i) Solve (G) locally. If $G^* < G_B^*$ found, update $\mathcal{P}^*$ and GOTO Step 2.
(ii) Solve (G) globally with $\mathcal{P} = L_l V_v$. If $G^* < G_B^*$, update $\mathcal{P}^*$ and GOTO Step 2.

4 Examples

The algorithm GLOPEQ is written in C and all the computational results reported in this paper were performed on a Hewlett Packard 9000/730 machine, which is rated at 76 MIPS (91 SPECfp). The solver MINOS5.4 is accessed as a subroutine. The executable C program is available directly from the authors, although prospective users will need a license for MINOS5.4. All the times reported are the total cpu time taken to obtain the equilibrium solution corresponding to a global minimum of the Gibbs free energy function. It should be noted that several of the examples are solved using more than one thermodynamic model. The results will of course be different for these models, and sometimes may yield solutions which have unequal numbers of phases (e.g. Example 4), as well as significant deviations in the phase and/or mol fractions. This highlights the importance of employing experimental data as available to evaluate the solutions to ensure that they qualitatively and quantitatively conform to the reported experimental behavior. All but one of the examples are for non–reacting systems. This is because there are very few examples of reacting systems of industrial relevance that use excess Gibbs free energy models. Most frequently, equations of state are employed in stoichiometric solution techniques for high pressure systems, which is outside the scope of this research. A detailed description of how GLOPEQ works for a challenging two component example is now given, followed by additional examples.

4.1 Illustrative example: n-Butyl Acetate – Water

The NRTL equation was used to model this system using parameters provided by Heidemann and Mandhane (1973). McDonald and Floudas (1995c) showed how the global solution contained two liquid phases. The Gibbs surface possesses multiple stationary points, making the problem very difficult for local solvers. A vapor phase is not considered. The initial charge is equimolar, so that $n_i^T = 0.5 \; \forall \; i$.

1. Initialization:

Setting $\kappa_G = 1$ (i.e. solve (G) locally once using MINOS5.4) with $\mathcal{P} = L_2$ yields a local LL solution with $G^* = -0.01961$. The values of the mol numbers for this solution are:

$$n_1^1 \;=\; 0.00213 \quad n_1^2 \;=\; 0.49787$$

$$n_2^1 = 0.46547 \quad n_2^2 = 0.03453$$

2. Stability check:

Solve (S) with $\mu_i^0(\boldsymbol{z}) = \{-0.03523, -0.00398\}$. The local search phase with $\kappa_S = 1$ (i.e. solve (S) locally with MINOS5.4 once) yields $\mathcal{F}^* = 0.0$. After 2 iterations of the global search, a negative tangent plane distance of $\mathcal{F}^* = -0.00070$ with $\boldsymbol{x}^* = \{0.59425, 0.40575\}$ is obtained. A better equilibrium solution must be sought.

3. Gibbs free energy search:
On the first pass, $l = l + 1 = 2$ and a global Gibbs search with two liquid phases is initiated. After 47 iterations of the GOP algorithm, an improved equilibrium solution with $G^* = -0.02020$ is found. The Gibbs energy search is therefore exited, and the next phase of the stability check is implemented.

4. Stability check:

The new solution supplies $\mu_i^0(\boldsymbol{z}) = \{-0.03642, -0.00398\}$. Solving (S) globally yields a non-negative tangent plane distance function as the global solution of (S). The candidate equilibrium solution therefore corresponds to a global minimum of the Gibbs free energy. The final solution is given as:

$$\begin{aligned} n_1^1 &= 0.00071 \quad n_1^2 = 0.49929 \\ n_2^1 &= 0.15588 \quad n_2^2 = 0.34412 \end{aligned}$$

This example illustrates some of the guiding principles of GLOPEQ. Firstly, the first stability check was exited very early after 2 iterations. In addition, the minimization of the Gibbs free energy was also terminated early. The total time taken was 0.69 cpu sec. For comparison, the total time taken to minimize the Gibbs free energy with two liquid phases postulated was 1.23 cpu sec. It is clear that the combined algorithm generates significant computational savings even though the number of local searches employed was very low at 1. If $\kappa = 20$ is used, then GLOPEQ finds the true equilibrium solution in 0.23 cpu secs. The actual input file used to generate the global solution is shown in Appendix A. Comment lines are begun using a hash mark (#). There are certain keywords (such as `GIBBS MODEL`, `PROBLEM NAME`, `NUMBER OF COMPONENTS`, and so on) that must be included in the file. Options are included between the `BEGIN/END OPTIONS` statements. The file shown runs the combined algorithm.

To minimize the Gibbs free energy for two liquid phases, the hash marks of the last three lines are simply removed to solve (G) alone. The output file generated by the above example is shown in Appendix A. A complete description of the package can be found in McDonald and Floudas (1994b).

The global solutions as obtained by the NRTL, UNIFAC and ASOG models are supplied in Table 1 for an equimolar feed charge at a temperature of 298 K and atmospheric pressure. A vapor phase is not considered. McDonald and Floudas (1994a,b) discuss this example extensively in the context of the minimization of the Gibbs free energy and the tangent plane distance function using the NRTL equation. Even though it is a small two component example, it demonstrates quite complex behavior, and provides a good test for any algorithm.

4.2 Example 2: SBA – DSBE – Water

This example is drawn from azeotropic distillation. Kovach and Seider (1988) supply a set of compromise interaction coefficients that can be used to model LLV equilibrium. The data for the problem is given in McDonald and Floudas (1995a). The Antoine coefficients for calculating the saturated vapor pressures was supplied by Kovach and Seider (1987). Widagdo *et al.* (1992) have supplied the phase diagrams on all five trays which feature complex connections of multiphase regions. Because of the sensitivity of this example to the data, it represents a very challenging test of the algorithm GLOPEQ. The solutions on all five trays studied in this work are given in Table 2, with the corresponding times. In all cases, the global solution was obtained in very reasonable time (i.e. under 20 cpu secs).

4.3 Example 3: n-Propanol – n-Butanol – Water

This example features a single immiscible pair between butanol and water. Block and Hegner (1976) obtained the NRTL binary parameters, and the LL interaction parameters for the UNIFAC equation were obtained from Magnussen *et al.* (1981). At a feed charge of $n_i^T = \{0.041, 0.267, 0.692\}$, corresponding to the conditions in the decanter which separates the bottom product into an organic and a water phase, the global equilibrium LL solutions for both models are given in Table 3. The temperature of the decanter is approximately 370 K which is well outside the recommended range of applicability of the UNIFAC parameters. However, it still provides a reasonable prediction of phase equilibrium at this feed charge.

4.4 Example 4: Ethylene Glycol – Lauryl Alcohol – Nitromethane – Water

Null (1970) used an extended version of the van Laar equation to model this system. A vapor phase does not form and there are a potential of three liquid phases. Chakravarty *et al.* (1985) obtained UNIQUAC coefficients and the parameters used in this work are supplied by McDonald and Floudas (1995a). The system is at a temperature of 295 K and 1 atm pressure. The UNIFAC equation was also used to model this system using the binary interaction parameters for the prediction of liquid–liquid equilibria supplied by Magnussen *et al.* (1981). The global solutions for both the UNIQUAC and UNIFAC equations are given in Table 4. The UNIFAC equation also predicted the presence of three liquid phases, the maximum number allowable in the system.

If water is added as a fourth component, and the temperature is increased to T = 350K and the pressure is reduced to P = 0.43 atm, then the UNIFAC equation using the LV binary interaction parameters of Gmehling *et al.* (1982) predicts two liquid phases and one vapor phase. If the LL binary interaction parameters of Magnussen *et al.* (1981) are used, then a global solution with three liquid phases and a vapor phase is obtained. The global equilibrium solutions and the computational results are supplied in Table 5. The temperature of the system does lie outside the recommended range of use for the LL parameters (283–313 K), but it does demonstrate the complex behavior the UNIFAC model is capable of predicting.

4.5 Example 5: Water – n-Propanol – n-Hexane

This is an example used by Fredenslund *et al.* (1977) to illustrate the calculation of phase equilibrium. For several values of the feed charge, they report equilibrium solutions with two liquid phases. This is the maximum number of phases they consider in their calculations. There are in fact three liquid phases at the global minimum of the Gibbs free energy. McDonald and Floudas (1995b) report a global solution containing three liquid phases using the VL parameters of Fredenslund *et al.* (1977) for two feed charges. ¿From experimental data, it is known that water and hexane is the only partially miscible pair of components of this system. However, the UNIFAC model predicts that the propanol–hexane binary pair is partially miscible. This demonstrates the complexity of the UNIFAC model, predicting phases that do not actually occur experimentally. In fact, Magnussen *et al.* (1981) observed that the UNIFAC equation was capable of predicting three liquid phases, quoting the xylene–acetonitrile–water system as one example and singling out systems involving 1-propanol or 2-propanol as especially troublesome. Special procedures had to be undertaken in order to avoid erroneous prediction of phase equilibrium for these systems, and interaction parameters were individually obtained for both propanols for the prediction of liquid–liquid equilibrium. Using the UNIFAC parameter table of Magnussen *et al.* (1981) results in much better prediction of this system, and a two phase solution is obtained. These solutions are reported in Table 6 for two feed charges. Conditions (i) and (ii) correspond to $n_i^T = \{0.5, 0.1, 0.25\}$ and $n_i^T = \{0.5, 0.4, 0.25\}$ respectively. They correlate the experimental data much better than the original parameters of Fredenslund *et al.* (1977).

4.6 Example 6: Ethanol – Benzene – Water

This example has been extensively studied due to the importance of the azeotropic distillation process used to separate ethanol and water using benzene as an entrainer. For example, Kovach and Seider (1983) used the UNIQUAC equation with parameters obtained form Prausnitz *et al.* (1980). It should be noted that they found that the predictions of Gmehling and Onken (1977) led to poor prediction of the liquid–liquid equilibrium data. For comparison, the results when the UNIFAC equation is used to model the liquid phase activity coefficients using interaction parameters obtained from Magnussen *et al.* (1981) are also supplied. These are results obtained when $n_i^T = \{0.2, 0.4, 0.4\}$, which lies within the region of immiscibility and the equilibrium solutions are given in Table 7. The temperature is 300 K and is too low to allow the formation of a vapor phase, and both models predict two liquid phases, in agreement with the experimental data at atmospheric pressure. The ASOG equation was not used as there are no interaction parameters for the aromatic and water groups, which represents a serious drawback of this equation.

4.7 Example 7: Ethanol – Ethyl Acetate – Water

Walraven and van Rompay (1988) used this example to test their phase–splitting algorithm for liquid–liquid immiscibility employing the NRTL coefficients obtained by van Zandijcke and Verhoeye (1974). This example was also studied by McDonald and Floudas (1995c). At a temperature of 343 K, and a feed charge of $n_i^T = \{0.08, 0.30, 0.62\}$, two liquid phases are predicted by the NRTL equation, the ASOG equation, and the UNIFAC equation. For the UNIFAC equation the LL interaction parameters of Magnussen *et al.* (1981) were employed, even though the temperature of the system was outside the recommended temperature range for these correlations. The results for all these activity coefficient correlations are presented in Table 8.

4.8 Example 8: Methanol – Methyl Acetate – Water

This example is considered at a temperature of 325 K and a pressure of 0.965 atm. The UNIFAC VLE interaction parameters were used to model the system. With $n_i^T = \{0.15, 0.45, 0.40\}$, an LLV solution is obtained, and this is reported in Table 9. When the ASOG equation was used at this value of the feed charge, a one phase vapor solution was obtained. and is thus incapable of predicting liquid and vapor phases simultaneously. The ability to predict LL and VL equilibrium simultaneously with a single set of interaction parameters is difficult for any activity coefficient equation. With $n_i^T = \{0.05, 0.25, 0.7\}$, and no vapor phase postulated, the ASOG equation predicts two liquid phases and this solution is also given in Table 9.

4.9 Example 9: Heptane – Hexane – Methanol

This example features two hydrocarbons and an alcohol at a temperature of 330 K and atmospheric pressure. Methanol forms a partially miscible pair with each of the hydrocarbons in the system. The NRTL parameters of Sørensen and Arlt (1980) (Page 133) were used to model the system as well as the LL UNIFAC binary parameters of Magnussen *et al.* (1981) and the ASOG binary parameters of Kojima and Tochigi (1979). All three activity coefficient models yield an equilibrium solution of two liquid phases and these are supplied in Table 10.

4.10 Example 10: Toluene – n-Propanol – Water

This example features three components and is modeled using the NRTL parameters of Sørensen and Arlt (1980) (Page 580), and the LL UNIFAC binary parameters of Magnussen *et al.* (1981). Note that the ASOG equation cannot be used due to the absence of interaction coefficients for the aromatic–water pair. Conditions at temperatures of 278 K and 298 K under atmospheric pressure are examined. A vapor phase does not form at these conditions. The difficulties associated in systems containing propanol has been mentioned in relation to the UNIFAC equation, where false predictions of extraneous phases can be obtained. In fact, for this example at a temperature of 278 K, the NRTL equation predicts three liquid phases; in addition, it calculates that toluene and water form a partially miscible pair. This discrepancy occurs because of the rapid change in the slopes of the tielines as the plait point is approached. On the other hand, the UNIFAC equation predicts two liquid phases and this is to be expected as the interaction parameters were individually reduced for propanol. The solutions at this temperature are supplied in Table 11. At the higher temperature, both models predict two liquid phases, agreeing with experiment, and the global equilibrium solutions are given in Table 12.

4.11 Example 11: Hexanol – Nitromethane – Water

This example is interesting as the phase diagram features a type-II curve emanating from the water corner and at a sufficiently low temperature, 1-hexanol and nitromethane are immiscible. The experimental data indicates (Sørensen and Arlt, 1980) that at low enough temperatures, these two regions coalesce to form three liquid phases. Temperatures of 294 K and 313 K at atmospheric pressure have been selected for analysis. At 294 K, Walas (1985) (Page 376) obtained the binary interaction coefficients and these are given in Table 13. At a feed charge of $n_i^T = \{0.2, 0.5, 0.3\}$, the UNIQUAC equation predicts three liquid phases (given in Table 14), while the UNIFAC equation predicts a single liquid phase, that is, the two regions of immiscibility are separated by a one phase region and never coalesce. At $n_i^T = \{0.3, 0.6, 0.1\}$ which lies within the 1-hexanol–nitromethane type-I region, the UNIFAC equation predicts two liquid phases and this solution is supplied in Table 14.

When the temperature is raised to 313K, the experimental data indicate that the 1-hexanol–nitromethane pair becomes miscible. With $n_i^T = \{0.1, 0.3, 0.6\}$, which lies within the type-II region, both the UNIQUAC equation using the parameters supplied by Sørensen and Arlt (1980) and the UNIFAC equation predict two liquid phases and these solutions are reported in Table 15. The ASOG equation could not be used as there are no binary interaction parameters for the water–NO_2 group pair.

4.12 Example 12: Phenol – Acetone – Water

This example features an "island curve" in the water rich corner of the phase equilibrium diagram. The NRTL parameters are obtained from Sørensen and Arlt (1980) (Page) at a temperature of 330 K and atmospheric pressure. The LL UNIFAC binary parameters of Magnussen *et al.* (1981) were also used to model this system. In both cases, a liquid–liquid solution was obtained and these are reported in Table 16. Because the group binary interaction coefficients between the aromatic OH and both the water and and ketone groups were not available, the ASOG equation could not be used to model this system.

4.13 Example 13: Esterification Reaction

The esterification reaction between ethanol and acetic acid to form ethyl acetate and water has been extensively studied in the literature. It demonstrates extreme sensitivity to the values used for the Gibbs free energies of formation. The values as used in this work were calculated by McDonald and Floudas (1995c). At a temperature of 355 K, all the models used predicted an LV solution. The Wilson parameters were obtained from (Suzuki *et al.*, 1969), the NRTL parameters were derived from these Wilson parameters as shown by McDonald and Floudas

(1995c), and the UNIQUAC binary interaction parameters were obtained from Gmehling *et al.* (1982). The equilibrium solutions are given in Table 17.

4.14 A summary of Computational Experience

Table 18 presents a summary of the computational results for many of the examples presented in this chapter. Clearly, the most challenging one is Example 4, where times of over 1000 cpu secs are required to obtain the true equilibrium solution. This demonstrates the difficulty and sensitivity of this particular four component example, whose solution has four phases present at equilibrium (experimentally it is unknown how many phases will in fact be present at these conditions). For many systems, it is evident that global solutions can be obtained in reasonable cpu time given that a global optimization approach is being employed. As the number of components increases, the computational effort will increase, and this will impose a practical limit on the size of problems that can be solved efficiently, a limitation of any global optimization approach. Having said that, the examples were all taken from the literature and represent important systems in the chemical process industry where problems in obtaining equilibrium solutions arise.

For those activity coefficient equations that are expressed as the difference of two convex functions, it is possible to achieve improved computational results by simply incorporating a portion of the concave portion of the objective function into the convex portion, assuming that the resulting function remains convex. This results in the following adjustment to Eqn. (A.1):

$$\begin{aligned} \frac{g(\boldsymbol{x})}{RT} &= \bar{\mathcal{C}}(\boldsymbol{x}) - \eta \cdot \sum_{i \in C} \varphi_i x_i \ln x_i \\ \text{with } \bar{\mathcal{C}}(\boldsymbol{x}) &= \mathcal{C}(\boldsymbol{x}) - (1-\eta) \cdot \sum_{i \in C} \varphi_i x_i \ln x_i \end{aligned}$$

Numerical experiments indicate that even down to values of $\eta = 0.2$, the eigenvalues of the function $\bar{\mathcal{C}}(\boldsymbol{x})$ remain nonnegative for thousands of randomly chosen points $\boldsymbol{x}$, that is, the function $\bar{\mathcal{C}}(\boldsymbol{x})$ remains convex. This strategy results in improved lower bounding characteristics with lower computational times as can be seen in Table 19 for the most computationally intensive UNIFAC examples using various values of η. In all cases, the same global solution was obtained as in the rigorous case where $\eta = 1$.

5 Conclusions

This work has presented an algorithm which is theoretically guaranteed to converge to the global equilibrium solution. A new computational tool, GLOPEQ, has been presented for the computation of equilibrium solutions corresponding to a global minimum of the Gibbs free energy function. The approach can be used for liquid phases that can be modeled using the NRTL, Wilson, modified Wilson, UNIQUAC, UNIFACand ASOG activity coefficient models. Vapor phases that behave ideally or that can be described by the B-truncated virial equation can also be handled. The combined algorithm uses two optimization formulations in tandem for maximum efficiency. The first of these problems is the minimization of the Gibbs free energy, and the second is the minimization of the tangent plane distance function. Results for many examples demonstrate that global solutions can be generated efficiently for various difficult and challenging problems.

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Solution for n-Butyl-Acetate (1) – Water (2) $T = 298$K, $P = 1.0$ atm					
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	$\hat{G}_I^*$ (—)	cpu (sec)
Solution using NRTL (Heidemann and Mandhane, 1973)					
$C_6H_{12}O_2$ (1)	0.50	0.59199	0.00456	-0.02020	0.23
H_2O (2)	0.50	0.40801	0.99544		
ϕ^k	(—)	0.84341	0.15659		
Solution using UNIFAC (Magnussen *et al.*, 1981)					
$C_6H_{12}O_2$ (1)	0.50	0.91717	0.00036	-0.03407	0.37
H_2O (2)	0.50	0.08283	0.99964		
ϕ^k	(—)	0.54498	0.45502		
Solution using ASOG (Kojima and Tochigi, 1979)					
$C_6H_{12}O_2$ (1)	0.50	0.80908	0.00152	0.28919	0.32
H_2O (2)	0.50	0.19092	0.99848		
ϕ^k	(—)	0.38273	0.61727		

Table 1: Solutions for Example 1

Solutions for SBA (1) – DSBE (2) – Water (3) on five trays						
Comp.	Tray No. G^*	Feed (mols)	Liquid I (—)	Liquid II (—)	Vapor (—)	cpu (sec)
$i = 1$	Tray 28	40.30707	0.51802	0.05667	0.34024	19.67
$i = 2$	-70.75208	5.14979	0.05110	0.0	0.08762	
$i = 3$		54.54314	0.43088	0.94333	0.57214	
ϕ^k			0.60729	0.15916	0.23355	
$i = 1$	Tray 25	35.18411	0.52037	0.04401	0.30236	16.41
$i = 2$	-81.89074	12.55338	0.15429	0.0	0.13931	
$i = 3$		52.26247	0.32534	0.95599	0.55833	
ϕ^k			0.39439	0.14128	0.46433	
$i = 1$	Tray 7	33.45195	0.48182	0.03759	0.28014	15.26
$i = 2$	-90.29375	18.21254	0.24579	0.0	0.16430	
$i = 3$		48.33661	0.27239	0.96241	0.55556	
ϕ^k			0.34476	0.06248	0.59276	
$i = 1$	Tray 5	31.39202	0.45250	0.03474	0.26923	14.48
$i = 2$	-91.64367	20.35994	0.29858	0.0	0.17512	
$i = 3$		48.24804	0.24892	0.96526	0.55565	
ϕ^k			0.36524	0.09488	0.53988	
$i = 1$	Tray 2	31.28600	0.44619	0.03419	0.26708	15.16
$i = 2$	-92.61758	21.00538	0.30924	0.0	0.17717	
$i = 3$		47.70862	0.24457	0.96581	0.55575	
ϕ^k			0.46349	0.15989	0.37662	

Table 2: Solutions for Example 2

Solution for n-Propanol (1) – n-Butanol (2) – Water (3) $T = 370$K, $P = 1.0$ atm					
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIFAC (Magnussen *et al.*, 1981) equation					
C_3H_7OH (1)	0.041	0.00629	0.05737	-0.34703	6.32
C_4H_9OH (2)	0.267	0.02820	0.37966		
H_2O (3)	0.692	0.96551	0.56297		
ϕ^k	(—)	0.32054	0.67946		
Solution using NRTL (Block and Hegner, 1976)					
C_3H_7OH (1)	0.041	0.00746	0.04432	-0.29723	1.33
C_4H_9OH (2)	0.267	0.02139	0.29134		
H_2O (3)	0.692	0.97115	0.66434		
ϕ^k	(—)	0.09016	0.90984		

Table 3: Solutions for Example 3

Solution for Ethylene Glycol (1) – Dodecanol (2) – Nitromethane (3) $T = 295$K, $P = 1.0$ atm						
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	Liquid III (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIFAC (Magnussen *et al.*, 1981)						
$(CH_2OH)_2$ (1)	0.4	0.10139	0.94758	0.35109	-0.13110	17.0
$C_{12}H_{25}OH$ (2)	0.1	0.00879	0.01323	0.42389		
CH_3CN (3)	0.5	0.88982	0.03918	0.22503		
ϕ^k	(—)	0.49440	0.28896	0.21664		
Solution using UNIQUAC (Chakravarty *et al.*, 1985)						
$(CH_2OH)_2$ (1)	0.4	0.02776	0.69280	0.27899	-0.16085	20.65
$C_{12}H_{25}OH$ (2)	0.1	0.00206	0.00399	0.49191		
CH_3CN (3)	0.5	0.97018	0.30321	0.22910		
ϕ^k	(—)	0.31705	0.48492	0.19803		

Table 4: Solutions for Example 4

Solution for Ethylene Glycol (1) – Dodecanol (2) – Nitromethane (3) – Water (4) $T = 350$K, $P = 0.43$ atm							
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	Liquid III (—)	Vapor (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIFAC (Magnussen *et al.*, 1981)							
$(CH_2OH)_2$ (1)	0.3	0.08338	0.70581	0.24274	0.00837	-3.43040	1921.6
$C_{12}H_{25}OH$ (2)	0.1	0.01565	0.00680	0.40924	0.00033		
CH_3CN (3)	0.5	0.88822	0.03099	0.31537	0.95268		
H_2O (4)	0.1	0.01275	0.25640	0.03264	0.03862		
ϕ^k	(—)	0.23277	0.31581	0.23002	0.22139		
Solution using UNIFAC (Gmehling *et al.*, 1982)							
$(CH_2OH)_2$ (1)	0.3	0.79546	0.18400	(—)	0.01166	-3.26552	1439.3
$C_{12}H_{25}OH$ (2)	0.1	0.00693	0.22059	(—)	0.00031		
CH_3CN (3)	0.5	0.06917	0.55733	(—)	0.81852		
H_2O (4)	0.1	0.12843	0.03808	(—)	0.16951		
ϕ^k	(—)	0.27016	0.44443	(—)	0.28541		

Table 5: Solutions for Example 4

Solution for Water (1) – n-Propanol (2) – n-Hexane (3) $T = 311$K, $P = 1.0$ atm						
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	Liquid III (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIFAC (Fredenslund *et al.*, 1977)						
H_2O (1)	0.5	0.00282	0.92272	0.45295	−0.08812	257.1
C_3H_7OH (2)	0.1	0.06676	0.07715	0.48501		
C_6H_{14} (3)	0.25	0.93042	0.00013	0.06204		
ϕ^k	(—)	0.30888	0.58396	0.10716		
Solution using UNIFAC (Magnussen *et al.*, 1981), Conditions (i)						
H_2O (1)	0.5	0.05088	0.92300	(—)	−0.16650	101.7
C_3H_7OH (2)	0.1	0.18431	0.07612	(—)		
C_6H_{14} (3)	0.25	0.76481	0.00089	(—)		
ϕ^k	(—)	0.38385	0.61615	(—)		
Solution using UNIFAC (Magnussen *et al.*, 1981), Conditions (ii)						
H_2O (1)	0.5	0.84154	0.31021	(—)	−0.50383	213.5
C_3H_7OH (2)	0.4	0.15379	0.40725	(—)		
C_6H_{14} (3)	0.25	0.00467	0.28254	(—)		
ϕ^k	(—)	0.23446	0.76554	(—)		

Table 6: Solutions for Example 5

Solution for Ethanol (1) – Benzene (2) – Water (3) $T = 298\text{K}$, $P = 1.0$ atm					
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIFAC (Magnussen *et al.*, 1981) equation					
C_2H_5OH (1)	0.2	0.16195	0.23552	-3.02954	15.25
C_6H_6 (2)	0.4	0.80995	0.01731		
H_2O (3)	0.4	0.02810	0.74717		
ϕ^k	(—)	0.48280	0.51720		
Solution using UNIQUAC (Prausnitz *et al.*, 1980)					
C_2H_5OH (1)	0.2	0.13566	0.25660	-2.99483	13.4
C_6H_6 (2)	0.4	0.82005	0.03045		
H_2O (3)	0.4	0.04429	0.71295		
ϕ^k	(—)	0.46802	0.53198		

Table 7: Solutions for Example 6

Solution for Ethanol (1) – Ethyl Acetate (2) – Water (3) $T = 343\text{K}$, $P = 1.0$ atm					
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIFAC (Magnussen *et al.*, 1981) equation					
C_2H_5OH (1)	0.08	0.03127	0.12436	-0.27823	7.8
$C_2H_5COOCH_3$ (2)	0.30	0.01446	0.55993		
H_2O (3)	0.62	0.95427	0.31571		
ϕ^k	(—)	0.47653	0.52347		
Solution using NRTL (van Zandijcke and Verhoeye, 1974)					
C_2H_5OH (1)	0.08	0.05601	0.10376	-0.30125	1.4
$C_2H_5COOCH_3$ (2)	0.30	0.08472	0.51320		
H_2O (3)	0.62	0.85927	0.38305		
ϕ^k	(—)	0.49757	0.50243		
Solution using ASOG (Kojima and Tochigi, 1979)					
C_2H_5OH (1)	0.08	0.06968	0.10288	-0.25457	2.1
$C_2H_5COOCH_3$ (2)	0.30	0.07645	0.79539		
H_2O (3)	0.62	0.85387	0.10173		
ϕ^k	(—)	0.68906	0.31094		

Table 8: Solutions for Example 7

Solution for Methanol (1) – Methyl Acetate (2) – Water (3) T = 325K, P = 0.965 atm						
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	Vapor (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIFAC (Gmehling *et al.*, 1982)						
CH_3OH (1)	0.15	0.17493	0.16602	0.11789	−1.33446	8.8
CH_3COOCH_3 (2)	0.45	0.10661	0.72941	0.76490		
H_2O (3)	0.40	0.71846	0.10457	0.11720		
ϕ^k	(—)	0.47259	0.10700	0.42041		
Solution (LL only) using ASOG (Kojima and Tochigi, 1979)						
CH_3OH (1)	0.05	0.04953	0.05081	(—)	0.24980	2.1
CH_3COOCH_3 (2)	0.15	0.08294	0.53740	(—)		
H_2O (3)	0.60	0.86753	0.41179	(—)		
ϕ^k	(—)	0.63241	0.36759	(—)		

Table 9: Solutions for Example 8

Solution for Heptane (1) – Hexane (2) – Methanol (3) $T = 330$K, $P = 1.0$ atm					
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIFAC (Magnussen *et al.*, 1981) equation					
C_7H_{16} (1)	0.2	0.32519	0.07709	-0.40584	11.1
C_6H_{14} (2)	0.2	0.31631	0.08581		
CH_3OH (3)	0.6	0.35849	0.83709		
ϕ^k	(—)	0.49539	0.50461		
Solution using NRTL (Sørensen and Arlt, 1980)					
C_7H_{16} (1)	0.2	0.34182	0.11313	-0.45738	1.8
C_6H_{14} (2)	0.2	0.32552	0.12311		
CH_3OH (3)	0.6	0.33266	0.76376		
ϕ^k	(—)	0.37986	0.62014		
Solution using ASOG (Kojima and Tochigi, 1979)					
C_7H_{16} (1)	0.2	0.42916	0.05265	-0.33066	3.4.
C_6H_{14} (2)	0.2	0.41604	0.06108		
CH_3OH (3)	0.6	0.15480	0.88627		
ϕ^k	(—)	0.39136	0.60864		

Table 10: Solutions for Example 9

Solution for Toluene (1) – n-Propanol (2) – Water (3) T = 278K, P = 1.0 atm						
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	Liquid III (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using NRTL (Sørensen and Arlt, 1980)						
C_7H_8 (1)	0.3	0.00154	0.69270	0.40457	−0.26734	4.0
C_3H_7OH (2)	0.2	0.04372	0.24270	0.38868		
H_2O (3)	0.5	0.95473	0.06460	0.20653		
ϕ^k	(—)	0.44006	0.25262	0.30732		
Solution using UNIFAC (Magnussen *et al.*, 1981)						
C_7H_8 (1)	0.3	0.52987	0.00040	(—)	−0.36462	8.9
C_3H_7OH (2)	0.2	0.32588	0.03594	(—)		
H_2O (3)	0.5	0.14425	0.96366	(—)		
ϕ^k	(—)	0.56584	0.43416	(—)		

Table 11: Solutions for Example 10

Solution for Toluene (1) – n-Propanol (2) – Water (3) T = 298K, P = 1.0 atm					
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using NRTL (Sørensen and Arlt, 1980)					
C_7H_8 (1)	0.3	0.55463	0.00254	−0.27606	3.1
C_3H_7OH (2)	0.2	0.32398	0.05517		
H_2O (3)	0.5	0.12139	0.94228		
ϕ^k	(—)	0.53878	0.46122		
Solution using UNIFAC (Magnussen *et al.*, 1981)					
C_7H_8 (1)	0.3	0.53377	0.00064	−0.35798	9.1
C_3H_7OH (2)	0.2	0.32086	0.04523		
H_2O (3)	0.5	0.14537	0.95413		
ϕ^k	(—)	0.47721	0.52279		

Table 12: Solutions for Example 10

Hexanol (1) – Nitromethane (2) – Water (3)					
Comp.	$q_i = q_i'$	r_i	$i-j$	$\Delta u_{ij}/R$	$\Delta u_{ji}/R$
$C_6H_{13}OH$	4.132	4.8031	$1-2$	331.76	468.898
CH_3CN	1.868	2.0086	$1-3$	64.177	360.85
H_2O	1.4	0.92	$2-3$	499.65	159.11

Table 13: Pure component and binary data for Example 11

Solution for Hexanol (1) – Nitromethane (2) – Water (3) $T = 294\text{K}$, $P = 1.0$ atm						
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	Liquid III (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIQUAC (Walas, 1985)						
$C_6H_{13}OH$ (1)	0.2	0.66132	0.00064	0.00017	-0.10229	7.0
CH_3CN (2)	0.5	0.04693	0.04464	0.95110		
H_2O (3)	0.3	0.29175	0.95472	0.04872		
ϕ^k	(—)	0.30210	0.19631	0.50159		
Solution using UNIFAC (Magnussen *et al.*, 1981)						
$C_6H_{13}OH$ (1)	0.3	0.51308	0.07921	(—)	-0.28494	11.0
CH_3CN (2)	0.6	0.36804	0.84035	(—)		
H_2O (3)	0.1	0.11888	0.08044	(—)		
ϕ^k	(—)	0.50888	0.49112	(—)		

Table 14: Solutions for Example 11

Solution for Hexanol (1) – Nitromethane (2) – Water (3) T = 313K, P = 1.0 atm					
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using UNIQUAC (Sørensen and Arlt, 1980)					
$C_6H_{13}OH$ (1)	0.1	0.19458	0.00127	−0.15819	9.5
CH_3CN (2)	0.3	0.55029	0.03872		
H_2O (3)	0.6	0.25513	0.96001		
ϕ^k	(—)	0.51074	0.48926		
Solution using UNIFAC (Magnussen *et al.*, 1981)					
$C_6H_{13}OH$ (1)	0.1	0.17404	0.00114	−0.16503	9.6
CH_3CN (2)	0.3	0.52467	0.00004		
H_2O (3)	0.6	0.30129	0.99881		
ϕ^k	(—)	0.57175	0.42825		

Table 15: Solutions for Example 11

Solution for Phenol (1) – Acetone (2) – Water (3) T = 330K, P = 1.0 atm					
Components	Feed (mols)	Liquid I (—)	Liquid II (—)	$\hat{G}^*$ (—)	cpu (sec)
Solution using NRTL (Sørensen and Arlt, 1980)					
C_6H_5OH (1)	0.10	0.27502	0.01663	−2.45737	0.9
CH_3COCH_3 (2)	0.05	0.13682	0.00864		
H_2O (3)	0.85	0.58816	0.97473		
ϕ^k	(—)	0.32265	0.67735		
Solution using UNIFAC (Magnussen *et al.*, 1981)					
C_6H_5OH (1)	0.10	0.44011	0.00334	−2.39238	4.7
CH_3COCH_3 (2)	0.05	0.21480	0.00316		
H_2O (3)	0.85	0.34509	0.99350		
ϕ^k	(—)	0.22131	0.77869		

Table 16: Solutions for Example 12

Ethanol (1) – Acetic Acid (2) – Ethyl Acetate (3) – Water (4) T = 355K, P = 1 atm.				
Component	Liquid (mol fraction)	Vapor (mol fraction)	G^* (—)	cpu (sec)
Solution using NRTL (McDonald and Floudas, 1995c)				
$EtOH$ (1)	0.03980	0.07830	−90.7795	3.0
HAc (2)	0.20181	0.06984		
$EtAc$ (3)	0.08163	0.44147		
H_2O (4)	0.67676	0.41038		
ϕ^k	0.04964	0.95036		
Solution using UNIFAC (Gmehling *et al.*, 1982)				
$EtOH$ (1)	0.08678	0.09382	−90.78438	90.1
HAc (2)	0.27450	0.05773		
$EtAc$ (3)	0.19776	0.44760		
H_2O (4)	0.44096	0.40085		
ϕ^k	0.16124	0.83876		
Solution using Wilson parameters (Suzuki *et al.*, 1969)				
$EtOH$ (1)	0.04898	0.08289	−90.7816	0.03
HAc (2)	0.20419	0.06570		
$EtAc$ (3)	0.11719	0.45408		
H_2O (4)	0.62965	0.39733		
ϕ^k	0.09970	0.90030		

Table 17: Global solutions for Example 13 at T=355K

Computational requirements for all examples in seconds				
Example	NRTL	UNIQUAC	UNIFAC	ASOG
Ex. 1	0.23	(—)	0.37	0.32
Ex. 2a	(—)	19.67	(—)	(—)
Ex. 2b	(—)	16.41	(—)	(—)
Ex. 2c	(—)	15.26	(—)	(—)
Ex. 2d	(—)	14.48	(—)	(—)
Ex. 2e	(—)	15.16	(—)	(—)
Ex. 3	1.33	(—)	6.32	(—)
Ex. 4a	(—)	20.65	17.0	(—)
Ex. 4b	(—)	(—)	1921.6	(—)
Ex. 4c	(—)	(—)	1439.3	(—)
Ex. 5	(—)	(—)	257.1	(—)
Ex. 5 (i)	(—)	(—)	101.7	(—)
Ex. 5 (ii)	(—)	(—)	213.5	(—)
Ex. 6	(—)	13.4	15.25	(—)
Ex. 7	1.4	(—)	7.8	2.1
Ex. 8	(—)	(—)	8.8	2.1
Ex. 9	1.8	(—)	11.1	3.4
Ex. 10a	4.0	(—)	8.9	(—)
Ex. 10b	3.1	(—)	9.1	(—)
Ex. 11a	(—)	7.0	11.0	(—)
Ex. 11b	(—)	9.5	9.6	(—)
Ex. 12	0.9	(—)	4.7	(—)
Ex. 13	3.0	(—)	90.1	(—)

Table 18: Summary of Computational results for all examples

Computation time (secs) for UNIFAC examples				
Example	$\eta = 1.0$	$\eta = 0.5$	$\eta = 0.35$	$\eta = 0.2$
Ex. 4b	1921.6	360.8	199.0	87.5
Ex. 4c	1439.3	305.3	154.8	65.7
Ex. 5	257.1	85.3	51.9	24.0
Ex. 5 (i)	101.7	85.3	51.9	24.0
Ex. 5 (ii)	213.5	75.2	47.8	29.0
Ex. 13	90.1	33.8	19.7	11.6

Table 19: Summary of results for some UNIFAC examples

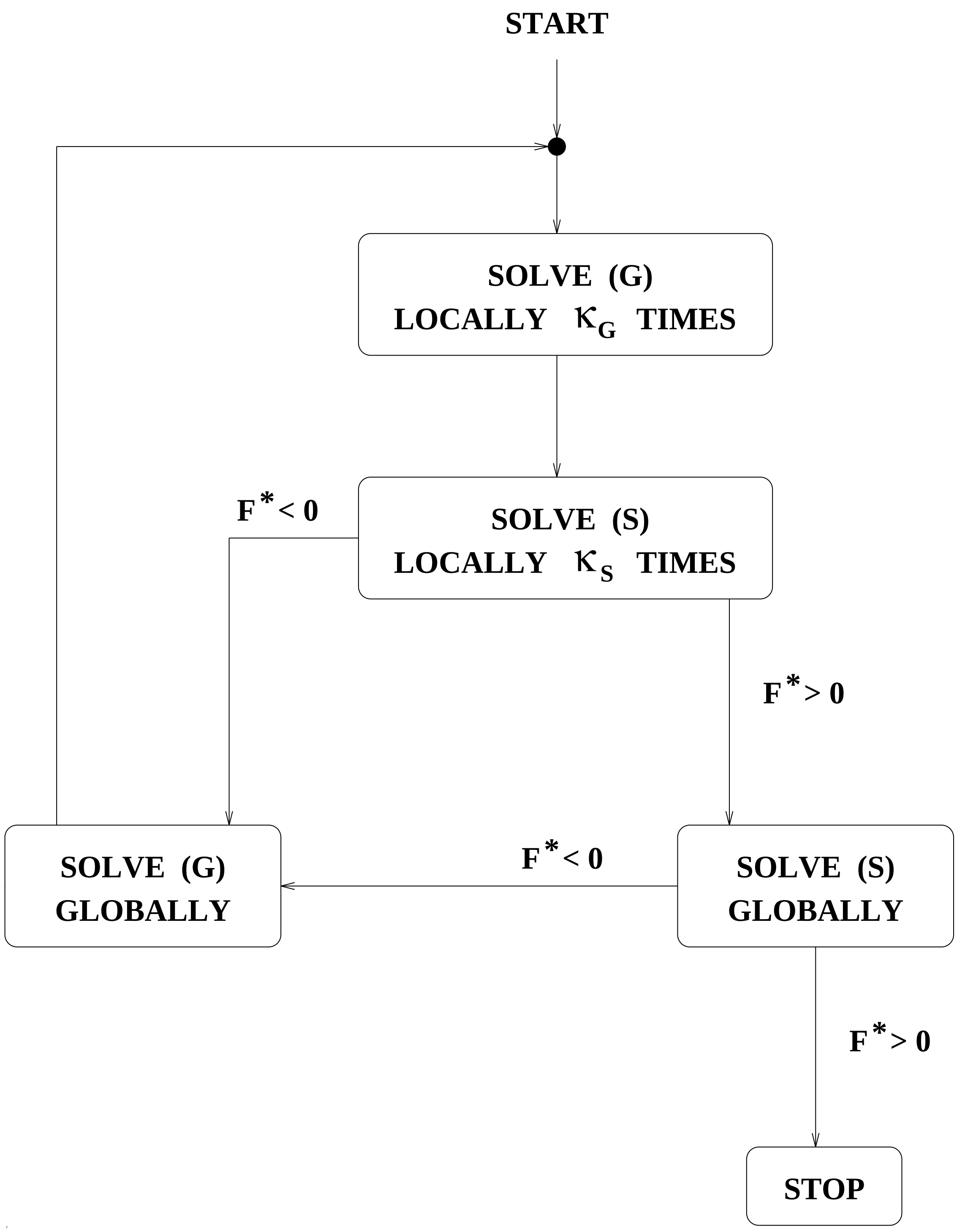

Figure 1: Outline of the combined algorithm GLOPEQ

Appendix A

Expressions for the Gibbs free energy

In this section, the expressions for the Gibbs free energy for the fugacity models used in GLOPEQ are given. The Gibbs functions can be transformed so that the objective function to be minimized will be either (i) bilinear, or (ii) the difference of two convex functions (D.C.). For the first of these classes, the Global OPtimization (GOP) of Floudas and Visweswaran (1990,1993) is used for cases where the nonconvexities of the formulations are of a bilinear form. which involves introducing a set of bilinear constraints into the formulation, and this is discussed in McDonald and Floudas (1995c) for the minimization of the Gibbs free energy, and in McDonald and Floudas (1995a) for the phase stability problem. For the second class, the branch and bound algorithm of Falk and Soland (1969) is used to obtain global solutions for the case when the nonconvexities are of a separable form.

Molar Gibbs function leading to a bilinear formulation

1. NRTL Equation (Renon and Prausnitz, 1968):

McDonald and Floudas (1995c) showed how the total Gibbs free energy could be transformed into the summation of a convex portion and a bilinear fractional portion. The molar Gibbs free energy when the NRTL equation is used to model the liquid phase is given by:

$$\frac{g(\boldsymbol{x})}{RT} = \sum_{i \in C} x_i \left\{ \Delta G_i^f + \ln x_i + \frac{\sum_{j \in C} \tau_{ij} \mathcal{G}_{ij} x_j}{\sum_{l \in C} \mathcal{G}_{lj} x_l} \right\}$$

Nonconvexities arise through the bilinear fractional term.

Molar Gibbs function leading to D.C. formulations

For the equations considered in this section, the objective function can be written as the difference of two convex functions, where the concave portion is separable. The convex portion is signified by $\mathcal{C}(\boldsymbol{x})$ and the coefficient designating the concave portion is φ_i so that the molar Gibbs function is defined as:

$$\frac{g(\boldsymbol{x})}{RT} = \mathcal{C}(\boldsymbol{x}) - \sum_{i \in C} \varphi_i x_i \ln x_i \qquad \text{(A.1)}$$

The definitions of $\mathcal{C}(\boldsymbol{x})$ and φ_i are now given for some activity coefficient correlations.

1. UNIQUAC Equation (Abrams and Prausnitz, 1975):

McDonald and Floudas (1994a) showed how the Gibbs free energy function can be transformed into the difference of two convex functions, leading to the following expressions:

$$\begin{aligned}
\mathcal{C}(\boldsymbol{x}) &= \sum_{i\in C} x_i \left\{ \Delta G_i^f - z_i^R r_i \ln r_i + \frac{z}{2} q_i \ln q_i \right\} \\
&+ z^A \cdot \sum_{i\in C} r_i x_i \ln \sum_{i\in C} r_i x_i + \sum_{i\in C} z_i^B r_i x_i \ln \frac{x_i}{\sum_{j\in C} r_j x_j} \\
&+ \frac{z}{2} \sum_{i\in C} x_i \ln \frac{q_i x_i}{\sum_{j\in C} q_j x_j} + \sum_{i\in C} q_i' x_i \ln \sum_{i\in C} q_i' x_i + \sum_{i\in C} q_i' x_i \ln \frac{x_i}{\sum_{j\in C} q_j' \tau_{ji} x_j} \\
\text{with} \quad \varphi_i &= q_i' + r_i \cdot z^A
\end{aligned}$$

The parameters of the model are q_i, q_i' and r_i with binary interaction parameters τ_{ij}. $z = 10$ is the coordination number. The introduced parameters (McDonald and Floudas, 1994a) are defined as follows:

$$\begin{aligned}
z_i^R &= \frac{\frac{z}{2} q_i - 1}{r_i} \\
z_i^B &= \sum_{j\neq i} \left[z_j^R - z_M^R \right] \quad \text{with} \quad z_M^R = \min_i \left\{ z_i^R \right\} \\
z^A &= z_i^R + z_i^B
\end{aligned}$$

2. UNIFAC Equation (Fredenslund *et al.*, 1977):

McDonald and Floudas (1995b) derived the following expressions for the UNIFAC equation:

$$\begin{aligned}
\mathcal{C}(\boldsymbol{x}) &= \sum_{i\in C} x_i \left\{ \frac{\Delta G_i^f}{RT} - z_i^R r_i \ln r_i + \frac{z}{2} q_i \ln q_i - v^{(i)} \right\} + z^A \cdot \sum_{i\in C} r_i x_i \ln \sum_{i\in C} r_i x_i \\
&+ \sum_{i\in C} z_i^B r_i x_i \ln \frac{x_i}{\sum_{j\in C} r_j x_j} + \frac{z}{2} \sum_{i\in C} q_i x_i \ln \frac{x_i}{\sum_{j\in C} q_j x_j} \\
&+ \sum_{i\in C} x_i q_i \ln \sum_{i\in C} x_i q_i + \sum_{i\in C} x_i \sum_{l\in G} v_{li} Q_l \ln \frac{x_i}{\sum_{j\in C} x_j \hat{v}_{lj}} \\
\text{with} \quad \varphi_i &= q_i + r_i \cdot z^A
\end{aligned}$$

The parameters of the original model are Q_l, R_l and v_{li} with binary interaction parameters Ψ_{lm}. The remaining parameters are defined as follows:

$$q_i = \sum_{l\in G} v_{li} Q_l$$

$$
\begin{aligned}
r_i &= \sum_{l \in G} \upsilon_{li} R_l \\
\hat{\upsilon}_{li} &= \sum_{m \in G} Q_m \upsilon_{mi} \Psi_{ml} \\
\upsilon^{(i)} &= \sum_{l \in G} \upsilon_{li} \ln \Gamma_l^{(i)} \\
\ln \Gamma_l^{(i)} &= Q_l \left\{ 1 - \ln \frac{\hat{\upsilon}_{li}}{q_i} - \sum_{m \in G} \frac{\upsilon_{mi} Q_m \Psi_{lm}}{\hat{\upsilon}_{mi}} \right\}
\end{aligned}
$$

z^A, z_i^R and z_i^B are defined exactly as for the UNIQUAC equation.

3. Wilson Equation (Wilson, 1964):

McDonald and Floudas (1995b) proved that the Wilson equation leads to a convex expression for the Gibbs energy. It is therefore incapable of describing liquid phase–splitting and a global optimization algorithm is not required. In this case:

$$
\frac{g(\boldsymbol{x})}{RT} = \sum_{i \in C} x_i \left\{ \Delta G_i^f + \ln \frac{x_i}{\sum_{j \in C} x_j \Lambda_{ij}} \right\} \tag{A.2}
$$

where Λ_{ij} are the binary interaction parameters of the system.

4. Modified Wilson Equation (Tsuboka and Katayama, 1975):

McDonald and Floudas (1995b) obtained the following expressions for the modified Wilson equation:

$$
\begin{aligned}
\mathcal{C}(\boldsymbol{x}) &= \sum_{i \in C} x_i \left\{ \Delta G_i^f + \ln \frac{x_i}{\sum_{j \in C} x_j \Lambda_{ji}} \right\} + \sum_{i \in C} \left[\sum_{j \in C} x_j \rho_{ji} \right] \ln \left[\sum_{j \in C} x_j \rho_{ji} \right] \\
&+ \sum_{i \in C} \sum_{j \neq i} x_j \rho_{ji} \ln \frac{x_j}{\sum_{l \in C} x_l \rho_{li}} \\
\text{with} \quad \varphi_i &= \sum_{j \neq i} \rho_{ji}
\end{aligned}
$$

The binary interaction parameters are given by Λ_{ij}. ρ_{ij} are the liquid volume ratios.

5. ASOG Equation (Kojima and Tochigi, 1979):

McDonald and Floudas (1995b) derived the following expressions for the ASOG equation:

$$\begin{aligned}
\mathcal{C}(\boldsymbol{x}) &= \sum_{i\in C} x_i \left\{ \Delta G_i^f + \ln \nu_i - v^{(i)} \right\} \\
&+ \sum_{i\in C} x_i \ln \frac{x_i}{\sum_{j\in C} x_j \nu_j} + \sum_{i\in C} x_i v_i^S \ln \sum_{i\in C} x_i v_i^S + \sum_{i\in C} x_i \sum_{l\in G} v_{li} \ln \frac{x_i}{\sum_{j\in C} x_j \hat{v}_{lj}} \\
\text{with} \quad \varphi_i &= v_i^S
\end{aligned}$$

The parameters of the model are ν_i, v_{li} and a_{lm} with the introduced parameters defined as:

$$\begin{aligned}
v_i^S &= \sum_{l\in G} v_{li} \\
\hat{v}_{li} &= \sum_{m\in G} v_{mi} a_{lm} \\
v^{(i)} &= \sum_{l\in G} v_{li} \ln \Gamma_l^{(i)} \\
\ln \Gamma_l^{(i)} &= 1 - \ln \frac{\hat{v}_{li}}{v_i^S} - \sum_{m\in G} \frac{v_{mi} \cdot a_{ml}}{\hat{v}_{mi}}
\end{aligned}$$

Appendix B

Both the input file used for Example 1 and the resulting output file are given in this Appendix.

```
#
# Example input file for GLOPEQ
#
# Example 1: n-Butyl-Acetate -- Water
#
# Parameters obtained from Heidemann and Mandhane (1973)
#
GIBBS MODEL
NRTL
#
PROBLEM NAME
n-Butyl Acetate (1) -- Water (2)
#
NUMBER OF COMPONENTS
2
#
TAU BINARY DATA
0.0         3.00498
4.69071     0.0
#
ALPHA BINARY DATA
0.0         0.391965
0.391965    0.0
#
BEGIN OPTIONS
#
TOTAL MOLS
0.5
0.5
#
LOCAL SOLVES
20
#
EPSA
0.0001
#
EPSR
0.0005
#
MAXIMUM ITERATIONS
1000
#
END OPTIONS
#
#MINIMIZE GIBBS
#NUMBER OF LIQUID PHASES
#2
```

```
        Welcome to GLOPEQ, Version 1.0.
        A GLobal Optimization package for the Phase and chemical EQuilibrium problem.
        Copyright (c) Conor M. McDonald and Christodoulos A. Floudas.
        Department of Chemical Engineering, Princeton University, Princeton, N.J.
        All rights reserved.

        All queries and bug reports should be sent to conor@titan.princeton.edu

PROBLEM TITLE:
==============

n-Butyl Acetate (1) -- Water (2)

HERE IS THE DATA YOU SUPPLIED FOR THE PROBLEM:
==============================================

PLEASE CHECK THE INPUT FOR POSSIBLE MISTAKES

ACTIVITY COEFFICIENT MODEL USED IS NRTL


BINARY COMPONENT INTERACTION PARAMETERS, TAU[I,J]

  C-1   C-2
C-1           0     3.00498
C-2     4.69071           0

BINARY COMPONENT INTERACTION PARAMETERS, G[I,J]

  C-1   C-2
C-1           1    0.307941
C-2    0.159041           1

  nT[i]   dG[L]   dG[V]   LIN[L]   LIN[V]
C-1     0.500000    0.000000    0.000000    0.000000    0.000000
C-2     0.500000    0.000000    0.000000    0.000000    0.000000


TEMPERATURE NOT SUPPLIED
PRESSURE    =  1.00000 ATM

NUMBER OF LOCAL SOLVES      =       1
MAXIMUM ITERATIONS ALLOWED  =     500
MAXIMUM SUBPROBLEMS ALLOWED =   50000

ABSOLUTE CONVERGENCE TOLERANCE = 0.00010
RELATIVE CONVERGENCE TOLERANCE = 0.00050

***** PHASE 1: GENERATING BEST SOLUTION USING 1 LOCAL SEARCH

MINIMIZING GIBBS FREE ENERGY FUNCTION LOCALLY

TOTAL NUMBER OF PHASES  = 2
NUMBER OF LIQUID PHASES = 2
NUMBER OF VAPOR PHASES  = 0
```

```
BEST SOLUTION AT PHASE 1 IS GIVEN AS:

MOL NUMBER VARIABLES:

  P-1   P-2
C-1     0.497866  0.00213431
C-2    0.0345301     0.46547

PHASE FRACTIONS:

  P-1   P-2
B-1     0.532396    0.467604

MOL FRACTION VARIABLES:

  P-1   P-2
C-1     0.935142  0.00456436
C-2    0.0648579    0.995436

CHEMICAL POTENTIALS:

  P-1   P-2
C-1   -0.0352296  -0.0352296
C-2    -0.003983   -0.003983


CHEMICAL POTENTIALS FOR USE IN NEXT PHASE:

  C-1   C-2
Y-1   -0.0352296   -0.003983

***** END OF PHASE 1 (CURRENT BEST SOLUTION DOES NOT CONTAIN A VAPOR PHASE)

   =========================================
   =========================================

***** PHASE 2 (i) STABILITY CHECK FOR LIQUID PHASE

MINIMIZING TANGENT PLANE DISTANCE FUNCTION FOR LIQUID PHASE


***********************************
***** BEGINNING GLOBAL SEARCH *****
***********************************

MINIMIZING TANGENT PLANE DISTANCE FUNCTION FOR 2 COMPONENTS



NEGATIVE TANGENT PLANE DISTANCE FUNCTION FOUND

RETURNING CONTROL TO MAIN PROGRAM

*** SUMMARY OF GLOBAL SEARCH ***
```

```
BEST SOLUTION AFTER 0 ITERATIONS HAS OF =    -0.000703300

MOL FRACTION VARIABLES:

  C-1   C-2
M-1     0.594248    0.405752

CHEMICAL POTENTIALS:

  C-1   C-2
M-1   -0.0359329 -0.00468629


LOWER BOUND = -100000000.000000000
UPPER BOUND =    -0.000703300


ABS DIFF    = 99999999.999296695

ABSOLUTE CONVERGENCE TOLERANCE   = 0.000100
RELATIVE CONVERGENCE TOLERANCE   = 0.000500

NUMBER OF ITERATIONS             =     0
NUMBER OF SUBPROBLEMS SOLVED     =     0
NUMBER OF SUBPROBLEMS STORED     =     0
NUMBER OF SUBPROBLEMS FATHOMED   =     0
NUMBER OF SUBPROBLEMS ELIMINATED =     0
FATHOMING RATE                   =  0.00

TIME TAKEN (in secs)             =  0.00

********************************
***** END OF GLOBAL SEARCH *****
********************************

***** ENDING PHASE 2 STABILITY CHECK
***** LIQUID PHASE UNSTABLE

***** PHASE 2 -- SEARCH FOR LOWER GIBBS ENERGY

MINIMIZING GIBBS FREE ENERGY FUNCTION LOCALLY

TOTAL NUMBER OF PHASES  = 2
NUMBER OF LIQUID PHASES = 2
NUMBER OF VAPOR PHASES  = 0

**********************************
***** BEGINNING GLOBAL SEARCH *****
**********************************

MINIMIZING GIBBS FREE ENERGY FUNCTION FOR 2 COMPONENTS

TOTAL NUMBER OF PHASES  = 2
NUMBER OF LIQUID PHASES = 2
```

```
NUMBER OF VAPOR PHASES  = 0

NO IMPROVEMENT FOUND USING 1 LOCAL SEARCHES

NO IMPROVEMENT FOUND USING 1 LOCAL SEARCHES

IMPROVED SOLUTION FOUND FOR GIBBS FREE ENERGY

RETURNING CONTROL TO MAIN PROGRAM

*** SUMMARY OF GLOBAL SEARCH ***

BEST SOLUTION AFTER 47 ITERATIONS HAS OF =    -0.020198312

MOL NUMBER VARIABLES:

  P-1   P-2
C-1     0.499286 0.000713609
C-2     0.344121    0.155879

PHASE FRACTIONS:

  P-1   P-2
B-1     0.843407    0.156593

MOL FRACTION VARIABLES:

  P-1   P-2
C-1     0.591987  0.00455711
C-2     0.408013    0.995443

CHEMICAL POTENTIALS:

  P-1   P-2
C-1   -0.0364191  -0.0364191
C-2  -0.00397755 -0.00397755


LOWER BOUND =    -0.025007944
UPPER BOUND =    -0.020198312


ABS DIFF    =     0.004809633

ABSOLUTE CONVERGENCE TOLERANCE   = 0.000100
RELATIVE CONVERGENCE TOLERANCE   = 0.000500

NUMBER OF ITERATIONS             =    47
NUMBER OF SUBPROBLEMS SOLVED     =   152
NUMBER OF SUBPROBLEMS STORED     =    98
NUMBER OF SUBPROBLEMS FATHOMED   =    54
NUMBER OF SUBPROBLEMS ELIMINATED =     2
FATHOMING RATE                   = 35.53

TIME TAKEN (in secs)             =  0.50
```

```
********************************
***** END OF GLOBAL SEARCH *****
********************************


MOL NUMBER VARIABLES:

  P-1   P-2
C-1     0.499286 0.000713609
C-2     0.344121    0.155879

PHASE FRACTIONS:

  P-1   P-2
B-1     0.843407    0.156593

MOL FRACTION VARIABLES:

  P-1   P-2
C-1     0.591987  0.00455711
C-2     0.408013    0.995443

CHEMICAL POTENTIALS:

  P-1   P-2
C-1   -0.0364191  -0.0364191
C-2  -0.00397755 -0.00397755


CHEMICAL POTENTIALS FOR USE IN NEXT PHASE:

  C-1   C-2
Y-1   -0.0364191 -0.00397755

***** END OF PHASE 2 (CURRENT BEST SOLUTION DOES NOT CONTAIN A VAPOR PHASE)

   =========================================
   =========================================

***** PHASE 3 (i) STABILITY CHECK FOR LIQUID PHASE

MINIMIZING TANGENT PLANE DISTANCE FUNCTION FOR LIQUID PHASE


***********************************
***** BEGINNING GLOBAL SEARCH *****
***********************************

MINIMIZING TANGENT PLANE DISTANCE FUNCTION FOR 2 COMPONENTS



*** SUMMARY OF GLOBAL SEARCH ***
```

```
CONVERGENCE AFTER 25 ITERATIONS HAS OF =     0.000000000

MOL FRACTION VARIABLES:

  C-1   C-2
M-1     0.591987    0.408013

CHEMICAL POTENTIALS:

  C-1   C-2
M-1   -0.0364191 -0.00397757


LOWER BOUND =    -0.000082477
UPPER BOUND =     0.000000000


ABS DIFF    =     0.000082477

ABSOLUTE CONVERGENCE TOLERANCE   = 0.000100
RELATIVE CONVERGENCE TOLERANCE   = 0.000500

NUMBER OF ITERATIONS             =    25
NUMBER OF SUBPROBLEMS SOLVED     =    50
NUMBER OF SUBPROBLEMS STORED     =    30
NUMBER OF SUBPROBLEMS FATHOMED   =    20
NUMBER OF SUBPROBLEMS ELIMINATED =     0
FATHOMING RATE                   = 40.00

TIME TAKEN (in secs)             =  0.11

********************************
***** END OF GLOBAL SEARCH *****
********************************

***** ENDING PHASE 3 STABILITY CHECK
***** LIQUID PHASE STABLE

***** GLOBALLY STABLE EQUILIBRIUM SOLUTION FOUND:

***** GIBBS FREE ENERGY VALUE IS:    -0.020198312


MOL NUMBER VARIABLES:

  P-1   P-2
C-1     0.499286 0.000713609
C-2     0.344121    0.155879

PHASE FRACTIONS:

  P-1   P-2
B-1     0.843407    0.156593

MOL FRACTION VARIABLES:
```

```
  P-1   P-2
C-1     0.591987  0.00455711
C-2     0.408013    0.995443

CHEMICAL POTENTIALS:

  P-1   P-2
C-1   -0.0364191  -0.0364191
C-2  -0.00397755 -0.00397755


TOTAL TIME TAKEN (in secs) =    0.66
```