DECOMPOSITION BASED AND BRANCH AND BOUND GLOBAL OPTIMIZATION APPROACHES FOR THE PHASE EQUILIBRIUM PROBLEM

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Submitted 10 October 1993; revised 11 March 1994;
To appear in *Journal of Global Optimization*, 1994.

Abstract

An increasingly popular approach when solving the phase and chemical equilibrium problem is to pose it as an optimization problem. However, difficulties are encountered due to the highly nonlinear nature of the models used to represent the behavior of the fluids, and because of the existence of multiple local solutions. This work shows how it is possible to guarantee ϵ-global solutions for a certain important class of the phase and chemical equilibrium problem, namely when the liquid phase can be modeled using either the Non-Random Two-Liquid (NRTL) equation, or the UNIversal QUAsi Chemical (UNIQUAC) equation. Ideal vapor phases are easily incorporated into the global optimization framework. A number of interesting properties are described which drastically alter the structure of the respective problems. For the NRTL equation, it is shown that the formulation can be converted into a biconvex optimization problem. The GOP algorithm of Floudas and Visweswaran [8, 9] can then be used to obtain ϵ-global solutions in this case. For the UNIQUAC equation, the new properties show how the objective function can be transformed into the difference of two convex functions (i.e. a D.C. programming problem is obtained), where the concave portion is separable. A branch and bound algorithm based on that of Falk and Soland [6] is used to guarantee convergence to an ϵ-global solution. Examples are presented which demonstrate the performance of both algorithms.

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Key words: Global optimization, phase equilibrium, biconvex and DC programming problems.

1 Introduction

A crucial step in the design of any separation process is the ability to predict the behavior of the fluids, when there may be several fluid phases and components that may or may not be reacting. For many separations processes, the assumption that the fluids are in equilibrium is made. The goal is to effectively model these processes over a potentially wide range of operating conditions. Such models can yield complex and nonlinear expressions with resultant difficulties in obtaining the solutions that actually describe the process.

For the phase and chemical equilibrium problem there have been essentially two basic approaches. The first of these is equation based, and is not considered in this work. A useful reference in this area is the book of Smith and Missen [21]. An increasingly popular approach is to explicitly minimize the thermodynamic function that describes the equilibrium condition. In the context of this work, this function will be the Gibbs free energy, and a *global* minimum implies that the system at hand is at equilibrium. Seider *et al.* [20] provide a review of the methods used to solve this optimization problem. Ohanomah and Thompson [14, 15, 16] give a comparative study of the available methods. These methods have typically been second-order Newton type methods with resultant dependency on starting point in terms of quality of the final solution. Other approaches have been used. Sun and Seider [22] use a Newton-homotopy continuation algorithm to obtain the stationary points of the Gibbs free energy surface. Paules and Floudas [17] employ the Global Optimal Search algorithm of Floudas *et al.* [7] to find the equilibrium solution. Eubank *et al.* [5] provide an interesting alternative approach based on integrating the area under the Gibbs free energy curve.

It is observed that all these algorithms share one drawback: there is no theoretical guarantee of convergence to the true equilibrium solution – or even to a proper local solution in some cases. This represents a serious disadvantage in attempting to describe phase equilibrium with or without chemical reaction. Due to the complex nature of the models used to describe the equilibrium situation, there may be several local solutions to the problem at hand. Thus, the certainty of convergence to the global solution for conventional methods will be highly dependent on starting point.

In this paper, the phase and chemical equilibrium problem is examined for the case where the liquid phase can be modeled by the NRTL and UNIQUAC equations, and the vapor phase is assumed to behave ideally. Both of these equations have the ability to predict liquid-liquid immiscibility and can describe multicomponent mixtures with binary parameters only.

The NRTL and UNIQUAC equations are algebraically complex and lead to highly nonconvex expressions for the Gibbs free energy function that usually lead to multiple local solutions.

In the following section, the requisite thermodynamic background for the phase and chemical equilibrium problem is provided, describing the assumptions that are made in this work. Then, a simplifying property for the NRTL equation is presented. It will be shown how the formulation for the NRTL equation can be transformed from its original nonconvex form into an optimization problem where a biconvex objective function is minimized subject to a bilinear set of constraints. This induced special structure allows the Global OPtimization (GOP) algorithm of Floudas and Visweswaran [8, 9] to be used to obtain global solutions to this problem. Next, the structure of the UNIQUAC equation is examined in detail. Two important properties are introduced which simplify the Gibbs energy expression, but still leave it in a nonconvex form. Additionally, some manipulation of terms reveal how this nonconvex expression can be transformed into the difference of two convex functions, where the concave portion of the objective function can be either nonseparable or separable. These changes occur purely in the objective function, so that it is not necessary to introduce new transformation variables as is the case for the NRTL equation. Having induced this special structure in the problem, an algorithm based on the branch and bound algorithm of Falk and Soland [6] is used to obtain the global solution of this problem. In summary, the main contribution of this work is to show that for ideal vapor phases and liquid phases whose behavior may be predicted by the NRTL or the UNIQUAC equation, *attainment of an ϵ-global solution can be guaranteed from <u>any</u> starting point.*

2 Problem Formulation

In this section, a general outline of the phase and chemical equilibrium problem will be given. The focus is on systems that attain equilibrium states under conditions of constant temperature and pressure, where the global minimum value of the Gibbs free energy describes the true equilibrium state. The set of components is represented by the index set $C = \{i\}$ and the elements that constitute these components are given by $E = \{e\}$. The set of phases is denoted by $P = \{k\}$ where it is composed of vapor and liquid phases, labeled P_V and P_L respectively, so that $P = P_V \cup P_L$. The problem may then be stated as follows:

> *Given i components participating in up to k potential phases under isothermal and isobaric conditions find the mol vector* $\mathbf{n}$ *that minimizes the value of the Gibbs free energy while also satisfying the appropriate material balance constraints.*

For a multicomponent, multiphase system, the criterion of equilibrium dictates that the Gibbs free energy function, $G(\mathbf{n})$, attain its minimum:

$$\min \quad G(\mathbf{n}) = \sum_{i \in C} \sum_{k \in P} n_i^k \left\{ \Delta G_i^{k,f} + RT \ln \frac{\hat{f}_i^k}{f_i^{k,0}} \right\} \tag{1}$$

where n_i^k is the number of moles of species i present in phase k, $\hat{f}_i^k$ and $f_i^{k,0}$ are the fugacity coefficients for the mixture and the pure component at the standard state respectively. The standard state is the fugacity of the component in its pure state at the temperature and pressure of the system. $\Delta G_i^{k,f}$ represents the Gibbs free energy of formation of component i in phase state k at the system temperature.

Difficulties in the use of Eqn. (1) arise due to the complicated expressions available for the expressions for fugacity. The liquid phase is modeled through the use of activity coefficients where the fugacity ratio is expressed as:

$$\frac{f_i^L}{f_i^{L,0}} = \gamma_i^L x_i^L \tag{2}$$

where x_i^L denotes the mole fraction of species i in the liquid phase, and γ_i^L is the corresponding activity coefficient at the system temperature and pressure.

The fugacity of the ideal vapor phase can be expressed as follows:

$$\frac{f_i^V}{f_i^{V,0}} = P y_i^V \tag{3}$$

where y_i^V represents the vapor phase mol fraction at a total system pressure P. The standard state for the vapor phase is taken as an ideal gas at unit fugacity at the system temperature where this quantity is usually equal to 1 atm.

Material Balances

The objective function as described by Eqn. (1) must yield a solution that will satisfy the conservation of mass requirements. These can take either of two forms depending on whether reaction occurs in the system and introduce a set of linear equality constraints into the formulation.

(a) *Elemental Constraints*: For simultaneous phase and chemical equilibrium where reaction does occur, conservation of the constituent atoms must be satisfied:

$$\sum_{i \in C} \sum_{k \in P} a_{ei} n_i^k \quad = b_e \quad \forall \quad e \in E \tag{4}$$

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.

(b) *Mass Balance Constraints*: These constraints are required for those systems where no chemical reaction takes place, and thus conservation over the components need only hold:

$$\sum_{k \in P} n_i^k \;=\; n_i^T \quad \forall \quad i \in C \tag{5}$$

where n_i^T is the total number of moles of component i in the initial charge.

For notational clarity, the material balance constraints for any system, reacting or non-reacting, will be written in the following general form:

$$\mathbf{A} \cdot \mathbf{n} \;-\; \mathbf{b} = 0 \tag{6}$$

where $\mathbf{n}$ represents the column vector of the component mol numbers, $\mathbf{A}$ is the appropriate elemental or compound abundance matrix, and $\mathbf{b}$ is the column vector of the total amounts of elements or compounds in the system.

Feasibility Constraints: Obviously a physically realizable solution requires that

$$0 \;\leq\; n_i^k \;\leq\; n^T \qquad \forall \; i \in C \,,\; k \in P \tag{7}$$

where n^T is the total number of mols in the system.

The complete formulation of the phase and chemical equilibrium for ideal vapor phases and liquid phases whose fugacities can be adequately modeled by the NRTL or UNIQUAC equation, is given by minimizing the expression of Eqn. (1) subject to the material balance constraints supplied by Eqn. (6) and the feasibility constraints of Eqn. (7). The variables of the formulation are the mol numbers n_i^k, noting that the mol fractions can be defined in terms of the mol numbers as $x_i^k = n_i^k / \sum_j n_j^k$ for all components and phases. There are two important observations in regard to the optimization formulation:

(i) The constraint set is of small size and linear.

(ii) The only nonlinearity appears in the objective function as $n_i \ln \hat{f}_i / f_i^0$.

If the system is ideal then any local solution will be the global one. However, the main difficulty is that due to the complex nature of the models used to predict fugacities, highly nonconvex functionalities result. This may lead to local or trivial solutions that are not true equilibrium solutions, and may lie far away from the correct optimal solution. The obtained solution will also be highly dependent on the chosen starting point.

3 Analysis for the NRTL Equation

In this section, the Gibbs free energy expression is analyzed for the case of an ideal vapor phase and liquid phases modeled using the NRTL activity coefficient expression. Renon and Prausnitz [19] derived the following equation for the liquid-phase activity coefficient:

$$\ln\gamma_i = \frac{\sum\limits_{j\in C}\tau_{ji}\mathcal{G}_{ji}x_j}{\sum\limits_{j\in C}\mathcal{G}_{ji}x_j} + \sum_{j\in C}\frac{\mathcal{G}_{ij}x_j}{\sum\limits_{l\in C}\mathcal{G}_{lj}x_l}\left\{\tau_{ij} - \frac{\sum\limits_{l\in C}\tau_{lj}\mathcal{G}_{lj}x_l}{\sum\limits_{l\in C}\mathcal{G}_{lj}x_l}\right\} \qquad \forall\ i\in C \tag{8}$$

where γ_i is the activity coefficient at mol fraction x_i, τ_{ij} and $\mathcal{G}_{ij}$ are non-symmetric binary interaction parameters. τ_{ij} can be negative but $\mathcal{G}_{ij}$ is always positive. One important feature of the NRTL equation is its capability of representing liquid-liquid immiscibility for multi-component systems with only binary parameters. Eqn. (8) yields exactly the same expression for mol numbers as for mol fractions. Substitution of Eqn. (8) into Eqn. (2) yields the correct liquid phase fugacity term, after rewriting the mol fractions in terms of mol numbers. Eqn. (3) is assumed to define the vapor phase fugacity. Again, the mol fractions are written in terms of the vapor mol number variables. Substitution of the resultant vapor and liquid phase fugacity equations into Eqn. (1) gives the Gibbs free energy function as follows:

$$\begin{aligned}\min\ \hat{G}(\boldsymbol{n}) \;=\;& \sum_{i\in C}\sum_{k\in P} n_i^k\left\{\frac{\Delta G_i^{k,f}}{RT} + \ln\frac{n_i^k}{\sum\limits_{j\in C}n_j^k}\right\}\\ &+ \sum_{i\in C}\sum_{k\in P_L} n_i^k\left\{\frac{\sum\limits_{j\in C}\tau_{ji}\mathcal{G}_{ji}n_j^k}{\sum\limits_{j\in C}\mathcal{G}_{ji}n_j^k} + \sum_{j\in C}\frac{\mathcal{G}_{ij}n_j^k}{\sum\limits_{l\in C}\mathcal{G}_{lj}n_l^k}\left\{\tau_{ij} - \frac{\sum\limits_{l\in C}\tau_{lj}\mathcal{G}_{lj}n_l^k}{\sum\limits_{l\in C}\mathcal{G}_{lj}n_l^k}\right\}\right\}\end{aligned} \tag{9}$$

where $\hat{G}(\boldsymbol{n}) = G(\mathbf{n})/RT$ (i.e. dimensionless G). Note that the pressure term associated with the fugacity of the vapor phase has been incorporated into the Gibbs energy of formation term, that is, $\Delta G_i^{V,f} = \Delta G_i^{V,f} + RT\ln P$. This is done in order to collect the linear terms of the objective function.

3.1 Analysis of the Gibbs free energy function:

As given by Eqn. (9), $\hat{G}(\boldsymbol{n})$ is a complex and nonconvex expression. However, the situation is ameliorated by the following property:

Property 3.1 *For each phase $k\in P$, the following relation is true:*

$$\sum_{i\in C} n_i^k\left\{\frac{\sum\limits_{j\in C}\tau_{ji}\mathcal{G}_{ji}n_j^k}{\sum\limits_{j\in C}\mathcal{G}_{ji}n_j^k}\right\} - \sum_{i\in C} n_i^k\left\{\sum_{j\in C}\frac{\mathcal{G}_{ij}n_j^k}{\sum\limits_{l\in C}\mathcal{G}_{lj}n_l^k}\,\frac{\sum\limits_{l\in C}\tau_{lj}\mathcal{G}_{lj}n_l^k}{\sum\limits_{l\in C}\mathcal{G}_{lj}n_l^k}\right\} = 0 \tag{10}$$

Proof: See Appendix A.

This property reduces the complexity of Eqn. (9) greatly, and it brings the crucial advantage of having bilinear, rather than trilinear, fractional functions in the expression for the objective function.

Property 3.2 *Let ρ_i be positive parameters defined $\forall\, i$. Define the real-valued function $f_i(\mathbf{n})$ with $\mathbf{n} > 0$ as follows:*

$$f_i(\mathbf{n}) = n_i \ln \frac{n_i}{\sum\limits_j \rho_j n_j}$$

then $f_i(\mathbf{n})$ is convex.

Proof: See Appendix B.

Remark: Based on Property 3.2, if $\mathcal{C}_N^k$ is defined as follows:

$$\mathcal{C}_N^k = \sum_{i \in C} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} + \ln \frac{n_i^k}{\sum\limits_{j \in C} n_j^k} \right\} \qquad \forall\, k \in P$$

then the quantity $\sum\limits_k \mathcal{C}_N^k$ is convex, since it is a summation of individually linear and convex terms.

This means that the objective function can now be written as a combination of a convex portion, and a nonconvex portion:

$$\min\ \hat{G}(\boldsymbol{n}) \;=\; \sum_{k \in P} \mathcal{C}_N^k + \sum_{i \in C} \sum_{k \in P_L} n_i^k \left\{ \sum_{j \in C} \frac{\mathcal{G}_{ij} \tau_{ij} n_j^k}{\sum\limits_{l \in C} \mathcal{G}_{lj} n_l^k} \right\} \tag{11}$$

The nonconvexities of Eqn. (11) now lie solely in the term to the right of the plus sign. The following NonConvex Formulation (NCF) is a new formulation:

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

where $\hat{G}(\boldsymbol{n})$ is defined by Eqn. (11) and is a much simpler form for the Gibbs free energy function than that customarily given by Eqn. (9).

3.2 Transformations and Partitioning

The general form of the optimization problem of interest is given as follows:

$$\left.\begin{array}{rrcl} \min\limits_{x,y} & f(x,y) & & \\ s.t. & h(x,y) & = & 0 \\ & g(x,y) & \leq & 0 \\ & x & \in & X \\ & y & \in & Y \end{array}\right\} \tag{12}$$

where X and Y are convex sets, $f(x,y)$ is the objective function to be minimized, and $h(x,y)$ and $g(x,y)$ represent the vectors of equality and inequality constraints respectively. These functions are assumed to be continuous and piecewise differentiable on $X \times Y$. The GOP algorithm of Floudas and Visweswaran [8, 9] can be used to to determine an ϵ-global solution for problems that satisfy the following conditions:

Conditions (A):

- $f(x,y)$ and $g(x,y)$ are convex in x for all fixed y and convex in y for all fixed x,
- $h(x,y)$ is affine in x for all fixed y, and affine in y for all fixed x,
- X and $Y \subseteq V$ are nonempty, compact convex sets and a constraint qualification is satisfied, where $V \equiv \{\ y\colon h(x,y) = 0, g(x,y) \leq 0,\ \text{for some } x \in X\}$.

It will now be shown how new variables are introduced so as to change the nature of the nonconvexities in the objective function defined by Eqn. (11). This is known as the *transformation* phase. Having augmented the variable set in this way, it is then *partitioned* into two variable subsets, so that *Conditions (A)* of the GOP are satisfied. If the following new variables are introduced:

$$\Psi_i^k = \frac{n_i^k}{\sum\limits_{j \in C} \mathcal{G}_{ji} n_j^k} \qquad \forall\ i \in C\ ,\ k \in P_L \tag{13}$$

then the transformed objective function becomes:

$$\min\ \hat{G}(\boldsymbol{n}) = \sum_{k \in P} \mathcal{C}_N^k + \sum_{i \in C} \sum_{k \in P_L} n_i^k \left\{ \sum_{j \in C} \mathcal{G}_{ij} \tau_{ij} \Psi_j^k \right\} \tag{14}$$

This objective function is now subject to the transformation constraints of Eqn. (13) (which are rewritten by bringing the denominator over to the left hand side so that they will be of bilinear form, rather than fractional), in addition to the material balance constraints as defined by Eqn. (6). The objective is to partition the variable set into two subsets so that if either of these subsets is held constant, an optimization problem with simpler structure remains. An examination of Eqn. (14) leads to the conclusion that the obvious partition of variables is that in which the y variable set contains the mol vector, with the x variable set containing the new variables:

$$y \leftarrow \left\{n_i^k\right\} \qquad x \leftarrow \left\{\Psi_i^k\right\} \tag{15}$$

Notice that if the mol number variable set is held constant, a linear objective function results. On the other hand, if the transformed variable set is held constant, a convex objective function is obtained. The equality constraints are of bilinear form and so will yield linear terms if either of the subsets is held constant. Thus, *Conditions (A)* of the GOP are satisfied. The form of the nonconvexities of the objective function have been changed, resulting in the introduction of additional bilinear equality constraints into the system.

3.3 The Primal Problem

The primal problem is defined as the subproblem that results when the y variable set is held fixed so that $y = \bar{y}$. In what follows, overbars on variables represent their values obtained from any given primal problem, which is defined as follows:

$$\left.\begin{array}{lll} \min & \displaystyle\sum_{k\in P} \bar{\mathcal{C}}_N^k + \sum_{i\in C}\sum_{k\in P_L} \bar{n}_i^k \left\{\sum_{j\in C} \mathcal{G}_{ij}\tau_{ij}\Psi_j^k\right\} & \\ s.t. & \Psi_i^k \cdot \left\{\displaystyle\sum_{j\in C} \mathcal{G}_{ji}\bar{n}_j^k\right\} = \bar{n}_i^k & \forall\ i \in C\ ,\ k \in P_L \end{array}\right\} \quad \text{(P)}$$

$\left\{\bar{n}_i^k\right\}$ represents the current value of the mol numbers (the y variable set). The primal problem (P) is always feasible provided that the mol vector satisfies the material balance constraints which are functions of the y variables alone. Hence they can be carried directly to the relaxed dual subproblems. This is the reason the material balance constraints are not included in (P). Notice that (P) is merely a function evaluation as the x variable set is completely specified by $\left\{\bar{n}_i^k\right\}$.

It will be necessary to use the Karush-Kuhn-Tucker (KKT) conditions for the primal problem in proceeding sections. The Lagrangian as constructed from the primal problem is given as:

$$
\begin{aligned}
L(x,\bar{y},\lambda) &= \sum_{k\in P} \bar{\mathcal{C}}^{k}_{N} + \sum_{i\in C}\sum_{k\in P_L} \bar{n}^{k}_{i}\left\{\sum_{j\in C}\mathcal{G}_{ij}\tau_{ij}\Psi^{k}_{j}\right\} \\
&+ \sum_{i\in C}\sum_{k\in P_L}\lambda_{\Psi^{k}_{i}}\left\{\Psi^{k}_{i}\cdot\sum_{j\in C}\mathcal{G}_{ji}\bar{n}^{k}_{j} - \bar{n}^{k}_{i}\right\}
\end{aligned}
\tag{16}
$$

where $\lambda_{\Psi^k_i}$ is the multiplier associated with the corresponding constraint that defines the x variable Ψ^k_i. The evaluation of the KKT conditions for the primal yields:

$$
\nabla_{\Psi^k_i} L(x,\bar{y},\lambda) = \sum_{j\in C}\mathcal{G}_{ji}\tau_{ji}\bar{n}^{k}_{j} + \lambda_{\Psi^k_i}\cdot\sum_{j\in C}\mathcal{G}_{ji}\bar{n}^{k}_{j} = 0 \qquad \forall\, i\ \in C\ ,\ k\ \in P_L \tag{17}
$$

The Lagrange multipliers from the primal are then explicitly calculated as:

$$
\bar{\lambda}_{\Psi^k_i} = -\frac{\sum\limits_{j\in C}\mathcal{G}_{ji}\tau_{ji}\bar{n}^{k}_{j}}{\sum\limits_{j\in C}\mathcal{G}_{ji}\bar{n}^{k}_{j}} \qquad \forall\, i\ \in C\ ,\ k\ \in P_L \tag{18}
$$

Thus, the multipliers from any primal problem are nonempty and bounded for all $y \in Y$, a required condition to guarantee ϵ-global convergence. In the special case that $\sum_j \mathcal{G}_{ji} n^k_j = 0$, it is clear that $n^k_i = 0\ \forall\ i \in C$, that is, the phase disappears. The corresponding primal constraints are then of the form $\Psi^k_i \cdot 0 = 0$. This implies that any value for the Lagrange multipliers can be chosen so that the KKT conditions will be satisfied for the primal problem and $\lambda_{\Psi^k_i} = 0\ \forall\ i\ \in C$ is one obvious choice. Thus, if for a given phase k, $n^k_i = 0\ \forall\ i\ \in C$, then set $\lambda_{\Psi^k_i} = 0\ \forall\ i\ \in C$; otherwise use Eqn. (18) to calculate the multipliers. This eliminates the problem of obtaining unbounded values for the multipliers from the primal problem. It is therefore seen that solving the primal problems and obtaining the corresponding multipliers amounts to simple function evaluations.

3.4 The Relaxed Dual problem

The primal problem establishes upper bounds on the solution. The relaxed dual subproblems supply lower bounds on the global solution. The details of the derivation of the Lagrangian for use in the relaxed dual is described in the following section.

3.4.1 Derivation of the Lagrangian

The first step in deriving the Lagrangian is to separate and collect all the x variable terms to obtain:

$$
\begin{aligned}
L(x,y,\bar{\lambda}) &= \sum_{i\in C}\sum_{k\in P_L} \Psi_i^k \left\{ \sum_{j\in C} \mathcal{G}_{ji}\tau_{ji} n_j^k + \bar{\lambda}_{\Psi_i^k} \cdot \sum_{j\in C} \mathcal{G}_{ji} n_j^k \right\} \\
&+ \sum_{k\in P} \mathcal{C}_N^k - \sum_{i\in C}\sum_{k\in P_L} n_i^k \bar{\lambda}_{\Psi_i^k}
\end{aligned}
\tag{19}
$$

Eqn. (19) is simplified by enacting the following steps:

(i) Subtract Eqns. (17) with $\lambda_{\Psi_i^k} = \bar{\lambda}_{\Psi_i^k}$ from the terms within the curly braces of Eqn. (19).

(ii) Use Eqns. (18) to modify the term to the right of the minus sign in Eqn. (19).

The following expression is then obtained:

$$
\begin{aligned}
L(x,y,\bar{\lambda}) &= \sum_{i\in C}\sum_{k\in P_L} \Psi_i^k \left\{ \sum_{j\in C} \mathcal{G}_{ji} \left[\tau_{ji} + \bar{\lambda}_{\Psi_i^k}\right] \left[n_j^k - \bar{n}_j^k\right] \right\} \\
&+ \sum_{k\in P} \mathcal{C}_N^k + \sum_{i\in C}\sum_{k\in P_L} n_i^k \left\{ \sum_{j\in C} \mathcal{G}_{ij}\tau_{ij} \bar{\Psi}_j^k \right\}
\end{aligned}
\tag{20}
$$

Note that if $n_i^k = \bar{n}_i^k \ \forall \ i \in C, k \in P_L$, then the Lagrangian equals the objective function value supplied by the primal at $\bar{n}_i^k$. By evaluating the gradients of the Lagrangian given by Eqn. (20) with respect to the x variables, the following equations are obtained:

$$
g_i^k(y) = \nabla_{\Psi_i^k} L(x,y,\bar{\lambda}) = \sum_{j\in C} \mathcal{G}_{ji} \left[\tau_{ji} + \bar{\lambda}_{\Psi_i^k}\right] \cdot \left[n_j^k - \bar{n}_j^k\right] \qquad \forall \ i \ \in C \ , \ k \ \in P_L \tag{21}
$$

These are the *qualifying constraints* written in terms of the x variables and describe the fundamental nature of the interaction of the two variable subsets. Notice that each x variable multiplies a *summation* of y variables, so that these constraints form hyperplanes that partition the y variable space. The next important step in the development is to obtain a much simpler set of partitioning hyperplanes. This is achieved by simply augmenting the set of x variables, so that each one of these new x variables will interact with a *single* y variable, rather than a summation of them. This augmented set of variables, denoted $\{\hat{\Psi}_{ij}^k\}$, is defined for each $\{i,k\} \in C \times P_L$ as follows:

$$\hat{\Psi}_{ij}^k = \Psi_i^k \qquad \forall\, j \in C \tag{22}$$

The x variables are now allowed to appear within the innermost summation of Eqn. (20) to yield an equivalent Lagrangian defined as follows:

$$\begin{aligned} L(x,y,\bar{\lambda}) &= \sum_{i\in C}\sum_{k\in P_L}\left\{\sum_{j\in C}\hat{\Psi}_{ij}^k\left[\mathcal{G}_{ji}\left\{\tau_{ji}+\bar{\lambda}_{\Psi_i^k}\right\}\right]\cdot\left[n_j^k-\bar{n}_j^k\right]\right\} \\ &+ \sum_{k\in P}\mathcal{C}_N^k+\sum_{i\in C}\sum_{k\in P_L} n_i^k\left\{\sum_{j\in C}\mathcal{G}_{ij}\tau_{ij}\bar{\Psi}_j^k\right\} \end{aligned} \tag{23}$$

Eqn. (23) now supplies the new form of the qualifying constraints, labeled $\hat{g}_{ij}^k(y)$, obtained from the modified Lagrangian of Eqn. (23) as:

$$\hat{g}_{ij}^k(y) = \nabla_{\hat{\Psi}_{ij}^k} L(x,y,\bar{\lambda}) \;=\; \mathcal{G}_{ji}\left[\tau_{ji}+\bar{\lambda}_{\Psi_i^k}\right]\cdot\left[n_j^k-\bar{n}_j^k\right] \quad \forall\, i\in C\ ,\ j\in C\ ,\ k\in P_L \tag{24}$$

Thus, each qualifying constraint is now a function of a single y variable, with the important result that the hyperplanes are now orthogonal to each other, and partition the y variable space into n-rectangles (i.e. simple boxes). The number of connected variables is given as:

$$N_{CV} = |C|\cdot|P_L| \tag{25}$$

where the braces signify the cardinalities of the appropriate sets.

In Eqn. (24), each qualifying constraint shares the same basic form, defined as $(n_j^k - \bar{n}_j^k)$. The only difference is the expression that premultiplies this term. These are constants that depend on the parameters of the NRTL model and information from the primal in the form of the Lagrange multipliers. Eqn. (7) delineates the feasible region as an n-rectangle. The initial *parent* region is described by this n-rectangle, and its bounds are represented by $R\{\mathcal{L}^R,\mathcal{U}^R\}$, where $\mathcal{L}^R = \{\mathcal{L}^R_{n_i^k}\}$ and $\mathcal{U}^R = \{\mathcal{U}^R_{n_i^k}\}$ comprise the regional bounds for the variables $\{n_i^k\}$. Upon choosing an initial point $\{\bar{n}_i^k\}$, this parent n-rectangle is partitioned by N_{CV} orthogonal hyperplanes passing through $\{\bar{n}_i^k\}$, so that $2^{N_{CV}}$ new n-rectangles are created. Within each of these new n-rectangles, the sign of $(n_i^k - \bar{n}_i^k)$ will be constant $\forall\ \ i \in C\ ,\ k \in P_L$. The bounds for each of these n-rectangles are described as the *box* bounds, denoted $B\{\mathcal{L}^B,\mathcal{U}^B\}$, with $\mathcal{L}^B = \{\mathcal{L}^B_{n_i^k}\}$ and $\mathcal{L}^B = \{\mathcal{U}^B_{n_i^k}\}$ representing the individual box bounds for the variables $\{n_i^k\}$. The set of all possible combinations of box bounds is denoted by CB, with its $2^{N_{CV}}$

members individually referred to as B_l. The parameter $s_{ik}^{B_l}$ is used to delineate each of these box regions and is defined over $C \times P_L \times CB$. It determines the partition of the y variable space for any given B_l as follows:

$$\left.\begin{array}{lll} \text{If} \quad s_{ik}^{B_l} = +1 & \text{then} & n_i^k - \bar{n}_i^k \geq 0 \\ \text{If} \quad s_{ik}^{B_l} = -1 & \text{then} & n_i^k - \bar{n}_i^k \leq 0 \end{array}\right\} \quad \forall\, i \,\in\, C\ ,\ k \,\in\, P_L$$

Figure 1 shows how $s_{ik}^{B_l}$ is used to create these regional and box bounds at the first iteration for the case of 2 connected variables, with $C \equiv \{i_1, i_2\}$ and $P_L \equiv \{k_1\}$. The initial point generates 4 subdomains denoted B_1 through B_4.

This implies that it is possible to construct Lagrangians that validly underestimate the global solution in each of these n-rectangles, within which an individual relaxed dual subproblem is solved. If the solution is greater than the current best upper bound obtained from the primal problem, it may be fathomed (i.e. discarded); otherwise, it is added to the set of candidate lower bounds. The infimum of all such solutions supplies the point for the next iteration, where the n-rectangle associated with this node will be partitioned into $2^{N_{CV}}$ n-rectangles to supply additional lower bounds on the final solution. In the context of Figure 1, suppose the infimum of the 4 lower bounds lies in B_2. At the next iteration, B_2 is divided into 4 regions, and so on.

A convenient way of describing this partitioning of the y variable space in the branch and bound approach is through the use of a tree structure. The starting point is represented by the *root* node, labeled R, and it generates $2^{N_{CV}}$ nodes at the first level of the tree. One of these leaf nodes becomes the next iteration node, in turn generating a further $2^{N_{CV}}$ additional nodes, and so on. Note that at any given iteration, all generated solution nodes share the same parent node, so that each n-rectangle is a refinement of its parent n-rectangle implying that the regional bounds for a given node are supplied by the box bounds of its parent node. This has the important implication that any given Lagrange function will be valid in any future n-rectangles that it spawns. In addition, retrieval of previous Lagrange functions for use in the current relaxed dual subproblem is easily achieved by employing a backward depth-first traversal through the solution tree from the current node to the root node, extracting the relevant information required to construct the Lagrange function at each node along the path. This set of previous iterations to be included in the subproblems of some iteration K is denoted $PL(K_P)$. Because a Lagrangian is not included for *all* previous iterations, but only for those whose nodes define the current node as a subdomain in the y variable space, each relaxed dual subproblem contains relatively few Lagrangians from previous iterations. Thus, each relaxed dual subproblem can be both generated and solved efficiently. The manner in which the x variable bounds are obtained and set on the basis of the qualifying constraints will now be described.

3.4.2 Bounds for the x variables

For any given n-rectangle defined by $B\{\mathcal{L}^B, \mathcal{U}^B\}$, it is necessary to establish upper and lower bounds on the x variables within this box. Recall that $\{\Psi_i^k\}$ are defined as linear fractionals. Any linear fractional is a pseudolinear function, that is, it is pseudoconvex *and* pseudoconcave. Thus, there is one local minimum and one local maximum that satisfy the KKT optimality conditions, and these will be unique global extrema. By examining the KKT conditions for the problem:

$$\left.\min \quad \Psi_i^k \quad s.t. \quad \mathcal{L}^B_{n_j^k} \leq n_j^k \leq \mathcal{U}^B_{n_j^k} \quad \forall \ j \in C \right\} \forall \, i \in C \ , \ \forall \, k \in P_L \tag{26}$$

the global minimum value for each Ψ_i^k in $B\{\mathcal{L}^B, \mathcal{U}^B\}$ can be evaluated and is labeled $\mathcal{L}_{\Psi_i^k}$. $-\Psi_i^k$ is minimized subject to the same constraints to obtain the corresponding maximum, $\mathcal{U}_{\Psi_i^k}$. The globally valid lower and upper bounds for Ψ_i^k (and hence $\hat{\Psi}_{ij}^k$) within the n-rectangle defined by $B\{\mathcal{L}^B, \mathcal{U}^B\}$ are given as:

$$\left.\mathcal{L}_{\Psi_i^k} = \frac{\mathcal{L}^B_{n_i^k}}{\mathcal{L}^B_{n_i^k} + \sum\limits_{j \neq i} \mathcal{G}_{ji}\, \mathcal{U}^B_{n_j^k}} \qquad \mathcal{U}_{\Psi_i^k} = \frac{\mathcal{U}^B_{n_i^k}}{\mathcal{U}^B_{n_i^k} + \sum\limits_{j \neq i} \mathcal{G}_{ji}\, \mathcal{L}^B_{n_j^k}} \qquad \right\} \ \forall \, i \in C \ , \ \forall \, k \in P_L \tag{27}$$

Having established the lower and upper bounds on the x variables it is necessary to decide at what bounds to set the modified x variable set, $\left\{\hat{\Psi}_{ij}^k\right\}$, for some $B_l \in CB$. Each term involving $(n_j^k - \bar{n}_j^k)$ is underestimated individually. This quantity alone does not determine the bounds at which the x variables are set. The terms that premultiply $(n_j^k - \bar{n}_j^k)$ must also be considered. Once the combined sign of the two terms has been established, the sign of the qualifying constraints as given by Eqns. (24) is known so that the x variables can be set at their appropriate bounds for the current *and* previous iterations as follows:

For each $\{i, j, k\} \in C \times C \times P_L$ perform the following steps:

1. Current Iteration K:

$$\text{If} \quad \mathcal{G}_{ji}\left[\tau_{ji} + \bar{\lambda}^K_{\Psi_i^k}\right] \cdot s_{jk}^{B_l^K} \geq 0 \quad \text{then} \quad \left(\hat{x}_{ij}^k\right)^K = \mathcal{L}_{\Psi_i^k}$$
$$\text{If} \quad \mathcal{G}_{ji}\left[\tau_{ji} + \bar{\lambda}^K_{\Psi_i^k}\right] \cdot s_{jk}^{B_l^K} < 0 \quad \text{then} \quad \left(\hat{x}_{ij}^k\right)^K = \mathcal{U}_{\Psi_i^k}$$

2. Previous Iterations $K_P \in PL(K_P)$:

$$\text{If} \quad \mathcal{G}_{ji}\left[\tau_{ji} + \bar{\lambda}^{K_P}_{\Psi_i^k}\right] \cdot \left[\left(\bar{n}_i^k\right)^{K_P} - \left(\bar{n}_i^k\right)^{K}\right] \geq 0 \quad \text{then} \quad \left(\hat{x}_{ij}^k\right)^{K_P} = \mathcal{L}_{\Psi_i^k}$$
$$\text{If} \quad \mathcal{G}_{ji}\left[\tau_{ji} + \bar{\lambda}^{K_P}_{\Psi_i^k}\right] \cdot \left[\left(\bar{n}_i^k\right)^{K_P} - \left(\bar{n}_i^k\right)^{K}\right] < 0 \quad \text{then} \quad \left(\hat{x}_{ij}^k\right)^{K_P} = \mathcal{U}_{\Psi_i^k}$$

For any given relaxed dual subproblem, these sets of bounds are denoted by $\hat{x}^{B_l^K}$ for the current iteration, and $\hat{x}^{B_l^{K_P}}$ for previous iterations.

3.5 Global Optimization Algorithm for the NRTL model

In what follows, k_S represents any node of the solution tree, with k_C and k_t corresponding to temporary nodes used in the selection of the set of previous Lagrange functions. I_{k_S} is the iteration number, K, at which node k_S is generated, with K_C denoting the current iteration number, and K_P representing some previous iteration. $\mathcal{S}_C$ represents the current node under consideration at any given iteration and is obviously a leaf node. The parent of any of these nodes is simply indicated by $p(k)$. The complete algorithm for the NRTL equilibrium model is now given.

STEP 0: Initialization

Select an initial mol vector $\bar{\mathbf{n}}^0$ and convergence tolerance ε.

Initialize $R_C\{\mathcal{L}^{\boldsymbol{R}},\mathcal{U}^{\boldsymbol{R}}\}$, $P^U = +\infty$, $M^L = -\infty$, $\mathcal{S}_C = R$, $k_S = \emptyset$, $I_{k_S} = \emptyset$.

STEP 1: Primal Problem

Evaluate (P) to give $P(\bar{\mathbf{n}}^K)$. Store $\bar{\lambda}^K$, $\bar{\mathbf{n}}^K$.

Solve (NCF) to give $\hat{G}^*$ and update $P^U = \min\left[P^U\ ,\ P(\bar{\mathbf{n}}^K)\ ,\ \hat{G}^*\right]$.

STEP 2: Select previous Lagrangians

Set $PL(K_P) = \emptyset$, $k_t = S_C$.

(1) Set $K_P = I_{k_t}$. Extract $\bar{\lambda}^{K_P}$, $\bar{\mathbf{n}}^{K_P}$. Set $PL(K_P) = PL(K_P) \cup K_P$ and $k_C = k_t$.

(2) Set $k_t = p(k_C)$. If $k_t = R$, proceed to STEP 3; otherwise, return to (1).

STEP 3: The Relaxed Dual Phase

(1) Choose a combination of box bounds, B_l from the set CB.

Evaluate $B_C\{\mathcal{L}^{\boldsymbol{B}},\mathcal{U}^{\boldsymbol{B}}\}$ and $\{\mathcal{L}_{\Psi_i^k},\mathcal{U}_{\Psi_i^k}\}$.

Set $\hat{x}^{B_l^K}$ and $\hat{x}^{B_l^{K_P}}$ and solve (RD) to give μ_B^* and n^*.

$$\left.\begin{array}{rcl} & \min\limits_{\substack{y\in Y\\ \mu_B}} & \mu_B \\ s.t.\ \mu_{\boldsymbol{B}} & \geq & L_K(\hat{x}^{B_l^K},\bar{\mathbf{n}}^K,y,\bar{\lambda}^K) \\ \mu_{\boldsymbol{B}} & \geq & L_{K_P}(\hat{x}^{B_l^{K_P}},\bar{\mathbf{n}}^{K_P},y,\bar{\lambda}^{K_P}) \quad \forall \quad K_P \in PL(K_P) \\ \mathcal{L}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} & \leq & n_{\boldsymbol{i}}^{\boldsymbol{k}} \ \leq \ \mathcal{U}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} \qquad \forall \ i \in C \ , \ k \in P_L \\ \mathbf{0} & = & \mathbf{A}\cdot\mathbf{n} \ - \ \mathbf{b} \end{array}\right\} \quad \text{(RD)}$$

where $L_K(\hat{x}^{B_l^K},\bar{\mathbf{n}}^K,y,\bar{\lambda}^K)$ is given by Eqn. (23).

(i) If $\mu_B^* \geq P^{\boldsymbol{U}} - \epsilon$, then fathom solution.

(ii) If $\mu_B^* < P^{\boldsymbol{U}} - \epsilon$, then set $k_{\boldsymbol{S}} = k_{\boldsymbol{S}} + 1$, $p\,(k_{\boldsymbol{S}}) = \mathcal{S}_C$, $I_{\boldsymbol{k}_S} = K$, $\mu^{\boldsymbol{k}_S} = \mu_B^*$, $n^{\boldsymbol{k}_S} = n^*$, $R_{\boldsymbol{k}_S}\{\mathcal{L}^R,\mathcal{U}^R\} = B\{\mathcal{L}^B,\mathcal{U}^B\}$.

(2) Choose another set of box bounds B_l from CB and return to (1).

If there are no remaining unchosen B_l in CB, then proceed to STEP 4.

STEP 4: Select mol vector for next iteration

Select infimum of all $\mu_B^{\boldsymbol{k}_S}$, and set $S_C = k_{\boldsymbol{S}}$, the associated node.
Set $\bar{\mathbf{n}}^{K+1} = \mathbf{n}^{\boldsymbol{k}_S}$, $M^L = \mu_B^{\boldsymbol{S}_C}$ and $R_{K+1}\{\mathcal{L}^{\boldsymbol{R}},\mathcal{U}^{\boldsymbol{R}}\} = R_{\boldsymbol{k}_S}\{\mathcal{L}^{\boldsymbol{R}},\mathcal{U}^{\boldsymbol{R}}\}$

STEP 5: Check for convergence

Check if $\left|\frac{P^U - M^L}{P^U}\right| \leq \epsilon$. If true, then STOP; otherwise set $K = K+1$, and return to Step 1.

It has been shown how all the conditions required to guarantee ϵ-global convergence of the GOP algorithm (Floudas and Visweswaran [8, 9]) are satisfied.

The main computational effort lies in solving the relaxed dual subproblems. There is a very simple way to reduce the number of connected variables. The material balance constraints appear affinely in the relaxed dual formulation. The material balance matrix represented by $\mathbf{A}$ has rank r so that r mol number variables can be written in terms of the others. In other words r connected variables are eliminated. Thus, the number of connected variables is now given as:

$$N_{CV} = \quad |C| \cdot |P| - \ r \tag{28}$$

For the phase equilibrium problem $r = |C|$. The derivation of the relaxed dual is exactly the same except that now the material balance constraints are not required to maintain feasibility.

Another computational aid is the fact that at a given stage of the algorithm, if the current point matches a previous point for some (or all) $i \in C$, $k \in P_L$, then there is no need for a partitioning hyperplane in that dimension. This reduces the number of relaxed dual subproblems to be solved at that iteration. A significant number of relaxed dual subproblems are typically eliminated in this way. Note that (NCF) can also be solved locally at each iteration (as well as evaluating the primal) to give a valid upper bound on the global solution.

3.6 Examples

Two examples are presented which demonstrate the GOP algorithm as it applies to the NRTL equation. Both these problems have two postulated liquid phases, so that the the Gibbs free energy of formation terms can be eliminated. The function to be minimized is then given as $\hat{G}_I = [G - \sum_i \Delta G_i^{L,f} n_i^T] / RT$. where G is defined by Eqn. (1).

All the examples have a degenerate set of trivial solutions where the component mol fractions in each of the liquid phases are the same. If one of these points is used to initiate the search for a local solver, then it will be unable to move from the trivial solution, a major problem for local optimization algorithms. The results show that the GOP successfully obtains the global solution even when supplied with such a trivial solution initial point.

It is possible to incorporate a simple local search technique into the framework of the global optimization algorithm. At the beginning of every iteration, MINOS5.3 is used to solve (NCF) as a nonconvex nonlinear programming problem, using the current mol numbers $\{\bar{n}_i^k\}$ as a starting point. If the resulting solution supplies a Gibbs free energy level less than the current best upper bound, then P^U is updated to equal this new solution. This is done because typically a point close to the global solution is generated at a relatively early stage of the algorithm, but this solution is not refined until a later point in the solution procedure. The advantage of such a strategy is that immediate refinement of solutions (local or global) will occur with the attractive benefit of improved upper bounds at an earlier stage of the algorithm, and a greater fathoming rate. In summary, the local search is an efficient way in which to generate valid and improved upper bounds, independently of the global optimization algorithm.

3.6.1 Example 1: n-Butyl-acetate – Water

The application of the GOP to a simple two component, two phase example is now considered. This illustrative example is taken from the thesis of Lin [13] and features two components, n-butyl-acetate (1) and water (2), at a temperature of 298K and a pressure of 1 atm. There are two possible liquid phases and they are modeled using the NRTL equation. Both phases share the same standard state, so that $\hat{G}_I$ supplies the function to be minimized. The binary parameters were obtained from Heidemann and Mandhane [10]:

$$\tau_{12} = 3.00498 \quad , \quad \tau_{21} = 4.69071$$
$$\mathcal{G}_{12} = 0.30794 \quad , \quad \mathcal{G}_{21} = 0.15904$$

The initial mixture charge is equimolar ($n_i^T = 0.5 \; \forall \; i$) and no reaction occurs in the system. It appears to be a simple example but there are multiple stationary points and local solutions. In fact, there is a local minimum *and* a local maximum, in addition to the global solution. There is also a line of trivial solutions that represents physical one phase behavior, but mathematically yields two phase solutions, that is, the mol fractions are the same in each distinct phase. These solutions are given in Table 1 where the superscript I represents the first liquid phase. The mol numbers for the second liquid phase are obtained as $n_i^{II} = n_i^T - n_i^I \; \forall \; i$. The Gibbs free energy surface as a function of the mol numbers in liquid phase I is pictured in Figure 2, with the trivial solutions lying along the line defined by $n_1^I - n_2^I = 0$. Lin [13] employed a successive continuation method to solve the problem and trace all possible solution branches. In this manner, all the local and global extrema were obtained. A local solver will have difficulty obtaining the global solution unless the starting point lies close to it, and the trivial solution or one of the local optima may be found. To illustrate this point, when (NCF) was solved using MINOS5.3 from 100 randomly selected starting points, the global solution was found in only 13 cases. The strong local minimum solution was found in 5 cases, and the trivial solution was obtained in the remaining 82 cases. The explicit mathematical formulation is given as:

$$\begin{aligned}
\min \; \hat{G}_I \;&=\; n_1^1 \ln n_1^1 + n_2^1 \ln n_2^1 - [n_1^1 + n_2^1] \ln [n_1^1 + n_2^1] \\
&+\; n_1^2 \ln n_1^2 + n_2^2 \ln n_2^2 - [n_1^2 + n_2^2] \ln [n_1^2 + n_2^2] \\
&+\; \mathcal{G}_{12}\tau_{12} n_1^1 \Psi_2^1 + \mathcal{G}_{21}\tau_{21} n_2^1 \Psi_1^1 + \mathcal{G}_{12}\tau_{12} n_1^2 \Psi_2^2 + \mathcal{G}_{21}\tau_{21} n_2^2 \Psi_1^2 \\
s.t. \quad & \Psi_1^1 \{ n_1^1 + \mathcal{G}_{21} n_2^1 \} = n_1^1 \\
& \Psi_2^1 \{ \mathcal{G}_{12} n_1^1 + n_2^1 \} = n_2^1 \\
& \Psi_1^2 \{ n_1^2 + \mathcal{G}_{21} n_2^2 \} = n_1^2 \\
& \Psi_2^2 \{ \mathcal{G}_{12} n_1^2 + n_2^2 \} = n_2^2
\end{aligned}$$

$$n_1^1 + n_1^2 = 0.5$$
$$n_2^1 + n_2^2 = 0.5$$
$$0 \leq n_1^1, n_2^1, n_1^2, n_2^2 \leq 0.5$$

By using the mass balance equality constraints to eliminate the variables of the second liquid phase, the number of connected variables can be reduced to $N_{CV} = 2$. Thus, a maximum of four relaxed dual problems must be solved at each iteration. Any variables associated with the eliminated phase are designated with a superscript E. The x-variable set for the eliminated phase is then defined as:

$$\hat{\Psi}_{ij}^E = \frac{n_i^T - n_i}{\sum\limits_{l \in C} (n_l^T - n_l)} \quad \forall \;\; i \, , \, j \, \in \, C$$

where $\{n_i\}$ are the variables of the non-eliminated phase and the formulation, noting that the superscript I has been dropped. The explicit Lagrangian was derived as Eqn. (23) and yields the following expression:

$$\begin{aligned}
L(n_i, \bar{n}_i, \hat{\Psi}_{ij}, \hat{\Psi}_{ij}^E, \bar{\lambda}_i, \bar{\lambda}_i^E) \;\; = \;\; & \{ n_1 \ln n_1 + n_2 \ln n_2 - (n_1 + n_2) \ln (n_1 + n_2) \\
+ \;\; & (n_1^T - n_1) \ln (n_1^T - n_1) + (n_2^T - n_2) \ln (n_2^T - n_2) \\
- \;\; & (n_1^T - n_1 + n_2^T - n_2) \ln (n_1^T - n_1 + n_2^T - n_2) \\
- \;\; & n_1 \bar{\lambda}_1 - n_2 \bar{\lambda}_2 - (n_1^T - n_1) \bar{\lambda}_1^E - (n_2^T - n_2) \bar{\lambda}_2^E \} \\
+ \;\; & \hat{\Psi}_{11} \bar{\lambda}_1 [n_1 - \bar{n}_1] + \hat{\Psi}_{12} \mathcal{G}_{21} \left[\tau_{21} + \bar{\lambda}_1 \right] [n_2 - \bar{n}_2] \\
+ \;\; & \hat{\Psi}_{21} \mathcal{G}_{12} \left[\tau_{12} + \bar{\lambda}_2 \right] [n_1 - \bar{n}_1] + \hat{\Psi}_{22} \bar{\lambda}_2 [n_2 - \bar{n}_2] \\
- \;\; & \hat{\Psi}_{11}^E \bar{\lambda}_1^E [n_1 - \bar{n}_1] - \hat{\Psi}_{12}^E \mathcal{G}_{21} \left[\tau_{21} + \bar{\lambda}_1^E \right] [n_2 - \bar{n}_2] \\
- \;\; & \hat{\Psi}_{21}^E \mathcal{G}_{12} \left[\tau_{12} + \bar{\lambda}_2^E \right] [n_1 - \bar{n}_1] - \hat{\Psi}_{22}^E \bar{\lambda}_2^E [n_2 - \bar{n}_2]
\end{aligned}$$

Notice that the term within curly braces is convex and that the interaction between the x and the y variable sets is purely bilinear. The derivatives of the Lagrangian with respect to the x variables yield linear functionalities in the y variables allowing the y space to be partitioned in a simple manner. The Lagrangian generated in Region 1 of Iteration 1 is shown in Figure 3, where $0.25 \leq n_i \leq 0.5 \; \forall \; i$.

A local solver will *not* converge to the global solution from the initial point considered above. The progress of the upper and lower bounds is charted in Table 2. The total cpu time required was 1.23 sec. It should be noted that for 33% of the total iterations, only 2 relaxed dual problems were solved, demonstrating the fact that the maximum number of problems need not be solved at every iteration of the algorithm. In addition, 66% of the solutions obtained from the relaxed dual problems were fathomed.

3.6.2 Example 2: n-Propanol – n-Butanol – Water

This system was one of two studied by Block and Hegner [4] in their modeling of three phase distillation towers. n-Butanol and water form the only partially miscible binary pair (i.e. it is a Type I system) with a relatively small domain of immiscibility. The binary parameters as obtained by them for use in the NRTL equation are supplied in Table 3. $\hat{G}_I$ supplies the objective function to be minimized, and $N_{CV} = 3$. Block and Hegner [4] conducted the liquid phase splitting computations independently of the vapor phase i.e. the parameters have no dependence on temperature. It is therefore meaningless to consider a vapor phase for this example. Walraven and Rompay [23] subsequently used this problem in order to test their phase splitting algorithm for a number of different feed charges. The explicit formulation is given below:

$$
\begin{aligned}
\min \hat{G}_I \;=\;& n_1^1 \ln n_1^1 + n_2^1 \ln n_2^1 + n_3^1 \ln n_3^1 - [n_1^1 + n_2^1 + n_3^1] \ln [n_1^1 + n_2^1 + n_3^1] \\
+\;& n_1^2 \ln n_1^2 + n_2^2 \ln n_2^2 + n_3^2 \ln n_3^2 - [n_1^2 + n_2^2 + n_3^2] \ln [n_1^2 + n_2^2 + n_3^2] \\
+\;& n_1^1 \left[\mathcal{G}_{12}\tau_{12}\Psi_2^1 + \mathcal{G}_{13}\tau_{13}\Psi_3^1\right] + n_2^1 \left[\mathcal{G}_{21}\tau_{21}\Psi_1^1 + \mathcal{G}_{23}\tau_{23}\Psi_3^1\right] + n_3^1 \left[\mathcal{G}_{31}\tau_{31}\Psi_1^1 + \mathcal{G}_{32}\tau_{32}\Psi_2^1\right] \\
+\;& n_1^2 \left[\mathcal{G}_{12}\tau_{12}\Psi_2^2 + \mathcal{G}_{13}\tau_{13}\Psi_3^2\right] + n_2^2 \left[\mathcal{G}_{21}\tau_{21}\Psi_1^2 + \mathcal{G}_{23}\tau_{23}\Psi_3^2\right] + n_3^2 \left[\mathcal{G}_{31}\tau_{31}\Psi_1^2 + \mathcal{G}_{32}\tau_{32}\Psi_2^2\right]
\end{aligned}
$$

$s.t.$

$$
\begin{aligned}
&\Psi_1^1\{n_1^1 + \mathcal{G}_{21}n_2^1 + \mathcal{G}_{31}n_3^1\} = n_1^1 \qquad && \Psi_1^2\{n_1^2 + \mathcal{G}_{21}n_2^2 + \mathcal{G}_{31}n_3^2\} = n_1^2 \\
&\Psi_2^1\{\mathcal{G}_{12}n_1^1 + n_2^1 + \mathcal{G}_{32}n_3^1\} = n_2^1 && \Psi_2^2\{\mathcal{G}_{12}n_1^2 + n_2^2 + \mathcal{G}_{32}n_3^2\} = n_2^2 \\
&\Psi_3^1\{\mathcal{G}_{13}n_1^1 + \mathcal{G}_{23}n_2^1 + n_3^1\} = n_3^1 && \Psi_3^2\{\mathcal{G}_{13}n_1^2 + \mathcal{G}_{23}n_2^2 + n_3^2\} = n_3^2
\end{aligned}
$$

$$
\begin{aligned}
&n_1^1 + n_1^2 = n_1^T \qquad && 0 \le n_1^1, n_1^2 \le n_1^T \\
&n_2^1 + n_2^2 = n_2^T && 0 \le n_2^1, n_2^2 \le n_2^T \\
&n_3^1 + n_3^2 = n_3^T && 0 \le n_3^1, n_3^2 \le n_3^T
\end{aligned}
$$

Two source feeds from the work of Walraven and Rompay [23] were examined, and these charges are given in Table 4. The first of these lies well within the immiscibility region – $\{n_i^T\} = \{0.04, 0.16, 0.80\}$ – and therefore causes little problem for a local solver. However, the second considered source charge of $\{n_i^T\} = \{0.148, 0.052, 0.800\}$ lies close to the plait point, an area in which it is notoriously difficult to obtain the correct equilibrium solution. The trivial solution objective function value is -1.1919705, while the two phase global solution has an objective function value of -1.1919716, a difference of only $11 \cdot 10^{-7}$! Solving (NCF) using a local solver succeeded in obtaining the global solution from only 8 out of 100 random starting points. Nonetheless, the GOP algorithm generated the global solution for this very difficult problem when supplied with a trivial solution starting point. This clearly demonstrates the effectiveness of the algorithm in generating global solutions for extremely challenging problems. The equilibrium solutions for the two sets of conditions considered here are given in Table 4. The difficulty of the problem when the source charge is close to the plait point is evident in the increased computational effort required to obtain the equilibrium solution for this case.

4 Analysis for the UNIQUAC Equation

A commonly used activity coefficient correlation is the UNIQUAC equation originally proposed by Abrams and Prausnitz [1], where the excess Gibbs energy is postulated to be composed of two contributions: a combinatorial part due to the differences in the sizes and shapes of the molecules, and a residual portion due to the interactions that take place between them. Thus, differences in molecular size are taken directly into account. To obtain improved agreement for systems containing water and alcohols, a modified version of the universal quasi-chemical equation for the correlation of liquid-phase activity coefficients was proposed by Anderson and Prausnitz [2, 3] and is given as:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad \forall \ i \in C \tag{29}$$

$$\text{where} \quad \ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j \in C} l_j x_j \tag{30}$$

$$\text{and} \quad \ln \gamma_i^R = q_i' \left\{ 1 - \ln \left(\sum_{j \in C} \tau_{ji} \theta_j' \right) - \sum_{j \in C} \frac{\tau_{ij} \theta_j'}{\sum_{l \in C} \theta_l' \tau_{lj}} \right\} \tag{31}$$

where γ_i^C and γ_i^R are the combinatorial and residual contributions respectively to the activity coefficient at mol fraction x_i, τ_{ij} are non-symmetric binary interaction parameters, q_i, q_i' and r_i are pure component structural parameters, and z is a lattice coordination number. l_i, θ_i, θ_i' and ϕ_i are defined by the following relationships:

$$l_i = \frac{z}{2} \cdot (r_i - q_i) - (r_i - 1) \qquad \forall \ i \in C \tag{32}$$

$$\theta_i = \frac{q_i x_i}{\sum_{j \in C} q_j x_j} \qquad \forall \ i \in C \tag{33}$$

$$\theta_i' = \frac{q_i' x_i}{\sum_{j \in C} q_j' x_j} \qquad \forall \ i \in C \tag{34}$$

$$\phi_i = \frac{r_i x_i}{\sum_{j \in C} r_j x_j} \qquad \forall \ i \in C \tag{35}$$

where θ_i and θ_i' are the average area fractions for the combinatorial and residual portions of the activity coefficient expression, and ϕ_i is the average segment fraction. Note that these ratios can be equivalently defined for mol numbers as for mol fractions for any given phase. In the original formulation of Abrams and Prausnitz [1] $q'_i = q_i$.

Eqn. (2) yields the relationship between the fugacities and the activity coefficients. If the following series of steps are undertaken:

(i) the first logarithmic term in x_i of Eqn. (30) is brought over to the left hand side,

(ii) the non-logarithmic term involving ϕ_i of Eqn. (30) is expanded out,

(iii) the terms involving θ'_i in Eqn. (31) are expanded out,

then the following expression is obtained:

$$\begin{aligned} \ln \gamma_i x_i \quad = \quad & \left(1 - \frac{z}{2} q_i\right) \ln \phi_i + \frac{z}{2} q_i \ln \theta_i + l_i - r_i \cdot \frac{\sum_{j \in C} l_j n_j}{\sum_{j \in C} r_j n_j} \\ & - q'_i \ln \left(\frac{\sum_{j \in C} q'_j \tau_{ji} n_j}{\sum_{j \in C} q'_j n_j} \right) + q'_i - q'_i \sum_{j \in C} \frac{q'_j \tau_{ij} n_j}{\sum_{l \in C} q'_l \tau_{lj} n_l} \end{aligned} \tag{36}$$

By substituting Eqn. (36) into the original objective function of Eqn. (1), it is possible to write the objective function for the case of multiple liquid phases in terms of the mol numbers in the following form:

$$\begin{aligned} \min\ \hat{G}(\boldsymbol{n}) \quad = \quad & \sum_{i \in C} \sum_{k \in P} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} + \left(1 - \frac{z}{2} q_i\right) \ln \phi_i^k + \frac{z}{2} q_i \ln \theta_i^k + l_i - r_i \cdot \frac{\sum_{j \in C} l_j n_j^k}{\sum_{j \in C} r_j n_j^k} \right. \\ & \left. - q'_i \ln \left(\frac{\sum_{j \in C} q'_j \tau_{ji} n_j^k}{\sum_{j \in C} q'_j n_j^k} \right) + q'_i - q'_i \sum_{j \in C} \frac{q'_j \tau_{ij} n_j^k}{\sum_{l \in C} q'_l \tau_{lj} n_l^k} \right\} \end{aligned} \tag{37}$$

where θ_i^k and ϕ_i^k are now defined for all phases k. This is a complex expression involving logarithmic and quadratic quotients, and is clearly nonconvex. However, by exploiting a number of properties associated with Eqn. (37), it is possible to obtain a more tractable form for the Gibbs energy. Several interesting new properties of the terms in Eqn. (37) are revealed.

4.1 Analysis of the Gibbs free energy function:

In the foregoing analysis, different ways to express the Gibbs free energy function defined by Eqn. (37) are presented. The final formulation will cast the minimization problem as the difference of two convex functions (a D.C. programming problem), where the convex part is nonseparable, but the concave portion of the objective function is manipulated in such a way as to make it separable. In the development that follows, the indices i, j, l and m are defined over the set of components C.

4.1.1 Simplification of the Gibbs free energy:

Two simplifying properties are now presented.

Property 4.1 *The following relation is true* $\forall\ k\ \in P_L$*:*

$$\sum_{i\in C} n_i^k \left\{ l_i - r_i \cdot \frac{\sum\limits_{j\in C} l_j n_j^k}{\sum\limits_{j\in C} r_j n_j^k} \right\} = 0$$

Proof: For each $k\ \in\ P_L$:

$$\begin{aligned}\sum_{i\in C} n_i^k \left\{ l_i - r_i \cdot \frac{\sum\limits_{j\in C} l_j n_j^k}{\sum\limits_{j\in C} r_j n_j^k} \right\} &= \sum_{i\in C} l_i n_i^k - \left\{ \sum_{i\in C} r_i n_i^k \right\} \cdot \left\{ \frac{\sum\limits_{j\in C} l_j n_j^k}{\sum\limits_{j\in C} r_j n_j^k} \right\} \\ &= \sum_{i\in C} l_i n_i^k - \sum_{j\in C} l_j n_j^k = 0\end{aligned}$$

This implies that the parameter l_i need not appear in the Gibbs free energy expression. □

Property 4.2 *The following relation is true* $\forall\ k\ \in P_L$*:*

$$\sum_{i\in C} n_i^k \left\{ q_i' - q_i' \cdot \sum_{j\in C} \frac{q_j' \tau_{ij} n_j^k}{\sum_{l\in C} q_l' \tau_{lj} n_l^k} \right\} \quad = \quad 0$$

Proof: For each $k\ \in\ P_L$:

$$\begin{aligned}\sum_{i\in C} n_i^k \left\{ q_i' - q_i' \cdot \sum_{j\in C} \frac{q_j' \tau_{ij} n_j^k}{\sum\limits_{l\in C} q_l' \tau_{lj} n_l^k} \right\} &= \sum_{i\in C} q_i' n_i^k - \sum_{j\in C} q_j' n_j^k \cdot \left\{ \frac{\sum\limits_{m\in C} q_m' \tau_{mj} n_m^k}{\sum\limits_{l\in C} q_l' \tau_{lj} n_l^k} \right\} \\ &= \sum_{i\in C} q_i' n_i^k - \sum_{i\in C} q_i' n_i^k = 0\end{aligned}$$

where the term in braces is seen to equal unity. □

Employing Properties 4.1 and 4.2 in Eqn. (37), the objective function can now be written as follows:

$$\begin{aligned}\min\ \hat{G}(\boldsymbol{n}) \ &= \ \sum_{i\in C}\sum_{k\in P} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} + \left(1 - \frac{z}{2}q_i\right)\ln\phi_i^k + \frac{z}{2}q_i \ln\theta_i^k \right. \\ &\qquad \left. + q_i'\ln\sum_{j\in C} q_j' n_j^k - q_i'\ln\sum_{j\in C} q_j'\tau_{ji} n_j^k \right\}\end{aligned} \tag{38}$$

Some new notation will now be introduced in order to demonstrate the special structure that Eqn. (38) naturally possesses. The following new parameter, z_i^R, is introduced to aid in this process and is defined as:

$$z_i^R \ = \ \frac{\left(\frac{z}{2}q_i - 1\right)}{r_i} \quad \geq \quad 0 \quad \forall \ i \ \in \ C \tag{39}$$

z is usually taken as 10, with $q_i \geq 0.2$, and therefore z_i^R is always positive. Using Eqn. (39) and expanding out ϕ_i^k in terms of the mol numbers, one obtains:

$$\sum_{i\in C} n_i^k \left(1 - \frac{z}{2}q_i\right)\ln\phi_i^k \ = \ -\sum_{i\in C} z_i^R r_i n_i^k \ln\frac{r_i n_i^k}{\sum_{j\in C} r_j n_j^k} \quad \forall\, k \ \in \ P_L$$

It is now convenient to make the following definitions:

$$\mathcal{A}^k \ = \ \sum_{i\in C} z_i^R r_i n_i^k \ln\frac{r_i n_i^k}{\sum_{j\in C} r_j n_j^k} \qquad \forall \ k \ \in \ P_L \tag{40}$$

$$\mathcal{B}^k \ = \ \frac{z}{2}\sum_{i\in C} q_i n_i^k \ln\frac{q_i n_i^k}{\sum_{j\in C} q_j n_j^k} \qquad \forall \ k \ \in \ P_L \tag{41}$$

$$\mathcal{C}^k \ = \ \left[\sum_{i\in C} q_i' n_i^k\right]\ln\left[\sum_{i\in C} q_i' n_i^k\right] \quad \forall \ k \ \in \ P_L \tag{42}$$

$$\mathcal{D}^k \ = \ -\sum_{i\in C} q_i' n_i^k \ln\sum_{j\in C} q_j'\tau_{ji} n_j^k \qquad \forall \ k \ \in \ P_L \tag{43}$$

Note that θ_i^k has been expanded out in terms of the mol numbers $\forall\, k \ \in \ P_L$ in the definition of $\mathcal{B}^k$. These definitions allow the objective function of Eqn. (38) to be equivalently written as follows:

$$\min\ \hat{G}(\boldsymbol{n}) = \sum_{i\in C}\sum_{k\in P_L} n_i^k \frac{\Delta G_i^{k,f}}{RT} + \sum_{k\in P_L} \left\{ -\mathcal{A}^k + \mathcal{B}^k + \mathcal{C}^k + \mathcal{D}^k \right\} \tag{44}$$

This objective function still yields a nonconvex optimization formulation but it is simpler than the objective function customarily employed.

4.1.2 D.C. Transformation

It will now be shown how the objective function of Eqn. (44) is converted into D.C. form. Firstly, the following property is required.

Property 4.3 *Let ρ_i be a positive parameter defined $\forall\, i$. Define the real-valued function $f(\mathbf{n})$ with $\mathbf{n} > 0$ as follows:*

$$f(\mathbf{n}) = \left\{\sum_i \rho_i n_i\right\} \ln \left\{\sum_i \rho_i n_i\right\}$$

then $f(\mathbf{n})$ is convex.

Proof: See Appendix C. □

Remark: A number of observations can be made on the basis of Properties 3.2 and 4.3 in relation to the terms of Eqn. (44), and are listed as follows:

(i) the term $\mathcal{A}^k$ as defined by Eqn. (40) is convex $\forall\, k \in P_L$ (apply Property 3.2). This also implies that $-\mathcal{A}^k$ is concave,

(ii) the term $\mathcal{B}^k$ as defined by Eqn. (41) is convex $\forall\, k \in P_L$ (apply Property 3.2),

(iii) The term $\mathcal{C}^k$ as defined by Eqn. (42) is convex $\forall\, k \in P_L$ (apply Property 4.3).

Property 4.4 *Define $\mathcal{D}_+^k$ and $\mathcal{D}_-^k$ $\forall\, k \in P_L$ as follows:*

$$\begin{aligned} \mathcal{D}_+^k &= \sum_i q_i' n_i^k \ln \frac{n_i^k}{\sum_j q_j' \tau_{ji} n_j^k} \\ \mathcal{D}_-^k &= \sum_i q_i' n_i^k \ln n_i^k \end{aligned}$$

then $\mathcal{D}_+^k$ and $\mathcal{D}_-^k$ are convex $\forall\, k \in P_L$. Further, $\mathcal{D}^k$ as defined by Eqn. (43) can be equivalently expressed as the difference of these two convex functions:

$$\mathcal{D}^k = \mathcal{D}_+^k - \mathcal{D}_-^k \qquad \forall\, k \in P_L \tag{45}$$

Proof: See Appendix D. □

Thus, it has been demonstrated how the majority of terms in Eqn. (44) are by themselves convex or concave. In one instance, it was necessary to transform a nonconvex term ($\mathcal{D}^k$)

into the summation of a convex and a concave term. It is now possible to write the objective function as follows:

$$\min\ \hat{G}(\boldsymbol{n}) \;=\; \left\{\sum_{i\in C}\sum_{k\in P} n_i^k \,\frac{\Delta G_i^{k,f}}{RT} + \sum_{k\in P}\left\{\mathcal{B}^k + \mathcal{C}^k + \mathcal{D}_+^k\right\}\right\} - \left\{\sum_{k\in P}\left\{\mathcal{A}^k + \mathcal{D}_-^k\right\}\right\} \tag{46}$$

The key feature to notice is that each term within braces is convex. The concave term $-\mathcal{D}_-^k$ is separable. However the concave term $-\mathcal{A}^k$ is nonseparable. Because it is easier to construct the convex envelope of a *separable* concave function than a nonseparable one, the following definitions are required so that the term $-\mathcal{A}^k$ can be written in a radically different form:

$$\left.\begin{aligned} z_M^R &= \min_i \{z_i^R\} \\ z^A &= z_M^R + \sum_{i\in C}\left[z_i^R - z_M^R\right] \\ z_i^B &= \sum_{j\neq i}\left[z_j^R - z_M^R\right] \qquad \forall\ i\in C \end{aligned}\right\} \tag{47}$$

On the basis of these definitions, the following property is derived:

Property 4.5 *If $\mathcal{A}_+^k$ and $\mathcal{A}_-^k$ are defined $\forall\ k\in P_L$ as follows:*

$$\begin{aligned} \mathcal{A}_+^k &= z^A\cdot\sum_{i\in C} r_i n_i^k \ln\sum_{i\in C} r_i n_i^k + \sum_{i\in C} z_i^B r_i n_i^k \ln\frac{n_i^k}{\sum_{j\in C} r_j n_j^k} - \sum_{i\in C} n_i^k\cdot z_i^R r_i \ln r_i \\ \mathcal{A}_-^k &= \sum_{i\in C} r_i\left[z_i^R + z_i^B\right]\cdot n_i^k \ln n_i^k \end{aligned}$$

then $\mathcal{A}_+^k$ and $\mathcal{A}_-^k$ are convex functions. Further, $-\mathcal{A}^k$ can be expressed as the difference of these two convex functions:

$$-\mathcal{A}^k = \mathcal{A}_+^k - \mathcal{A}_-^k \tag{48}$$

Proof: See Appendix E. □

Property 4.5 allows the nonseparable, concave term $-\mathcal{A}^k$ to be replaced by the difference of two convex functions, defined in Eqn. (48). The key change is that the concave part of the new expression is now separable as shown below:

$$\min\ \hat{G}(\boldsymbol{n}) \;=\; \left\{\sum_{i\in C}\sum_{k\in P} n_i^k \,\frac{\Delta G_i^{k,f}}{RT} + \sum_{k\in P}\left\{\mathcal{A}_+^k + \mathcal{B}^k + \mathcal{C}^k + \mathcal{D}_+^k\right\}\right\} - \left\{\sum_{k\in P}\left\{\mathcal{A}_-^k + \mathcal{D}_-^k\right\}\right\} \tag{49}$$

The terms $\mathcal{A}^k$, $\mathcal{A}^k_+$, $\mathcal{A}^k_-$, $\mathcal{B}^k$, $\mathcal{C}^k$, $\mathcal{D}^k_+$ and $\mathcal{D}^k_-$ have been shown to be convex. Thus, the terms contained within the braces of Eqn. (49) are convex, i.e. $\hat{G}(\boldsymbol{n})$ is now given by the difference of two convex functions. At this point, it is convenient to collect the convex portions of the objective function together, defined as $\mathcal{C}^k_U \ \forall\ k \in P_L$, to yield:

$$\begin{aligned}
\mathcal{C}^k_U \;&=\; \sum_{i\in C} n_i^k \left\{ \frac{\Delta G_i^{k,f}}{RT} - z_i^R r_i \ln r_i \right\} \\
&+\; z^A \cdot \left\{ \sum_{i\in C} r_i n_i^k \right\} \ln \left\{ \sum_{i\in C} r_i n_i^k \right\} + \sum_{i\in C} z_i^B r_i n_i^k \ln \frac{n_i^k}{\sum_{j\in C} r_j n_j^k} \\
&+\; \frac{z}{2} \sum_{i\in C} q_i n_i^k \ln \frac{q_i n_i^k}{\sum_{j\in C} q_j n_j^k} + \left\{ \sum_{i\in C} q_i' n_i^k \right\} \ln \left\{ \sum_{i\in C} q_i' n_i^k \right\} + \sum_{i\in C} q_i' n_i^k \ln \frac{n_i^k}{\sum_{j\in C} q_j' \tau_{ji} n_j^k}
\end{aligned} \tag{50}$$

Furthermore, if the parameter φ_i is defined as follows:

$$\varphi_i \;=\; q_i' + r_i \left[z_i^R + z_i^B \right] \quad \forall\ i \in C \tag{51}$$

then (DC) is defined as:

$$\left.\begin{aligned}
\min\ \hat{G}(\boldsymbol{n}) \;&=\; \sum_{k\in P_L} \mathcal{C}^k_U - \sum_{i\in C} \sum_{k\in P_L} \varphi_i\, n_i^k \ln n_i^k \\
s.t. \qquad \mathbf{0} \;&=\; \mathbf{A}\cdot\mathbf{n} - \mathbf{b} \\
\mathbf{0} \;&\le\; \mathbf{n} \;\le\; \mathbf{n}^T
\end{aligned}\right\} \text{(DC)}$$

where $\mathcal{C}^k_U$ is defined by Eqn. (50). The objective function consists of a convex, nonseparable portion, and a separable, concave portion, with a convex constraint set. The expression for $\hat{G}(\boldsymbol{n})$ in (DC) is very different from the original Gibbs energy function defined by Eqn. (37). The analysis of the original function has revealed interesting properties in terms of the algebra *and* in terms of its convexity properties. It has been shown that this equation can be expressed as the sum of convex and concave parts. The specially induced structure will be used to full advantage in solving (DC).

4.2 Branch and Bound Algorithm

It is worthwhile to point out the salient features of the formulation for the phase and chemical equilibrium problem, as given by (DC):

(i) the objective function is D.C. with a separable concave portion,

(ii) the feasible region is an n-rectangle,

(iii) the constraint set is closed and convex (a set of linear equality constraints).

One of the first algorithms proposed to solve problems of the above nature was that of Falk and Soland [6]. It is a branch and bound type algorithm, where a branching scheme successively refines the feasible region into smaller and smaller n-rectangles, in each of which a convex subproblem is solved that supplies a lower bound on the global solution of (DC). In this manner, a sequence of nondecreasing lower bounds is generated that converges under certain conditions to the global solution. The algorithm used to solve (DC) in this work is based on the original paper of Falk and Soland [6]. The approach of this algorithm and several others has been generalized and discussed in the book of Horst and Tuy [11]. The algorithm shares many similarities with that used for the NRTL equation, except for slight variations in the partitioning scheme, and significant differences in the structure of the subproblems used to provide lower bounds for the global solution. Thus, in what follows, the notation used will in as far as possible be the same as that of Section 3.

4.2.1 Convex envelope of the Gibbs free energy

In order to obtain valid lower bounds, the approach is to derive convex underestimators for the concave portion of the objective function in successive partitions of the feasible region. Suppose that at a given stage in the algorithm, the partition currently under consideration is an n-rectangle defined as follows:

$$\mathcal{L}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} \leq n_{\boldsymbol{i}}^{\boldsymbol{k}} \leq \mathcal{U}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} \qquad \forall \ i \in C \ , \ k \in P_L \tag{52}$$

The manner in which the partition defined by these box bounds is obtained is described in the next section. A lower bound is required for the objective function defined in (DC). The simplest such bound can be obtained by constructing the convex envelope of $\hat{G}(\boldsymbol{n})$. The concave portion of the objective function is replaced by its convex envelope, which for a separable concave function is simply the affine function that joins the two endpoints of the region under consideration. This is shown for the one variable case in Figure 4 where the concave function $-n \ln n$ and its convex envelope, $\Psi(n)$, are plotted between the lower and upper bounds $\mathcal{L}^{B}_{\boldsymbol{n}}$ and $\mathcal{U}^{B}_{\boldsymbol{n}}$. Thus, the convex envelope of each concave function, labeled $\Psi_{\boldsymbol{i}}^{\boldsymbol{k}}$, in the region whose bounds are given by Eqn. (52) is:

$$\Psi_{\boldsymbol{i}}^{\boldsymbol{k}} \ = \ -\mathcal{L}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} \ln \mathcal{L}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} + \left[\frac{\mathcal{L}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} \ln \mathcal{L}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} - \mathcal{U}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} \ln \mathcal{U}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k}}{\mathcal{U}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} - \mathcal{L}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k}} \right] \cdot \left[n_{\boldsymbol{i}}^{\boldsymbol{k}} - \mathcal{L}^{\boldsymbol{B}}_{\boldsymbol{n}_i^k} \right] \ \forall \ i \in C, k \in P_L \tag{53}$$

Thus, the convex envelope of the concave portion of the objective function is then the summation of these individual affine functions. The convex envelope of the convex portion of the objective function is obviously the function itself; this implies that the convex envelope of (DC) is a convex function and any local solution to the following problem will be a global one:

$$\left.\begin{aligned} \min\ \mu &= \sum_{k\in P} \mathcal{C}^k + \sum_{i\in C}\sum_{k\in P_L} \varphi_i\ \Psi_i^k \\ s.t. \qquad & \mathcal{L}^B_{n_i^k} \leq n_i^k \leq \mathcal{U}^B_{n_i^k} \\ \mathbf{0} &= \mathbf{A}\cdot\mathbf{n} - \mathbf{b} \end{aligned}\right\}\text{(UES)}$$

Formulation (UES) provides a lower bound on the global solution in the region defined by $B\{\mathcal{L}^B, \mathcal{U}^B\}$. Solving subproblems of type (UES) in successive refinements of the feasible region will generate a nondecreasing subsequence of lower bounds.

4.2.2 Partitioning Scheme

When the GOP was used to solve the phase and chemical equilibrium problem for the NRTL equation, the initial n-rectangle defined by Eqn. (7) was successively subdivided into more and more n-rectangles. For the case of the UNIQUAC equation, the branching scheme is similar but there is one major difference. For the UNIQUAC as few as 2 subproblems need be solved at each iteration to guarantee convergence to the ϵ-global solution, whereas for the NRTL, upto N_{CV} hyperplanes were used to partition the current partition into as many as $2^{N_{CV}}$ regions. For consistency, the number of variables that appear in the concave portion of the objective function is also labeled N_{CV}. Obviously, $N_{CV} = |C| \cdot |P_L|$.

The same basic tree structure that was used for the NRTL equation is also employed here. Each n-rectangle within which a subproblem of type (UES) is solved has a node, k_S, associated with it. An initial point is chosen labeled $\{\bar{n}_i^k\}$. This parent n-rectangle is then partitioned by a number of hyperplanes, labeled N_P, passing through the point $\{\bar{n}_i^k\}$. The number of these hyperplanes can vary as follows:

$$1 \leq N_P \leq N_{CV}$$

This means that 2^{N_P} box regions are created at each iteration. In each of these subrectangles Problem (UES) is solved to provide a lower bound; if this lower bound lies below the current best upper bound, then the solution is stored as μ^{k_S} and $\mathbf{n}^{k_S}$, so that each solution node k_S has these quantities, as well as its box bounds, associated with it. It is important to realize that N_P is a user specified parameter, and that it can vary from one iteration to the next. The trade-off is tighter lower bounds for higher values of N_P and less subproblems to be solved for lower N_P. If it is set at one, then only two subproblems are solved for that iteration.

The important question of how to decide the partitioning remains. One natural means is to measure the distance, labeled δ_i^k, between the concave function and its convex envelope at the value of the current point:

$$\delta_i^k = \left| -\bar{n}_i^k \ln \bar{n}_i^k - \Psi_i^k(\bar{n}_i^k) \right| \qquad \forall \ i \in C \ , \ k \in P_L$$

where $\bar{n}_i^k$ represents the solution value obtained as the solution of the current node, S_C. Intuitively, one expects that the larger this distance, the greater the need for further refinement. Horst and Tuy [11] prove (see Chapter VII.4) that if the current n-rectangle is divided into two (or more) n-rectangles about the variable with the largest value of δ_i^k, then the branch and bound algorithm to be defined in the next section will converge to an ϵ-global solution of (DC). In the version of the algorithm used here, more than two n-rectangles may be created at each iteration, if desired. Therefore, the distances δ_i^k are rank-ordered from highest to lowest. The set of parameters $\{\mathcal{H}_i^k\}$ determines if there is a partitioning hyperplane for the corresponding variable n_i^k. If $\mathcal{H}_i^k = 1$ then a hyperplane is used to divide the region for that particular variable as $n_i^k \leq \bar{n}_i^k$ and $n_i^k \geq \bar{n}_i^k$. This is shown in Figure 5 for the first iteration where $N_P = 1$. Suppose that the greatest distance between the concave function and its convex envelope occurs for the variable n_1, so that $\mathcal{H}_1 = 1$ and $\mathcal{H}_2 = 0$. This means that the initial feasible region is divided into two box regions, labeled B_1^1 and B_2^1, where the superscript corresponds to the iteration number, and two subproblems are solved. In the general case, N_P hyperplanes are used to divide the current region into 2^{N_P} n-rectangles for the largest N_P distances. For the remaining variables, no dividing hyperplane is used so that $\mathcal{H}_i^k = 0$ and the box bounds for these variables are simply their regional bounds, i.e. $\mathcal{L}_{n_i^k}^B = \mathcal{L}_{n_i^k}^R$ and $\mathcal{U}_{n_i^k}^B = \mathcal{U}_{n_i^k}^R$.

Having solved a set of subproblems of type (UES) at a given iteration, the manner in which the value of the y variables is chosen for the next iteration is exactly the same as the GOP algorithm for the NRTL. Having chosen the infimum of all lower bounds, the region associated with this particular node is divided into 2^{N_P} new n-rectangles to obtain successively tighter lower bounds. In the context of Figure 5, assume that the infimum of the lower bounds occurs in box region 1 of Iteration 1. At Iteration 2 with $N_P = 1$ again, suppose that the distance is now greatest for n_2, so that $\mathcal{H}_2 = 1$, but $\mathcal{H}_1 = 0$. This implies that at Iteration 2, the region is divided into two box regions, B_1^2 and B_2^2 (see Figure 5), wherein (UES) is solved to obtain two new lower bounds on the global solution. Thus, 2^{N_P} new nodes are generated in the solution tree at a given iteration. Experience has shown that convergence properties are not significantly altered by tinkering with N_P. It is worthwhile to set N_P higher in earlier iterations to get tighter bounds, and reduce it as the algorithm proceeds to avoid adding excessive numbers of nodes to the solution tree.

4.2.3 Branch and Bound algorithm

The algorithm shares many similarities with that used for the NRTL equation, and the notation is therefore the same as that used in Section 3. The main difference lies in how it obtains lower bounds on the global solution. In this case, only *one* underestimating function is included when generating lower bounds for (DC). The complete branch and bound algorithm for the phase and chemical equilibrium problem when the liquid phase is modeled using the UNIQUAC equilibrium model is now given.

STEP 0: Initialization

Select an initial mol vector $\bar{\mathbf{n}}^0$ and convergence tolerance ε.

Initialize $R_C\{\mathcal{L}^R,\mathcal{U}^R\}$, $P^U = +\infty$, $M^L = -\infty$, $\mathcal{S}_C = R$, $k_S = \emptyset$, $\{\mathcal{H}_i^k\} = 0$, $N_P = 0$.

STEP 1: Primal Problem

Solve (DC) locally to give $\hat{G}^*$ and update $P^U = \min\left[P^U \ , \ \hat{G}^*\right]$.

STEP 2: Convex underestimation phase

(1) Choose a combination of box bounds, B_l from the set CB ($|CB| = 2^{N_P}$).

Use $s_{i,k}^{B_l}$, $\mathcal{H}_i^k$ and $R_K\{\mathcal{L}^R,\mathcal{U}^R\}$ to set $B_K\{\mathcal{L}^B,\mathcal{U}^B\}$.

Construct Ψ_i^k based on $B_K\{\mathcal{L}^B,\mathcal{U}^B\}$ and solve (UES) to yield μ^* and $\mathbf{n}^*$.

(i) If $\mu^* \geq P^U - \epsilon$, then fathom solution.

(ii) If $\mu^* < P^U - \epsilon$, then $k_S = k_S + 1$, $p\,(k_S) = \mathcal{S}_C$, $\mu^{k_S} = \mu^*$, $\mathbf{n}^{k_S} = \mathbf{n}^*$, $R_{k_S}\{\mathcal{L}^R,\mathcal{U}^R\} = B_K\{\mathcal{L}^B,\mathcal{U}^B\}$.

(2) Choose another set of bounds B_l from CB and return to (1).

If there are no remaining unchosen B_l in CB, then proceed to Step 3.

STEP 3: Select mol vector for next iteration

Select infimum of all $\mu_B^{k_S}$, and set $S_C = k_S$, the associated node.

Set $\bar{\mathbf{n}}^{K+1} = \mathbf{n}^{\boldsymbol{k}_S}$, $M^L = \mu_B^{\boldsymbol{S}_C}$ and $R_{K+1}\{\mathcal{L}^{\boldsymbol{R}},\mathcal{U}^{\boldsymbol{R}}\} = R_{\boldsymbol{k}_S}\{\mathcal{L}^{\boldsymbol{R}},\mathcal{U}^{\boldsymbol{R}}\}$

Choose $1 \leq N_P \leq N_{\boldsymbol{CV}}$. Set $D = \{i,k\} \equiv C \times P_L$, $\{\mathcal{H}_{\boldsymbol{i}}^{\boldsymbol{k}}\} = 0$.

for $m = 1,\ldots,N_P$

$$\begin{aligned} \{i^*,k^*\} &= \underset{D}{\text{argmax}} \left| -\bar{n}_{\boldsymbol{i}}^{\boldsymbol{k}} \ln \bar{n}_{\boldsymbol{i}}^{\boldsymbol{k}} - \Psi_{\boldsymbol{i}}^{\boldsymbol{k}}(\bar{n}_{\boldsymbol{i}}^{\boldsymbol{k}}) \right| \\ \mathcal{H}_{\boldsymbol{i}^*}^{\boldsymbol{k}^*} &= 1 \\ D &= D \backslash \{i^*,k^*\} \end{aligned}$$

end

STEP 4: Check for convergence

Check if $\left|\frac{P^U - M^L}{P^U}\right| \leq \epsilon$. If true, then STOP; otherwise set $K = K + 1$, and return to Step 1.

Convergence to an ϵ-global solution of (DC) by the above algorithm has been proven by Horst and Tuy [11].

Note that it is also possible to use the GOP algorithm for the case of the UNIQUAC equation. New variables, labeled $\Psi_{\boldsymbol{i}}^{\boldsymbol{k}}$, would be introduced so that $\Psi_{\boldsymbol{i}}^{\boldsymbol{k}} = n_{\boldsymbol{i}}^{\boldsymbol{k}}\ \forall\ i \in C, k \in P_L$. The nonconvex terms of the objective function then take the form $-n_{\boldsymbol{i}}^{\boldsymbol{k}} \ln \Psi_{\boldsymbol{i}}^{\boldsymbol{k}}$. This transformation will clearly satisfy *Conditions (A)* of the GOP. If the y variables (i.e. $n_{\boldsymbol{i}}^{\boldsymbol{k}}$) are held fixed, then a convex objective function results. If the x variables (i.e. $\Psi_{\boldsymbol{i}}^{\boldsymbol{k}}$) are kept constant, then a convex objective function is also obtained. However, because the linear convex envelope derived in Section 4.2.1 represents the tightest possible convex underestimator of the objective function, it is clear that the bounds generated by the GOP algorithm will not be as tight as those generated in the branch and bound algorithm just described.

4.3 Example 3: Toluene (1) – Water (2)

This example was studied by Lantagne *et al.* [12]. They used the modified version of the UNIQUAC equation for systems containing alcohols or water as proposed by Anderson and Prausnitz [3]. It is assumed that there is an equimolar charge of toluene and water ($n_1^T = n_2^T = 0.5$). There are two postulated liquid phases, so that $P_L \equiv \{k_1, k_2\}$; these phases share the same standard state so that the Gibbs free energy of formation terms can be eliminated as for Example 1. The pure component structural parameters and the binary interaction data were obtained from Prausnitz *et al.* [18] and these are given as:

$$\begin{array}{llll} q_1 = 2.97 & q_1' = 2.97 & r_1 = 3.92 & l_1 = 1.83 \\ q_2 = 1.40 & q_2' = 1.00 & r_2 = 0.92 & l_2 = -2.32 \end{array}$$

The parameters l_i are supplied even though they are not used in the formulation. The interaction parameters are given as:

$$\tau_{12} = 0.09867 \ , \ \tau_{21} = 0.59673$$

The parameters introduced to convert the original formulation into a D.C. programming problem are then defined as:

$$\begin{aligned} z_1^R &= \tfrac{5q_1-1}{r_1} & z_2^R &= \tfrac{5q_2-1}{r_2} \\ &= 3.53316 & &= 6.52174 \end{aligned}$$

$$\begin{aligned} z_M^R &= \min \{ z_1^R, z_2^R \} \\ &= z_1^R \\ &= 3.53316 \end{aligned}$$

$$\begin{aligned} z^A &= z_M^R + (z_1^R - z_M^R) + (z_2^R - z_M^R) \\ &= z_2^R \\ &= 6.52174 \end{aligned}$$

$$\begin{aligned} z_1^B &= z_2^R - z_M^R & z_2^B &= z_1^R - z_M^R \\ &= 2.98858 & &= 0 \end{aligned}$$

$$\begin{aligned} \varphi_1 &= q_1' + r_1 \cdot (z_1^R + z_1^B) &= 28.53522 \\ \varphi_2 &= q_2' + r_2 \cdot (z_2^R + z_2^B) &= 7.0 \end{aligned}$$

This allows the explicit formulation to be written as follows:

$$\begin{aligned} \min\ \hat{G}_I &= -n_1^T z_1^R r_1 \ln r_1 - n_2^T z_2^R r_2 \ln r_2 \\ &+ z^A \left[r_1 n_1^1 + r_2 n_2^1\right] \ln \left[r_1 n_1^1 + r_2 n_2^1\right] + z_1^B r_1 n_1^1 \ln \frac{n_1^1}{r_1 n_1^1 + r_2 n_2^1} \\ &+ z^A \left[r_1 n_1^2 + r_2 n_2^2\right] \ln \left[r_1 n_1^2 + r_2 n_2^2\right] + z_1^B r_1 n_1^2 \ln \frac{n_1^2}{r_1 n_1^2 + r_2 n_2^2} \\ &+ \frac{z}{2} q_1 n_1^1 \ln \frac{q_1 n_1^1}{q_1 n_1^1 + q_2 n_2^1} + \frac{z}{2} q_2 n_2^1 \ln \frac{q_2 n_2^1}{q_1 n_1^1 + q_2 n_2^1} \\ &+ \frac{z}{2} q_1 n_1^2 \ln \frac{q_1 n_1^2}{q_1 n_1^2 + q_2 n_2^2} + \frac{z}{2} q_2 n_2^2 \ln \frac{q_2 n_2^2}{q_1 n_1^2 + q_2 n_2^2} \\ &+ \left[q_1' n_1^1 + q_2' n_2^1\right] \ln \left[q_1' n_1^1 + q_2' n_2^1\right] + q_1' n_1^1 \ln \frac{n_1^1}{q_1' n_1^1 + \tau_{21} q_2' n_2^1} + q_2' n_2^1 \ln \frac{n_2^1}{\tau_{12} q_1' n_1^1 + q_2' n_2^1} \\ &+ \left[q_1' n_1^2 + q_2' n_2^2\right] \ln \left[q_1' n_1^2 + q_2' n_2^2\right] + q_1' n_1^2 \ln \frac{n_1^2}{q_1' n_1^2 + \tau_{21} q_2' n_2^2} + q_2' n_2^2 \ln \frac{n_2^2}{\tau_{12} q_1' n_1^2 + q_2' n_2^2} \\ &- \varphi_1 \left[n_1^1 \ln n_1^1 + n_1^2 \ln n_1^2\right] - \varphi_2 \left[n_2^1 \ln n_2^1 + n_2^2 \ln n_2^2\right] \end{aligned}$$

s.t.

$$n_1^1 + n_1^2 = 0.5$$
$$n_2^1 + n_2^2 = 0.5$$
$$0 \leq n_1^1, n_2^1, n_1^2, n_2^2 \leq 0.5$$

The last line of the objective function contains the nonconvex portion (which is separable and concave). The equality constraints can be used to eliminate the variables of the second liquid phase in the same manner as was done in Examples 1 and 2. This reduces the number of connected variables to $N_{CV} = 2$. If a trivial solution starting point is used, the algorithm converges in 343 iterations to the global solution which is given in Table 5. If such a starting point is supplied to a local solver, it will fail to converge to the global solution. The total time taken to solve the problem was 3.3 cpu sec and 64% of the solutions were fathomed. Because the size of the problem is small, $2^2 = 4$ subproblems were solved at each iteration (i.e. $N_P = N_{CV}$ for all iterations), even though it is necessary to solve only two at each iteration

The algorithm has been used to solve several other examples with more components and phases. The number of variables stays relatively small so that the tested problems stay of manageable size. This is because the effort of obtaining the interaction coefficients, τ_{ij}, becomes prohibitive for more than four components.

5 Conclusions

It has been demonstrated how the Gibbs free energy function can be radically altered when the liquid phase is modeled using the NRTL or UNIQUAC equations (and an ideal vapor phase). Numerous simplifications and properties of the equations have been revealed that allow the structures of the problems to be fully exploited. The GOP algorithm was used to obtain an ϵ-global solution for the NRTL equation, where a biconvex function is minimized over a set of bilinear equality constraints. A branch and bound algorithm based on that of Falk and Soland [6] was used to likewise guarantee obtaining an ϵ-global solution for the UNIQUAC equation. Examples were presented which demonstrate the effectiveness of the algorithms in obtaining global solutions of a number of difficult phase equilibrium problems, for which no previous approaches could make the same guarantees.

Acknowledgement: The authors gratefully acknowledge financial support from the National Science Foundation under Grants CBT-8857013 and CTS-9221411, as well as support from Amoco Chemical Co., Exxon Co., Tennessee Eastman Co., Mobil Co., and Shell Development.

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Appendix A

In what follows the mol number phase superscripts are dropped for clarity of presentation. It is required to prove that the following relation is true:

$$\sum_{i\in C} n_i \left\{ \frac{\sum\limits_{j\in C} \tau_{ji}\mathcal{G}_{ji}n_j}{\sum\limits_{j\in C} \mathcal{G}_{ji}n_j} \right\} - \sum_{i\in C} n_i \left\{ \sum_{j\in C} \frac{\mathcal{G}_{ij}n_j}{\sum\limits_{l\in C} \mathcal{G}_{lj}n_l} \frac{\sum\limits_{l\in C} \tau_{lj}\mathcal{G}_{lj}n_l}{\sum\limits_{l\in C} \mathcal{G}_{lj}n_l} \right\} = 0 \tag{A.1}$$

The basis of the proof is to extract the common term $\sum_j \mathcal{G}_{ji}n_j$ from the denominator of Eqn. (A.1). Rewriting the term to the left of the minus sign of Eqn. (A.1) yields:

$$\sum_i n_i \left\{ \frac{\sum_j \tau_{ji}\mathcal{G}_{ji}n_j}{\sum_j \mathcal{G}_{ji}n_j} \right\} = \sum_i \frac{1}{\sum\limits_j \mathcal{G}_{ji}n_j} \cdot n_i \cdot \sum_j \tau_{ji}\mathcal{G}_{ji}n_j \tag{A.2}$$

The first term in the denominator of the term to the right of the minus sign of Eqn. (A.1), $\sum_l \mathcal{G}_{lj}n_l$, is extracted and summed over the index i, that is, it is changed to $\sum_m \mathcal{G}_{mi}n_m$. In doing so, the indices of $\mathcal{G}_{ij}$ in the numerator of the term to the right of the minus sign of Eqn. (A.1) are swapped to give $\mathcal{G}_{ji}$ and the second indices in the l summation terms change from j to i as follows:

$$\begin{aligned}
&\sum_{i\in C} n_i \left\{ \sum_{j\in C} \frac{\mathcal{G}_{ij}n_j}{\sum\limits_l \mathcal{G}_{lj}n_l} \frac{\sum\limits_l \tau_{lj}\mathcal{G}_{lj}n_l}{\sum\limits_l \mathcal{G}_{lj}n_l} \right\} \\
&= \sum_i \frac{1}{\sum\limits_m \mathcal{G}_{mi}n_m} \cdot n_i \cdot \sum_j \mathcal{G}_{ji}n_j \cdot \frac{\sum\limits_l \tau_{li}\mathcal{G}_{li}n_l}{\sum\limits_l \mathcal{G}_{li}n_l} \\
&= \sum_i \frac{1}{\sum\limits_j \mathcal{G}_{ji}n_j} \cdot n_i \cdot \sum_l \tau_{li}\mathcal{G}_{li}n_l
\end{aligned} \tag{A.3}$$

noting that the indices of the terms $\sum_j \mathcal{G}_{ji}n_j$ and $\sum_l \mathcal{G}_{li}n_l$ run independently of each other and therefore cancel. Subtracting Eqn. (A.3) from Eqn. (A.2) yields the desired result:

$$\begin{aligned}
&\sum_i \frac{1}{\sum\limits_j \mathcal{G}_{ji}n_j} \cdot n_i \cdot \sum_j \tau_{ji}\mathcal{G}_{ji}n_j - \sum_i \frac{1}{\sum\limits_j \mathcal{G}_{ji}n_j} \cdot n_i \cdot \sum_l \tau_{li}\mathcal{G}_{li}n_l \\
&= \sum_i \frac{1}{\sum\limits_j \mathcal{G}_{ji}n_j} \cdot n_i \cdot \left\{ \sum_j \tau_{ji}\mathcal{G}_{ji}n_j - \sum_l \tau_{li}\mathcal{G}_{li}n_l \right\} \\
&= 0
\end{aligned}$$

realizing that the indices of the terms in braces run independently of each other and are therefore equal to zero. The same result can be obtained for any phase k. $\square$

Appendix B

It is required to establish if the following function is convex:

$$f_{\bar\imath} = n_{\bar\imath} \ln \frac{n_{\bar\imath}}{\sum\limits_{j=1,\dots,p} \rho_j n_j} \quad \text{for any} \quad \bar\imath = 1, \dots, p$$

where p represents the number of variables of the problem. There are a number of ways to prove its convexity. The chosen method here is to explicitly evaluate the eigenvalues for $f_{\bar\imath}$. For notational convenience, $u = \sum_j \rho_j n_j$ in the foregoing. A necessary and sufficient condition for convexity requires that all the eigenvalues of the Hessian, $\mathbf{H}$, be nonnegative. These are obtained by evaluating the roots of the characteristic equation of the matrix $(\mathbf{H} - \lambda\mathbf{I})$. The approach utilizes the following two properties:

(i) The determinant of a matrix changes sign if two rows (or two columns) are exchanged,

(ii) Adding a multiple of one row to another leaves the determinant unchanged (viz. for columns).

Step 1: Evaluation of $(\mathbf{H} - \lambda\mathbf{I})$

As a first step, the second order derivatives of the function $f_{\bar\imath}$ are given as follows:

$$\frac{\partial^2 f_{\bar\imath}}{\partial n_i \partial n_j} = \begin{cases} \frac{(\rho_{\bar\imath} n_{\bar\imath} - u)^2}{n_{\bar\imath} u^2} & i = j = \bar\imath \\ \rho_j \frac{\rho_{\bar\imath} n_{\bar\imath} - u}{u^2} & i = \bar\imath, j \neq i \\ \rho_i \rho_j \frac{n_{\bar\imath}}{u^2} & i \neq \bar\imath, j \neq \bar\imath \end{cases}$$

If $\bar n$ is substituted for $\rho_{\bar\imath} n_{\bar\imath}$ and n for $n_{\bar\imath}$, then $(\mathbf{H} - \lambda\mathbf{I})$ is given explicitly as:

$$(\mathbf{H} - \lambda\mathbf{I}) = \begin{pmatrix} \frac{(\bar n - u)^2}{n u^2} - \lambda & \rho_2 \frac{\bar n - u}{u^2} & \rho_3 \frac{\bar n - u}{u^2} & \cdots & \\ \rho_2 \frac{\bar n - u}{u^2} & \rho_2^2 \frac{n}{u^2} - \lambda & \rho_2 \rho_3 \frac{n}{u^2} & \rho_2 \rho_4 \frac{n}{u^2} & \\ \rho_3 \frac{\bar n - u}{u^2} & \rho_3 \rho_2 \frac{n}{u^2} & \rho_3^2 \frac{n}{u^2} - \lambda & \rho_3 \rho_4 \frac{n}{u^2} & \ddots \\ \vdots & \rho_4 \rho_2 \frac{n}{u^2} & \rho_4 \rho_3 \frac{n}{u^2} & \rho_4^2 \frac{n}{u^2} - \lambda & \ddots \\ & \vdots & & \ddots & \ddots \end{pmatrix}$$

The $\bar\imath$'th row and column have been pivoted into the first row and column, leaving the determinant unchanged because of Property (i). The set of parameters $\{\rho_2, \dots, \rho_p\}$ are assumed to be equivalent to the set $\{\rho_1, \dots, \rho_p\} \setminus \rho_{\bar\imath}$. Thus, the above form can be equivalently obtained for any $\bar\imath = 1, \dots, p$. □

Step 2: Transformation of $(\mathbf{H}-\lambda\mathbf{I})$

By Property (ii), the following operations change the structure of $(\mathbf{H}-\lambda\mathbf{I})$ without changing its determinant:

for $i = 3, \ldots, p$
  for $i' = i, \ldots, p$
    for $j = 1, \ldots, p$
      $a_{i',j} = a_{i',j} - \left[\frac{\rho_{i'}}{\rho_{i-1}}\right] a_{i-1,j}$
    end
  end
end

where a_{ij} is the $i-j$'th entry of the matrix $(\mathbf{H}-\lambda\mathbf{I})$. This yields the following result:

$$
|\mathbf{H}-\lambda\mathbf{I}| \equiv \begin{vmatrix}
\frac{(\bar{n}-u)^2}{nu^2}-\lambda & \rho_2\frac{\bar{n}-u}{u^2} & \rho_3\frac{\bar{n}-u}{u^2} & \cdots & \\
\rho_2\frac{\bar{n}-u}{u^2} & \rho_2^2\frac{n}{u^2}-\lambda & \rho_2\rho_3\frac{n}{u^2} & \rho_2\rho_4\frac{n}{u^2} & \cdots \\
0 & \frac{\rho_3}{\rho_2}\lambda & -\lambda & 0 & \\
0 & 0 & \frac{\rho_4}{\rho_3}\lambda & -\lambda & 0 \\
\vdots & \vdots & & \ddots & \ddots
\end{vmatrix}
$$

One more operation on the second row is required:

for $i = 2$
  for $j = 1, \ldots, p$
    $a_{i,j} = a_{i,j} - \left[\rho_2\frac{n}{\bar{n}-u}\right] a_{1,j}$
  end
end

The characteristic equation is then equivalently given by the following determinant:

$$
|\mathbf{H}-\lambda\mathbf{I}| \equiv \begin{vmatrix}
\frac{(\bar{n}-u)^2}{nu^2}-\lambda & \rho_2\frac{\bar{n}-u}{u^2} & \rho_3\frac{\bar{n}-u}{u^2} & \cdots & \\
\rho_2\frac{n}{\bar{n}-u}\lambda & -\lambda & 0 & 0 & \cdots \\
0 & \frac{\rho_3}{\rho_2}\lambda & -\lambda & 0 & \\
0 & 0 & \frac{\rho_4}{\rho_3}\lambda & -\lambda & 0 \\
\vdots & \vdots & & \ddots & \ddots
\end{vmatrix}
$$

This determinant is evaluated by expanding the cofactors down the first column so that:

$$
|\mathbf{H}-\lambda\mathbf{I}| = \left[\frac{(\bar{n}-u)^2}{nu^2}-\lambda\right] |A_{11}| + \left[\rho_2\frac{n}{\bar{n}-u}\right](-\lambda)|A_{21}| \tag{B.1}
$$

where A_{ij} is the appropiate minor obtained by deleting the i'th row and j'th column of $(\mathbf{H} - \lambda\mathbf{I})$. □

Step 3: Evaluation of $\mid A_{11} \mid$ and $\mid A_{21} \mid$

Because A_{11} is lower triangular, it is clear that:

$$\mid A_{11} \mid = (-\lambda)^{p-1} \tag{B.2}$$

A_{21} is a $(p-1) \times (p-1)$ square matrix. By extracting the common term in the first row, its determinant is given as:

$$\mid A_{21} \mid \;=\; \frac{\bar{n} - u}{u^2} \begin{vmatrix} \rho_2 & \rho_3 & \rho_4 & \cdots & \\ \frac{\rho_3}{\rho_2}\lambda & -\lambda & 0 & \cdots & \\ 0 & \frac{\rho_4}{\rho_3}\lambda & -\lambda & 0 & \cdots \\ 0 & 0 & \frac{\rho_5}{\rho_4}\lambda & -\lambda & \ddots \\ \vdots & & \ddots & \ddots & \ddots \end{vmatrix} \tag{B.3}$$

$$= \frac{\bar{n} - u}{u^2} \mid \mathcal{A}^{p-1} \mid \tag{B.4}$$

where $\mathcal{A}^{p-1}$ is the $(p-1) \times (p-1)$ matrix of the form given in Eqn. (B.3). Its determinant can be determined inductively by expanding across the top column, noting that the minors will be upper triangular to yield:

$$\rho_2 \mid \mathcal{A}^{p-1} \mid \;=\; (-\lambda)^{p-2} \cdot \left[\, \rho_2^2 + \cdots + \rho_p^2 \,\right] \tag{B.5}$$

$$= (-\lambda)^{k-2} \cdot \mathcal{T}$$

$$\text{where} \quad \mathcal{T} \;=\; \sum_{\substack{j=1,\ldots,p \\ j \neq i}} \rho_j^2 \tag{B.6}$$

in the general case. This simple relation allows the determinant of the original matrix to be easily calculated. □

Step 4: Evaluation of $\mid \mathbf{H} - \lambda\mathbf{I} \mid$

The original determinant may now be obtained by substituting Eqns. (B.2) and (B.4) into Eqn. (B.1) – noting that $\rho_2 \mid \mathcal{A}^{p-1} \mid = \mathcal{T} \cdot (-\lambda)^{p-2}$ by Eqn. (B.6) – to yield:

$$\begin{aligned} \mid \mathbf{H} - \lambda\mathbf{I} \mid \;&=\; (-\lambda)^{p-1} \left[\frac{(\bar{n} - u)^2}{nu^2} - \lambda \right] + \left[\frac{n}{\bar{n} - u} \right] \left[\frac{\bar{n} - u}{u^2} \right] (-\lambda)\, \rho_2 \mid \mathcal{A}^{p-1} \mid \\ &=\; (-\lambda)^{p-1} \left[\frac{(\bar{n} - u)^2}{nu^2} + \frac{n\mathcal{T}}{u^2} - \lambda \right] \end{aligned}$$

The eigenvalues are calculated as $\left|\mathbf{H}-\lambda\mathbf{I}\right| = 0$:

$$\begin{aligned}\lambda_{\bar{\imath}} &= \frac{(\bar{n}-u)^2 + n^2\mathcal{T}}{nu^2} \quad \geq \quad 0 \\ \lambda_j &= 0 \quad \forall \quad j \neq \bar{\imath}\end{aligned}$$

Recall that $\bar{n} = \rho_{\bar{\imath}}\, n_{\bar{\imath}}$, $u = \sum_{j=1,\ldots,p} \rho_j n_j$, $n = n_{\bar{\imath}}$, and $\mathcal{T} = \sum_{\substack{j=1,\ldots,p \\ j\neq\bar{\imath}}} \rho_j^2$.

As a check, notice that $\lambda_{\bar{\imath}} = \text{trace } \mathbf{H}$, because $\sum_{j\neq\bar{\imath}} \lambda_j = 0$. Thus, there is exactly one nonnegative eigenvalue and the rest are zero. This is precisely the necessary and sufficient condition for convexity. □

Appendix C

A proof of the convexity of the following function is required:

$$f(\mathbf{n}) = \left\{ \sum_{i=1,\ldots,p} \rho_i n_i \right\} \ln \left\{ \sum_{i=1,\ldots,p} \rho_i n_i \right\}$$

The method used is essentially the same as that employed in Appendix B. For notational convenience, $u = \sum_i \rho_i n_i$ in the foregoing. As a first step, the second order derivatives of the function $f(\mathbf{n})$ are given as follows:

$$\frac{\partial^2 f}{\partial n_i \partial n_j} = \frac{\rho_i \rho_j}{u}$$

$(\mathbf{H}-\lambda\mathbf{I})$ is constructed as for Appendix B, and the following operations will leave this matrix unchanged:

> **for** $i = 2, \ldots, p$
>   **for** $i' = i, \ldots, p$
>   **for** $j = 1, \ldots, p$
> $a_{i',j} = a_{i',j} - \left[\frac{\rho_{i'}}{\rho_{i-1}}\right] a_{i-1,j}$
>   **end**
>   **end**
> **end**

where a_{ij} is the $i-j$'th entry of the matrix $(\mathbf{H}-\lambda\mathbf{I})$. This yields the following result:

$$\mid \mathbf{H}-\lambda\mathbf{I} \mid \equiv \begin{vmatrix} \frac{\rho_1^2}{u}-\lambda & \frac{\rho_1\rho_2}{u} & \frac{\rho_1\rho_3}{u} & \cdots & \\ \frac{\rho_2}{\rho_1}\lambda & -\lambda & 0 & 0 & \cdots \\ 0 & \frac{\rho_3}{\rho_2}\lambda & -\lambda & 0 & \\ 0 & 0 & \frac{\rho_4}{\rho_3}\lambda & -\lambda & 0 \\ \vdots & \vdots & & \ddots & \ddots \end{vmatrix}$$

This determinant is evaluated by expanding the cofactors down the first column so that:

$$\mid \mathbf{H}-\lambda\mathbf{I} \mid = \left[\frac{\rho_1^2}{u}-\lambda\right] \mid A_{11} \mid + \left[\frac{\rho_2}{\rho_1}\right](-\lambda) \mid A_{21} \mid \tag{C.1}$$

where A_{11} is given by Eqn. (B.2) and A_{21} is defined as:

$$A_{21} = \frac{\rho_1}{u} \mid \mathcal{A}^{p-1} \mid \tag{C.2}$$

with A^{p-1} defined by Eqn. (B.5). This means that the determinant can be calculated as:

$$\begin{aligned} \mid \mathbf{H}-\lambda\mathbf{I} \mid &= (-\lambda)^{p-1}\left[\frac{\rho^2}{u}-\lambda\right] + \left[\frac{1}{u}\right](-\lambda)^{p-1}\left[\rho_2^2+\cdots+\rho_p^2\right] \\ &= (-\lambda)^{p-1}\left[\frac{\mathcal{T}}{u}-\lambda\right] \end{aligned}$$

but with $\mathcal{T}$ now defined as:

$$\mathcal{T} = \sum_{i=1,\ldots,p} \rho_i^2$$

The eigenvalues are calculated as $\left|\mathbf{H}-\lambda\mathbf{I}\right| = 0$:

$$\begin{aligned} \lambda_1 &= \frac{\mathcal{T}}{u} \geq 0 \\ \lambda_j &= 0 \quad \forall \quad j = 2,\ldots,p \end{aligned}$$

As a check, notice that $\lambda_1 = \text{trace } \mathbf{H}$, because $\sum_{j\neq 1}\lambda_j = 0$. Thus, there is exactly one nonnegative eigenvalue and the rest are zero. This is precisely the necessary and sufficient condition for convexity. □

Appendix D

Add and subtract the term $\sum_i q_i' n_i^k \ln n_i^k$ to the original term $\mathcal{D}^k$ of Eqn. (44):

$$\mathcal{D}^k \equiv \sum_{i\in C} q_i' n_i^k \ln n_i^k - \sum_{i\in C} q_i' n_i^k \ln \sum_{j\in C} q_j' \tau_{ji} n_j^k - \sum_{i\in C} q_i' n_i^k \ln n_i^k$$

$$\begin{aligned} &= \sum_{i\in C} q_i' n_i^k \ln \frac{n_i^k}{\sum\limits_{j\in C} q_j' \tau_{ji} n_j^k} - \sum_{i\in C} q_i' n_i^k \ln n_i^k \\ &= \left[\sum_{i\in C} q_i' n_i^k \ln \frac{n_i^k}{\sum\limits_{j\in C} q_j' \tau_{ji} n_j^k}\right] - \left[\sum_{i\in C} q_i' n_i^k \ln n_i^k\right] \end{aligned}$$

The first term in square brackets is the term defined as $\mathcal{D}_+^k$, while the second term is $\mathcal{D}_-^k$. Therefore Eqn. (45) is seen to be valid. It remains to prove that the terms $\mathcal{D}_+^k$ and $\mathcal{D}_-^k$ are convex. Setting and $q_j'\tau_{ji} = \rho \ \forall \ j$, each individual i'th term of the nonlinear part of $\mathcal{D}_+^k$ is seen to be convex. The sum of linear and convex functions is itself a convex function. Hence $\mathcal{D}_+^k$ is convex. $\mathcal{D}_-^k$ is a summation of separable terms of the form $n \ln n$, which are clearly convex terms because $q_i' > 0 \ \forall \ i$, i.e. $\mathcal{D}_-^k$ is convex. □

Appendix E

The original term $\mathcal{A}^k$ of Eqn. (44) is defined as:

$$\begin{aligned} -\mathcal{A}^k &\equiv -\sum_{i\in C} z_i^R r_i n_i^k \ln \frac{r_i n_i^k}{\sum\limits_{j\in C} r_j n_j^k} \\ &= -\sum_{i\in C} z_i^R r_i n_i^k \ln r_i n_i^k + \sum_{i\in C} z_i^R r_i n_i^k \ln \sum_{j\in C} r_j n_j^k \end{aligned}$$

A term is now added and subtracted from each i'th term as follows:

$$\begin{aligned} -\mathcal{A}^k &= -\sum_{i\in C} z_i^R r_i n_i^k \ln r_i n_i^k \\ &+ \sum_{i\in C} \Bigg\{ z_i^R r_i n_i^k \ln \sum_{j\in C} r_j n_j^k \\ &\qquad + (z_i^R - z_M^R) \sum_{j\neq i} r_j n_j^k \ln \left(\sum_{l\in C} r_l n_l^k\right) + (z_i^R - z_M^R) \sum_{j\neq i} r_j n_j^k \ln n_j^k \\ &\qquad - (z_i^R - z_M^R) \sum_{j\neq i} r_j n_j^k \ln \left(\sum_{l\in C} r_l n_l^k\right) - (z_i^R - z_M^R) \sum_{j\neq i} r_j n_j^k \ln n_j^k \Bigg\} \end{aligned}$$

This expression can be equivalently written as follows:

$$\begin{aligned} -\mathcal{A}^k &= -\sum_{i\in C} z_i^R r_i n_i^k \ln r_i n_i^k + \left[z_M^R + \sum_{i\in C} (z_i^R - z_M^R)\right] \left(\sum_{j\in C} r_j n_j^k\right) \ln \left(\sum_{j\in C} r_j n_j^k\right) \\ &+ \sum_{i\in C} \left[\sum_{j\neq i} \left(z_j^R - z_M^R\right)\right] r_i n_i^k \ln \frac{n_i^k}{\sum\limits_{j\in C} r_j n_j^k} - \sum_{i\in C} \left[\sum_{j\neq i} \left(z_j^R - z_M^R\right)\right] r_i n_i^k \ln n_i^k \end{aligned}$$

Recalling the definitions of z_M^R, z^A and z_i^B as given by Eqns. (47), the following relation is obtained:

$$\begin{aligned}
-\mathcal{A}^k &= \left\{-\sum_{i\in C} n_i^k z_i^R r_i \ln r_i + z^A \left(\sum_{j\in C} r_j n_j^k\right) \ln\left(\sum_{j\in C} r_j n_j^k\right) + \sum_{i\in C} z_i^B r_i n_i^k \ln \frac{n_i^k}{\sum_{j\in C} r_j n_j^k}\right\} \\
&- \left\{\sum_{i\in C} n_i^k \ln n_i^k r_i \left[z_i^R + z_i^B\right]\right\}
\end{aligned}$$

The first term within curly braces corresponds to the definition of $\mathcal{A}_+^k$. Its first term is linear. The next is convex by Property 4.3, while the third term is convex by Property 3.2. Thus the first term within curly braces is convex. The second term within curly braces is seen to be the definition of $\mathcal{A}_-^k$. It is clearly separable and convex. These two terms correspond to the definitions of $\mathcal{A}_+^k$ and $\mathcal{A}_-^k$ as given in Property 4.5 so that:

$$-\mathcal{A}^k = \mathcal{A}_+^k - \mathcal{A}_-^k \tag{E.1}$$

where $\mathcal{A}_+^k$ and $\mathcal{A}_-^k$ have been shown to be convex.

Solution for n-Butyl-Acetate (1) – Water (2) $T = 298$K, $P = 1.0$ atm				
Components	Feed (mols)	Liquid I (mols)	Liquid II (mols)	$\hat{G}_I^*$ (—)
$C_6H_{12}O_2$ (1)	0.50	0.00071	0.49929	-0.02020
H_2O (2)	0.50	0.15588	0.34412	(Global minimum)
$C_6H_{12}O_2$ (1)	0.50	0.00213	0.49787	-0.01961
H_2O (2)	0.50	0.46547	0.03453	(Local minimum)
$C_6H_{12}O_2$ (1)	0.50	0.00173	0.49827	-0.01730
H_2O (2)	0.50	0.37544	0.12456	(Local maximum)

Table 1: Solutions for Example 1

Iteration	M^L	$P(\bar{\mathbf{n}}^K)$
1	-0.42615	-0.01758
2	-0.23027	-0.01758
3	-0.22209	0.00507
4	-0.11446	-0.01754
48	-0.02408	-0.01980
74	-0.02166	-0.01988
87	-0.02059	-0.02002
91	-0.02042	-0.02018
106	-0.02021	-0.02020

Table 2: Progress of bounds for Example 1

n-Propanol (1) – n-Butanol (2) – Water (3): τ_{ij} and α_{ij} dimensionless					
Components ij	i	j	τ_{ij}	τ_{ji}	$\alpha_{ij} = \alpha_{ji}$
C_3H_8O – $C_4H_{10}O$	1	2	-0.61259	0.71640	0.30
C_3H_8O – H_2O	1	3	-0.07149	2.7425	0.30
$C_4H_{10}O$ – H_2O	2	3	0.90047	3.51307	0.48

Table 3: Binary data for Example 2

Solutions for n-Propanol (1) – n-Butanol (2) – Water (3) at T, $P = 1$ atm							
Component	Feed (mols)	Liquid I (mols)	Liquid II (mols)	$\hat{G}^*_{II}$ (—)	cpu (sec)	N_I (—)	N_F (%)
C_3H_8O (1)	0.040	0.0049	0.0351	-1.24112	5.2	268	65
$C_4H_{10}O$ (2)	0.160	0.0095	0.1505				
H_2O (3)	0.800	0.4153	0.3847				
C_3H_8O (1)	0.148	0.1280	0.0200	-1.1919716	17.31	932	26
$C_4H_{10}O$ (2)	0.052	0.0456	0.0064				
H_2O (3)	0.800	0.6549	0.1451				

Table 4: Global solutions for Example 2

	G^*	n_1^I	n_2^I
Global Minimum	-0.01976	0.00045	0.47733
Local Minimum	0.30919	0.25	0.25

Table 5: Solutions for Example 3

Iteration	Lower bound	Upper bound
1	-3.77305	0.30923
2	-3.65550	0.18812
3	-1.28319	0.18812
4	-1.13669	0.05711
12	-0.40768	0.00389
22	-0.15547	-0.00787
36	-0.06343	-0.00760
42	-0.04459	-0.00657
49	-0.03744	-0.00547
52	-0.03553	-0.01968
122	-0.02088	-0.01975
190	-0.02004	-0.01976
343	-0.01978	-0.01976

Table 6: Progress of bounds for Example 3

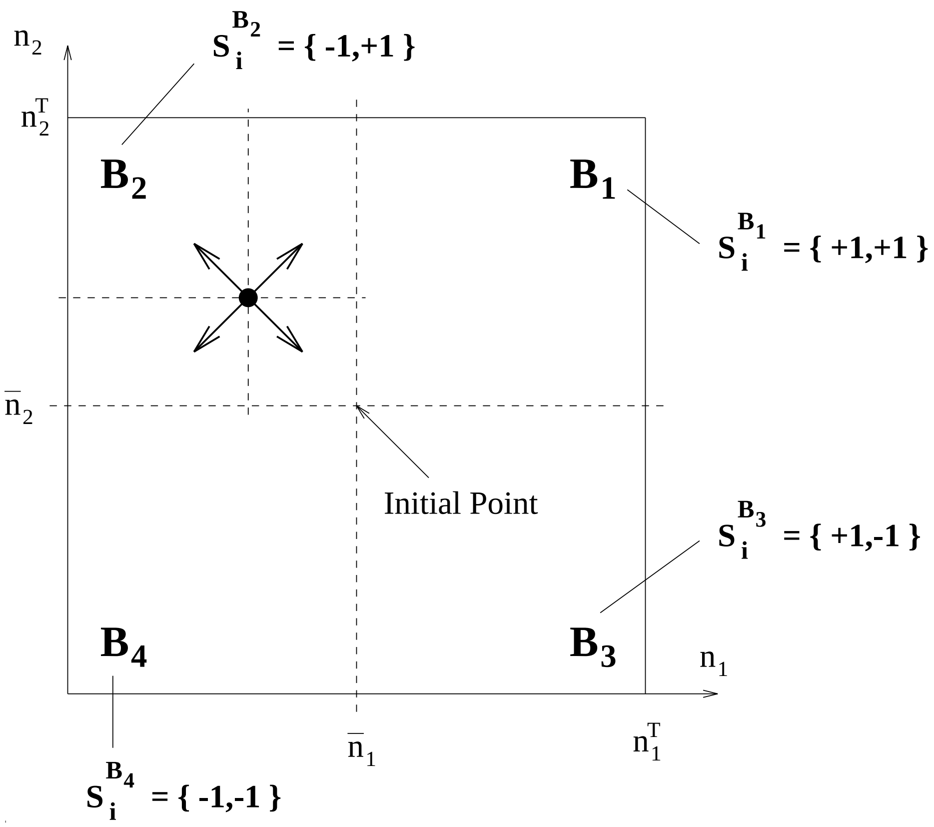

Figure 1: Example for two connected variables

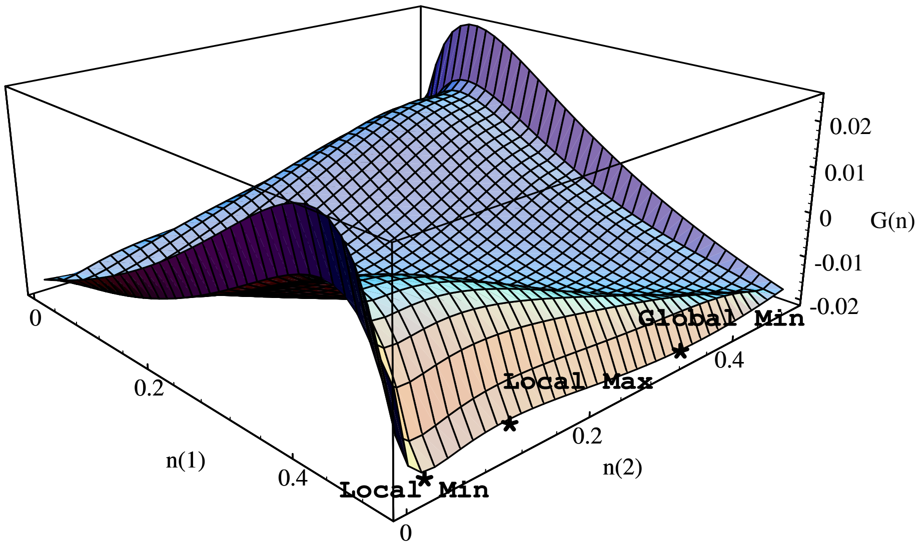

Figure 3: Gibbs surface and Lagrangian for Region 1 of Iteration 1 of Example 1

Figure 2: Gibbs energy surface for Example 1

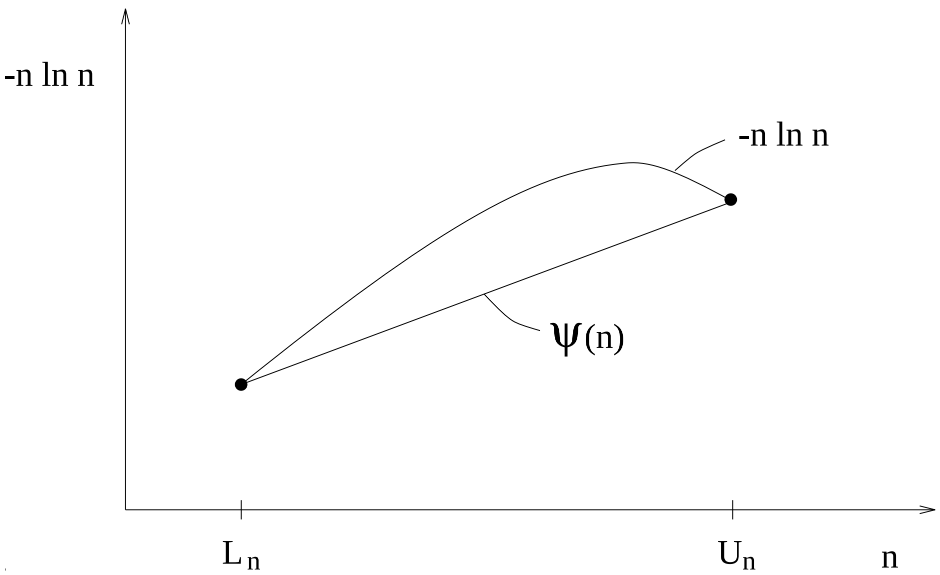

Figure 4: Concave function and its convex envelope

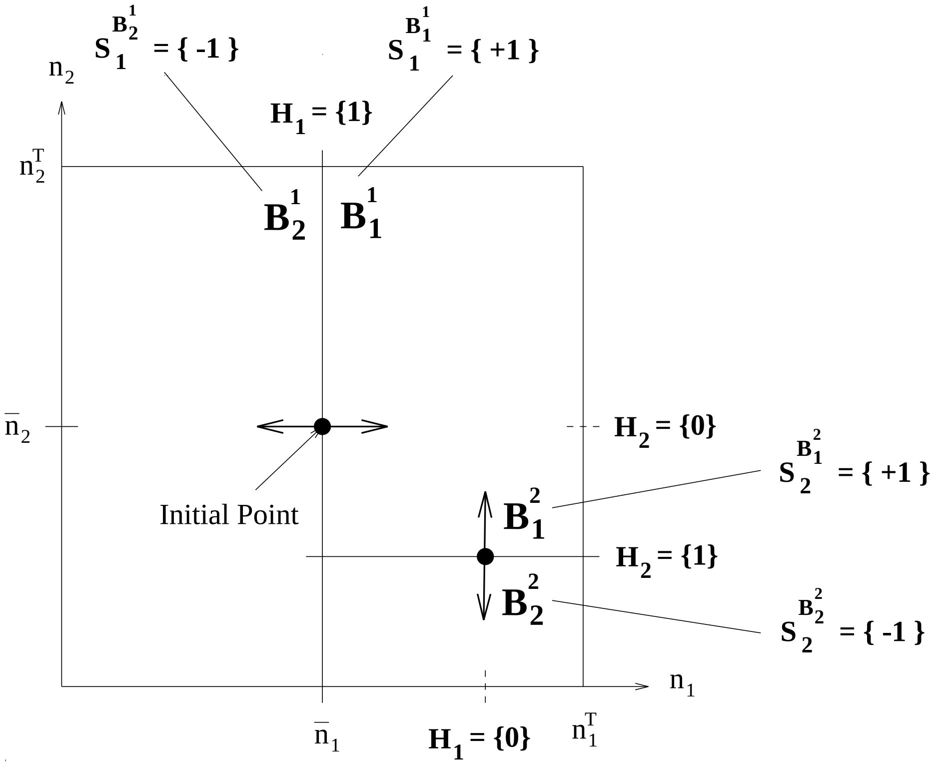

Figure 5: Box regions of UNIQUAC example