A Review on Global Optimization Methods for Phase Equilibrium Modeling and Calculations

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Abstract. The phase equilibrium modeling for multi-component systems is essential in process systems engineering. In particular, phase stability analysis, Gibbs free energy minimization and estimation of parameters in thermodynamic models are challenging global optimization problems involved in phase equilibrium calculations and modeling for both reactive and non-reactive systems. To date, many significant works have been performed in the area of global optimization, and several algorithms and computational contributions of global optimization have been used for solving these problems; global optimization methods used include both deterministic and stochastic algorithms. To the best of our knowledge, there is no review in the literature that focuses on the global optimization methods and their applications to phase equilibrium modeling and calculations. In this paper, we briefly describe selected deterministic and stochastic optimization algorithms, and then review their use for phase stability analysis, Gibbs free energy minimization and parameter estimation in phase equilibrium models. In short, we provide a general overview of global optimization for modeling and calculating the phase behavior of systems with and without chemical reactions including the prediction of azeotropes and critical points.

Keywords: Global optimization, Gibbs free energy minimization, Parameter estimation, Phase stability analysis, Phase and chemical equilibrium calculations.

1. INTRODUCTION

The phase equilibrium modeling for multi-component systems is essential in the design, operation, optimization and control of separation schemes. Novel processes handle complex mixtures, severe operating conditions, or even incorporate multi-functional unit operations (e.g. reactive distillation and extractive distillation). Therefore, phase behavior of multi-component systems has significant impact on process design including equipment and energy costs of separation and purification strategies [1]. Phase equilibrium calculations are usually executed thousands of times in process simulators, and are especially important in chemical, petroleum, petrochemical, pharmaceutical and other process industries where separation units are the core of process performance. Hence, these calculations must be performed reliably and efficiently, to avoid uncertainties and errors in process design.

Global optimization problems abound in the mathematical modeling of phase equilibrium for both reactive and non-reactive systems. Specifically, several thermodynamic calculations can be formulated as global optimization problems, and they include three applications: a) phase stability analysis, b) Gibbs free energy minimization and c) estimation of parameters in thermodynamic models. Formally, the optimization problems of these applications can be stated as follows: minimize $F_{obj}(\boldsymbol{u})$ subject to $h_j(\boldsymbol{u}) = 0$ for $j = 1, 2, \ldots, m$ and $\boldsymbol{u} \in \Omega$ where $\boldsymbol{u}$ is a vector of n continuous variables in the domain $\Omega \in \Re^n$, m is the number of equality constraints arising from the specific thermodynamic application, and $F_{obj}(\boldsymbol{u}) : \Omega \Rightarrow \Re$ is a real-valued function. The domain Ω is defined by the upper and lower limits of each decision variable.

The major challenge of solving global optimization problems for phase equilibrium modeling is because $F_{obj}(\boldsymbol{u})$ is generally non-convex and highly non-linear with many decision variables. Thus, the objective functions involved in phase equilibrium modeling and calculations may have several local optima including trivial and non-physical solutions especially for multi-component and multi-phase systems. Therefore, traditional optimization methods are not suitable for solving these thermodynamic problems because they are prone to severe computational difficulties and may fail to converge to the correct solution when initial estimates are not suitable [1,2]. In general, finding the global optimum is more challenging than finding a local optimum, and the location of this global optimum for phase equilibrium problems is crucial because only it corresponds to the correct and desirable solution [1,3].

The development and evaluation of global optimization methods had played and continue to play a major role for modeling the phase behavior of multi-component systems [1-3]. Until now, many deterministic and stochastic global optimization methods have been used for phase equilibrium

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calculations and modeling. Studies on the use of deterministic methods for phase equilibrium problems have been focused on the application of branch and bound optimization, homotopy continuation method and interval-Newton/generalized bisection algorithm. The stochastic optimization techniques applied for solving phase equilibrium problems include point-to-point, population-based and hybrid stochastic methods.

There have been significant developments in global optimization and their applications to phase equilibrium problems. But, to the best of our knowledge, there is no review in the literature that focuses on the global optimization methods for phase equilibrium modeling and calculations. Therefore, use of both deterministic and stochastic global optimization methods to solve phase equilibrium problems in multi-component systems is reviewed in this paper. In particular, we focus on applications of global optimization for phase stability analysis, Gibbs free energy minimization in both reactive and non-reactive systems, parameter estimation in phase equilibrium models, and the prediction of azeotropes and critical points. The performance and capabilities of many global optimization methods for these thermodynamic calculations are discussed. The remainder of this review is organized as follows. The formulation of optimization problems for phase equilibrium modeling and calculations is presented in Section 2. In Section 3, we briefly describe the deterministic and stochastic optimization methods used for solving the optimization problems outlined in Section 2. Section 4 reviews the phase equilibrium modeling and calculations using global optimization algorithms. Finally, concluding remarks are given in Section 5 of this review.

2. PHASE EQUILIBRIUM MODELING AND CALCULATIONS

This section introduces the basic concepts and description of phase equilibrium problems considered in this review. Specifically, a brief description of the global optimization problems including the objective function, decision variables and constraints, for phase stability, physical and chemical equilibrium, and phase equilibrium modeling is given in the following sections.

2.1. Phase Stability

Phase stability analysis is a fundamental stage in phase equilibrium calculations. This analysis allows identification of the thermodynamic state that corresponds to the global minimum of Gibbs free energy (globally stable equilibrium). Additionally, the results of stability analysis can be used to begin phase-split calculations. According to the Gibbs criterion, a mixture at a fixed temperature T, pressure P and overall composition is stable if and only if the Gibbs free energy surface is at no point below the tangent plane to the surface at the given overall composition [1,4]. This statement is a necessary and sufficient condition for global stability. Generally, stability analysis is performed using the tangent plane distance function (TPDF). So, the phase stability of a non-reactive mixture with c components and overall composition $z = \{z_1, ..., z_c\}$ in mole fraction units, at constant P and T, requires the global minimization of:

$$TPDF = \sum_{i=1}^{c} y_i \left(\mu_i\big|_y - \mu_i\big|_z \right) \tag{1}$$

where $\mu_i\big|_y$ and $\mu_i\big|_z$ are the chemical potentials of component i calculated at a trial composition y and z, respectively. Physically, TPDF is the vertical distance between the Gibbs free energy surface at y and the tangent plane constructed to this surface at z. For more details on the explanation, derivation and implications of TPDF, see the work of Michelsen [4].

To perform stability analysis, TPDF must be globally minimized with respect to composition of a trial composition y, which is subject to an equality constraint. This constrained global optimization problem can be written as

$$\begin{aligned} &\min_{y} \ TPDF \\ &\text{subject to } \sum_{i=1}^{c} y_i = 1 \\ &0 \le y_i \le 1 \ \ i = 1, ..., c \end{aligned} \tag{2}$$

where the decision variables in phase stability problems are the mole fractions y_i. If the global minimum of $TPDF(y) < 0$, the mixture under analysis is unstable; else, it is a globally stable system. Note that the constrained problem given by Equation (2) can be transformed into an unconstrained problem by using new decision variables β_i instead of y_i as the decision vector [5-7]. These new decision variables $\beta_i \in (0,1)$ are related to mole fraction variables y_i as follows

$$n_{iy} = \beta_i z_i n_F \quad i = 1, ..., c \tag{3}$$

$$y_i = n_{iy} \Big/ \sum_{j=1}^{c} n_{jy} \quad i = 1, ..., c \tag{4}$$

where $n_F = \sum_{i=1}^{c} n_{iF}$ is the total number of moles in the (feed) mixture used for stability analysis, and n_{iy} is the mole numbers of component i in the trial phase y, respectively. Note that feed mole fractions z_i are given by $z_i = n_{iF} / n_F$. Thus, the unconstrained global optimization problem for phase stability analysis is:

$$\begin{aligned} &\min_{\beta} \ TPDF \\ &0 \le \beta_i \le 1 \ \ i = 1, ..., c \end{aligned} \tag{5}$$

Using this unconstrained approach, the number of decision variables is c for a non-reactive system of c components.

As an alternative to the optimization procedure, phase stability can be also determined by finding all solutions of the stationary conditions of TPDF:

$$\mu_i\big|_y - \mu_i\big|_z - \mu_c\big|_y + \mu_c\big|_z = 0 \ \ i = 1, ..., c-1 \tag{6}$$

where $c-1$ mole fractions of trial phase y are the unknowns of Equation (6), assuming that $\sum_{i=1}^{c} y_i = 1$. If TPDF at any of the solutions obtained by this set of equations is negative, then the postulated mixture z is unstable and will exhibit phase-split. From Equation (6), note that the trivial solution ($y = z$) is always present in this thermodynamic problem, and it corresponds to the global minimum of TPDF for the case of stable mixtures.

As suggested by Michelsen [4], the stability criterion is also applicable to chemically equilibrated phases, and consequently almost any method proposed for stability analysis of non-reactive systems can be extended to reactive mixtures.

2.2. Phase Equilibrium Calculations

After identifying an unstable system in phase stability analysis, the subsequent stage corresponds to phase equilibrium/split calculation. In these calculations, main objectives are to establish the correct number and types of phases at equilibrium as well as the composition and quantity of each phase [1]. At constant temperature T and pressure P, a c multi-component and π multi-phase non-reactive system achieves equilibrium when its Gibbs free energy is at the global minimum. There are two main approaches for performing phase equilibrium calculations: a) equation solving approach and b) Gibbs free energy minimization approach [2]. The former involves solving a set of non-linear equations arising from mass balances and equilibrium relationships, whereas the latter involves the direct minimization of Gibbs free energy function. Although the first approach seems to be faster and simple, the solution obtained may not correspond to the global minimum of free energy function. Moreover, it needs a priori knowledge of phases existing at equilibrium [2]. Therefore, minimization of Gibbs free energy is a natural approach for calculating the equilibrium state of a mixture.

In a non-reactive system with c components and π phases, the thermodynamic function for phase equilibrium calculations is expressed as a linear combination of the chemical potential of each component in each phase:

$$G = \sum_{j=1}^{\pi} \sum_{i=1}^{c} n_{ij}\mu_{ij} \tag{7}$$

where n_{ij} and μ_{ij} are respectively the number of moles and chemical potential of component i in phase j. The expression for G and its mathematical properties depend on the thermodynamic equation(s) chosen to model each of the phases that may exist at equilibrium. For a non-reactive system, G must be minimized with respect to the set of n_{ij} subject to mass balance constraints. Thus, the constrained global optimization problem for Gibbs free energy minimization is:

$$\min_{n} \; G$$

$$\text{subject to } \sum_{j=1}^{\pi} n_{ij} = z_i n_F \quad i = 1,...,c \tag{8}$$

$$0 \le n_{ij} \le z_i n_F \quad i = 1,...,c \quad j = 1,...,\pi$$

where z_i is the mole fraction of component i in the feed used for phase split calculations.

One can use new variables instead of n_{ij} as decision variables in the above optimization problem. Introduction of the new variables eliminates the restrictions imposed by material balances, reduces problem dimensionality and the optimization problem is transformed to an unconstrained one. For multi-phase non-reactive systems, real variables $\beta_{ij} \in (0, 1)$ are defined and employed as decision variables by using the following expressions:

$$n_{i1} = \beta_{i1} z_i n_F \quad i = 1,...,c \tag{9}$$

$$n_{ij} = \beta_{ij}\left(z_i n_F - \sum_{m=1}^{j-1} n_{im} \right) \quad i = 1,...,c; \quad j = 2,...,\pi - 1 \tag{10}$$

$$n_{i\pi} = z_i n_F - \sum_{m=1}^{\pi-1} n_{im} \quad i = 1,...,c \tag{11}$$

Thus, the unconstrained global Gibbs energy minimization problem is defined as

$$\min_{\beta} \; G$$
$$0 \le \beta_{ij} \le 1 \quad i = 1,...,c \quad j = 1,...,\pi - 1 \tag{12}$$

For Gibbs energy minimization, the number of phases existing at the equilibrium is usually assumed to be known *a priori*, and the number of decision variables in the unconstrained approach is $c\,(\pi - 1)$ for non-reactive systems.

2.3. Simultaneous Chemical and Physical Equilibrium

Reactive phase equilibrium calculations, also known as chemical equilibrium, are performed if a reaction is possible in the system under study. Note that reactions increase the complexity and dimensionality of phase equilibrium problems, and so phase split calculations in reactive systems are more challenging due to non-linear interactions among phases and reactions. The phase distribution and composition at equilibrium of a reactive mixture are determined by the global minimization of Gibbs free energy subject to mass balances and chemical equilibrium constraints. Based on the handling of material balance constraints, available strategies can be classified as either stoichiometric or non-stoichiometric [8].

For reactive phase equilibrium, the mass balance restrictions and non-negativity requirements are usually formulated using the conservation of chemical elements in the components [9]. Therefore, to determine the phase equilibrium compositions in reactive systems using this approach, it is necessary to solve the following constrained global optimization problem:

$$\min_{n} \; G$$

$$\text{subject to } \sum_{i=1}^{c}\sum_{j=1}^{\pi} d_{li} n_{ij} = b_l \qquad l = 1,...,m_e \tag{13}$$

$$0 \le d_{li} n_{ij} \le b_l \qquad i = 1,...,c;\ j = 1,...,\pi;\ \ l = 1,...,m_e$$

where d_{li} represents the number of gram-atoms of element l in component i, b_l is the total number of gram-atoms of element l in the feed mixture and m_e is the number of elements. The constrained global minimization of G is with respect to $c\pi$ decision variables n_{ij}.

For modeling reactive systems, the chemical equilibrium condition can be evaluated from either Gibbs free energy data or chemical equilibrium constants determined experimentally. Accordingly, we can use different objective functions for the constrained minimization of Gibbs energy function. In addition, this thermodynamic problem can be also formulated using transformed composition variables. For more details on different objective functions using both conventional and transformed composition variables as the decision vector for G minimization in reactive systems, see the recent study by Bonilla-Petriciolet *et al*. [10].

In particular, the constrained Gibbs free energy minimization using conventional composition variables is better in terms of computer time and numerical implementation, for reactive phase equilibrium calculations [10]. For a c multi-component and π multi-phase system subject to r independent chemical reactions, the objective function for reactive phase equilibrium calculations can be defined, using reaction equilibrium constants, as

$$G_K = \Delta g - \sum_{j=1}^{\pi} \ln \mathbf{K}_{eq} \mathbf{N}^{-1} \mathbf{n}_{ref,j} \tag{14}$$

where Δg is the Gibbs free energy of mixing, $\ln \boldsymbol{K}_{eq}$ is a row vector of logarithms of chemical equilibrium constants for r independent reactions, $\boldsymbol{N}$ is an invertible, square matrix formed from the stoichiometric coefficients of a set of reference components chosen from the r reactions, and $\boldsymbol{n}_{ref}$ is a column vector of moles of each of the reference components. Equation (14) must be globally minimized subject to the mass balance restrictions. Formally, the constrained global minimization of G_K can be stated as

$$\min_{n_{ij}} \ G_K$$

$$\text{subject to } \sum_{j=1}^{\pi} \left(n_{ij} - \mathbf{v}_i \mathbf{N}^{-1} \mathbf{n}_{ref,j} \right) = n_{iF} - \mathbf{v}_i \mathbf{N}^{-1} \mathbf{n}_{ref,F} \quad i = 1, \ldots, c - r \tag{15}$$

$$n_{ij} > 0 \ \ i = 1,...,c \ \ j = 1,...,\pi$$

where $n_{i,F}$ is the initial moles of component i in the feed, $\boldsymbol{v}_i$ is the row vector (of dimension r) of stoichiometric coefficients of component i in r reactions, and n_{ij} is the number of moles of component i in phase j. The constrained global optimization problem can be solved by minimizing G_K with respect to $c\ (\pi - 1) + r$ decision variables n_{ij}. In this formulation, the mass balance equations are rearranged to reduce the number of decision variables of the optimization problem and to eliminate equality constraints. For more details on the development of Equation (15), see the recent study of Bonilla-Petriciolet *et al*. [10].

2.4. Phase Equilibrium Modeling

The estimation of parameters in thermodynamic models is an important requirement and a common task in many areas of chemical engineering because these models form the basis for synthesis, design, optimization and control of process systems. In the case of separation processes, thermodynamic models play a major role with respect to energy requirements, phase equilibrium and equipment sizing. The parameter estimation problem refers to determining values of model parameters that provide the best fit to a set of measured data such as vapor-liquid or liquid-liquid equilibrium. In particular, estimation of parameters in non-linear thermodynamic models for vapor-liquid equilibrium (VLE) modeling has been of great interest in the chemical engineering literature. VLE data modeling using thermodynamic equations is generally based on classical least squares or maximum likelihood approaches [11]. In the classical least squares, it is assumed that there is a set of independent variables not subject to measurement error and only the dependent variables have errors, while errors in all measured variables are accounted in the maximum likelihood approach.

Consider a set of observations q_{ij} of i = 1, …, nd dependent/response variables from j = 1, …, ne experiments are available for the system, where the responses can be expressed by an explicit model $q_{ij} = f_i\ (\ \boldsymbol{r}_j,\ \boldsymbol{\theta})$, with independent variables $\boldsymbol{r}_j = (r_{1,j},\ldots,r_{nd,j})^T$ and $npar$ parameters $\boldsymbol{\theta} = (\theta_1,\ldots,\theta_{npar})^T$. Measurement errors in $\boldsymbol{r}_j$ can either be treated or neglected; depending on this choice, we can have either least squares (when errors in independent variable are neglected) or maximum likelihood formulation (when independent variables have measurement errors). For the case of classical least squares (LS) criterion, the objective function can be defined as:

$$F_{LS} = \sum_{j=1}^{ne}\sum_{i=1}^{nd} \left(\frac{q_{ij} - f_i\left(\mathrm{r}_j, \theta\right)}{q_{ij}} \right)^2 \tag{16}$$

This function is minimized with respect to the model parameters $\boldsymbol{\theta}$ inside specified bounds. Then, the global optimization problem is:

$$\begin{aligned} &\min_{\theta}\ F_{LS} \\ &\theta_{i,\min} \le \theta_i \le \theta_{i,\max}\ i = 1,...,npar \end{aligned} \tag{17}$$

For modeling VLE data (i.e., x–y–P at constant T, or x–y–T at constant P), excess Gibbs energy equations are widely employed. Therefore, the objective function commonly used for VLE data fitting is based on activity coefficients, and is usually defined as

$$F_{LS} = \sum_{j=1}^{ne}\sum_{i=1}^{c} \left(\frac{\gamma_{ij}^{\exp} - \gamma_{ij}^{calc}}{\gamma_{ij}^{\exp}} \right)^2 \tag{18}$$

where $\gamma_{ij}^{\exp}$ is the experimental value for the activity coefficient of component i in j^{th} experiment, γ_{ij}^{calc} is the calculated value for the activity coefficient of component i in j^{th} experiment, and c is the number of components in the mixture. Experimental data of activity coefficients $\gamma_i^{\exp}$ can be calculated from VLE data as follows:

$$\gamma_i^{\exp} = \frac{y_i^{\exp} P}{x_i^{\exp} P_i^0} \quad i=1,\ldots,c \tag{19}$$

where $x_i^{\exp}$ and $y_i^{\exp}$ are, respectively, the measured mole fraction of component i in the liquid and vapor phases at equilibrium, P_i^0 is the vapor pressure of pure component i at the system temperature T, and P is the pressure of the system. For Eq. (19), it is assumed that, at low pressure, the fugacity coefficients of pure components cancel each other and the values of Poynting corrections are very close to one. Thus, the global minimization of LS objective function can be done as an unconstrained optimization problem using local composition models under these conditions.

On the other hand, if we assume that there are measurement errors in all the variables z_{ij} (which include both independent and response variables) for the experiments of the system to be modeled, the minimization problem to be solved is the error-in-variable (EIV) formulation of the form:

$$F_{EIV} = \sum_{j=1}^{ne} \sum_{i=1}^{nest} \frac{\left(z_{ij}^t - z_{ij}\right)^2}{\sigma_i^2} \tag{20}$$

Here, *nest* is the number of state variables, z_{ij}^t is the unknown "true" value of i^{th} state variable in j^{th} measurement, and σ_i is the standard deviation associated with the measurement of i^{th} state variable. The decision variables of EIV problem are the set of z_{ij}^t and the model parameters $\boldsymbol{\theta}$. Formally, we have to solve a constrained global optimization problem, which is given by

$$\min_{z^t,\theta} F_{EIV}$$

$$\text{subject to } \mathrm{g}\left(z_{ij}^t, \theta\right) = 0 \quad i = 1,...,nest \quad j = 1,...,ne \tag{21}$$

$$\theta_{i,\min} \le \theta_i \le \theta_{i,\max} \quad i = 1,...,npar$$

$$z_{ij,\min}^t \le z_{ij}^t \le z_{ij,\max}^t \quad i = 1,...,nest \quad j = 1,...,ne$$

where $\boldsymbol{g}$ is a vector of np model functions. In the EIV formulation, there is a substantial increase in the dimensionality of the optimization problem, which depends on the number of experiments. If the model functions $\boldsymbol{g}$ are explicit in z_{ij}, then they can be eliminated by direct substitution of z_{ij} in the objective function, and the above optimization can be solved as an unconstrained problem. For the case of VLE data, the state variables are x, y, P and T with standard deviations (σ_x, σ_y, σ_P and σ_T). Therefore, the common objective function for VLE data modeling using the EIV approach is

$$F_{obj} = \sum_{j=1}^{ne} \sum_{i=1}^{c} \left[\frac{\left(x_{ij}^t - x_{ij}\right)^2}{\sigma_{x_i}^2} + \frac{\left(y_{ij}^t - y_{ij}\right)^2}{\sigma_{y_i}^2} \right] + \sum_{j=1}^{ne} \left[\frac{(T_j^t - T_j)^2}{\sigma_T^2} + \frac{(P_j^t - P_j)^2}{\sigma_P^2} \right] \tag{22}$$

which is optimized with respect to $npar + c \times ne$ decision variables.

2.5. Calculation of Critical points and Azeotropes

Both critical points and azeotropes are special cases of phase equilibrium calculations, and are important topics because of their theoretical and practical implications for design of separation processes. They can occur in both reactive and nonreactive mixtures, and a mixture may have one, more than one or no critical points and/or azeotropes. Therefore, the correct prediction of phase behavior requires the determination of all critical points and azeotropes, or determining with certainty that there are none in the domain of interest [12, 13].

For nonreactive mixtures, homogeneous azeotropes occur when the compositions of vapor and liquid phases at equilibrium are identical. The same definition applies for homogeneous azeotropes in reactive systems but using reaction-invariant composition space [14]. For a mixture of c components, the thermodynamic conditions that a homogeneous azeotrope should satisfy is based on the equality of chemical potentials

$$\mu_{iL} - \mu_{iV} = 0 \quad i=1,\ldots,c \tag{23}$$

Equation (23) is a system of c non-linear equations with $c-1$ unknown compositions, x_i^{azeo} plus the unknown temperature or pressure of the azeotrope.

On the other hand, definition of the critical point of a mixture is as follows: at the critical point, the intensive properties of two phases in equilibrium become identical [15]. In particular, the Heidemann-Khalil formulation of the criticality conditions is the most widely used criteria in the literature for calculation of critical points [16]. Specifically, the criticality conditions for a mixture of c components are given by

$$Q\Delta\boldsymbol{n} = 0,\ \Delta\boldsymbol{n}^{\mathrm{T}}\Delta\boldsymbol{n} = 1 \tag{24}$$

$$\sum_{i=1}^{c}\sum_{j=1}^{c}\sum_{k=1}^{c} A_{ijk}\Delta n_i \Delta n_j \Delta n_k = 0 \tag{25}$$

In Eq. (24), the $c \times c$ matrix Q has elements

$$Q_{ij} = A_{ij} = \left(\frac{\partial^2 A}{\partial n_i \partial n_j} \right)_{T,V} \tag{26}$$

$$A_{ijk} = \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k} \right)_{T,V} \quad (27)$$

In the above equations, A is the Helmholtz free energy and n_i, n_j and n_k are the component mole numbers. The derivatives A_{ij} and A_{ijk} are evaluated at the given mixture composition $n_0 = (n_{1,0}, n_{2,0},\ldots, n_{c,0})$. Equations (24) and (25) is a system of $c + 2$ non-linear equations in $c + 2$ variables: T, V and $\Delta \boldsymbol{n} = (\Delta n_1, \Delta n_2,\ldots, \Delta n_c)$, where each element represents a nonzero perturbation in the component mole number. Note that Equations (23), (24) and (25) can be used for prediction of both homogeneous azeotropes and critical points in reactive systems if reaction invariant composition variables are used [14, 17].

The prediction of both azeotropes and critical points is reduced to locating all roots of a system of non-linear equations. Such systems of equations can be transformed to an optimization problem in order to use global optimization methods. Specifically, the objective function used for these thermodynamic calculations is given by

$$F_{obj} = \sum_{i=1}^{nle} f_i^2 \quad (28)$$

where f_i is given by Eq. (23) for azeotrope calculations or Eqs. (24) and (25) for critical point determination. If F_{obj} (x*) = 0, then it implies that x* is a global minimum and subsequently $f_1(x^*) = f_2(x^*) = \ldots = f_{nle}(x^*) = 0$, and thus x* is a root (i.e., azeotrope or critical point) for the corresponding system of equations. Finding all x* such that $F_{obj}(x^*) = 0$ corresponds to locating all roots of the system.

3. GLOBAL OPTIMIZATION METHODS

As stated, global optimization problems involved in the modeling and calculation of phase equilibrium are very challenging. This is because the objective functions are multivariable, non-convex and highly non-linear. For example, global minimization of TPDF and G are difficult tasks and require robust numerical methods, since these objective functions often have unfavorable attributes such as discontinuity and non-differentiability (e.g., when cubic equations of state or asymmetric models are used for modeling thermodynamic properties). Additional complexities arise near the phase boundaries, in the vicinity of critical points or saturation conditions, and when the same model is used for determining the thermodynamic properties of the mixture [1, 2]. Consequently, TPDF and G may have several local minima including trivial and non-physical solutions.

Parameter estimation problems too can be very difficult to solve reliably even for simple thermodynamic models [18-20]. Specifically, a number of pitfalls and difficulties may be faced in parameter estimation for VLE modeling; these include convergence to a local minimum, flat objective function in the neighborhood of the global optimum, badly scaled model functions and non-differentiable terms in thermodynamic equations. In addition, the number of optimization variables can be very large, especially for EIV problems. Failure to find the globally optimal parameters for a thermodynamic model and using locally optimal parameters instead, can have significant consequences in phase equilibrium calculations and predictions, may cause errors and uncertainties in equipment design and erroneous conclusions about model performance. Recent studies have shown that using the locally optimal parameters may result in incorrect predictions of the azeotropic states with local composition models and in qualitative discrepancies of the phase behavior such as prediction of spurious phase split and modeling of homogeneous azeotropes as heterogeneous [18,19]. In summary, several studies have demonstrated the challenging nature of global optimization problems for phase equilibrium modeling and calculations, and they have highlighted the need for reliable numerical techniques to overcome these difficulties.

Global optimization methods can be classified into two broad categories: deterministic and stochastic methods [21]. The former methods can provide a guaranteed global optimum but they require certain properties of objective function and constraints such as continuity and convexity. In some cases, problem reformulation is needed depending on the characteristics of the model under study. The stochastic methods generally require little or no assumption on the characteristics of the optimization problem, and yet provide a high probabilistic convergence to the global optimum. Further, stochastic methods are easy to understand, implement and use. Although they do not guarantee global optimality, they can often locate the global optimum in modest computational time compared to deterministic methods [22]. This section provides the basic concepts and description of deterministic and stochastic methods used for global optimization in phase equilibrium calculations and modeling.

3.1. Deterministic Methods

Deterministic optimization methods are those which exploit analytical properties of the problem to generate a deterministic sequence of points (finitely or infinitely) converging to a global optimum [23]. These methods include branch and bound global optimization, homotopy continuation methods, Lipschitz optimization and interval analysis [3]. In the following sections, we briefly summarize different deterministic global optimization methods applied to phase equilibrium calculations and modeling.

3.1.1. Branch and Bound Global Optimization

Branch and bound algorithms are a variety of adaptive partition strategies that have been proposed to solve global optimization problems [3]. These methods are based upon partitioning, sampling, and subsequent lower and upper bounding procedures. These operations are iteratively applied to the collection of active (i.e., candidate) subsets within the feasible set D. Branch and bound methods are non-heuristic, in the sense that they maintain provable upper and lower bounds on the globally optimal objective value; they terminate with a certificate that the optimal point found is ε-suboptimal.

Branch and bound methods include many specific approaches, and allow for a variety of implementations. These methods typically rely on some a priori knowledge of objective function characteristics and in developing proper structures (i.e., convex terms) of the optimization problem. The general branch and bound methodology is applicable to broad classes of global optimization problems. In general, these optimization algorithms are often slow and require a significant numerical effort that grows exponentially with problem size [1, 24].

3.1.2. Homotopy Continuation Methods

A continuation method is considered as a global method since it has the capability of finding all roots of a set of nonlinear equations. In brief, homotopy continuation methods provide a smooth transition between an approximate solution (often linear or nearly linear) and the true solution(s) of a nonlinear equation system, $\boldsymbol{f}(\boldsymbol{u}) = \boldsymbol{0}$ by gradually introducing the nonlinearities through the use of a scalar homotopy parameter t [25, 26]. These methods are global methods for finding the zeros of nonlinear functions. For global optimization, $\boldsymbol{f}(\boldsymbol{u})$ is a system of non-linear equations obtained from the stationary conditions of the optimization problem. Newton homotopy is usually used in the literature, and it has the form:

$$\boldsymbol{H}(\boldsymbol{u}, t) = t\,\boldsymbol{f}(\boldsymbol{u}) - (1 - t)\,\boldsymbol{g}(\boldsymbol{u}) = \boldsymbol{0} \tag{29}$$

where $\boldsymbol{f}(\boldsymbol{u})$ is the system of equations to be solved, $\boldsymbol{g}(\boldsymbol{u})$ is a simple system of equations for which a solution is known or easily found and t is a scalar homotopy parameter, which is gradually varied from 0 to 1 as the path is tracked from the starting point to the true solution.

Note that starting at $t = 0$, $\boldsymbol{H}(\boldsymbol{u}, 0) = 0$ is trivial to solve given any initial vector, $\boldsymbol{u}^0$. A homotopy path is generated as t increases to unity, where the true solutions occur. A predictor-corrector method can be applied to trace the homotopy paths by integrating along their arc lengths. Beginning on the homotopy path, a tangent vector is computed and a step is taken along the direction of its arc length (Euler's method). The algorithm calculates tangent vectors by solving an initial-value problem. The resulting homotopy paths resemble the solution diagrams obtained through parameterization. When a unique and continuous path exists for $\boldsymbol{H}(\boldsymbol{u}, t)$ from $t = 0$ to $t = 1$, the Newton homotopy-continuation algorithm guarantees global convergence to a single solution; however, it does not guarantee global convergence to multiple solutions. Note that success in finding all solutions along a single path has only been demonstrated for simple polynomials when all variables are relaxed from the real to the complex domain. Therefore, continuation methods can be implemented in both real and complex search spaces [27].

3.1.3. Interval Analysis

The interval analysis method is a general-purpose computational method to solve nonlinear equations to find all solutions lying within the variable bounds [28, 29]. Specifically, consider the solution of a nonlinear equation system, $\boldsymbol{f}(\boldsymbol{u}) = \boldsymbol{0}$ where $\boldsymbol{u} \in \boldsymbol{U}^0$ and the goal is to enclose, within very narrow intervals, all roots of the equation system in $\boldsymbol{U}^0$. The algorithm is applied to a sequence of intervals, beginning with the initial interval vector $\boldsymbol{U}^0$ specified by the user. For an interval $\boldsymbol{U}^k$ in the sequence, the first step in the solution procedure is the function range test. The interval extension $\boldsymbol{F}(\boldsymbol{U}^k)$ of $\boldsymbol{f}(\boldsymbol{u})$ over the current interval $\boldsymbol{U}^k$ is computed and tested to determine whether it contains zero. If not, then clearly there is no root of $\boldsymbol{f}(\boldsymbol{u}) = \boldsymbol{0}$ in this interval and can be discarded. If $\boldsymbol{U}^k$ passes the function range test, then the next step is the interval Newton test. This step requires an interval extension of the Jacobian matrix of $\boldsymbol{f}(\boldsymbol{u})$ and involves setting up and solving the interval Newton equation (a system of linear interval equations) for a new interval, which is usually referred as the image. Comparison of this image to the current interval being tested provides an existence and uniqueness test for roots of the equation system. Note that a reasonable initial interval should be wide enough so that the interval Newton method provides all the solutions of local minima and maxima, saddle points and global minimum for the optimization problem under study [30, 31].

3.2. Stochastic Methods

Stochastic optimization methods involve probabilistic elements and use random sequences in the search for the global optimum [21]. These methods employ heuristics for exploring (diversification) and exploiting (intensification) the search space, and learning strategies are used to find quickly near-optimal solutions [22]. The balance between diversification and intensification is important to equilibrate between reliability and computational efficiency (i.e., improve the effectiveness) of finding the global optimum by the stochastic algorithm. Stochastic optimization methods manipulate a single (i.e., point-to-point methods) or a collection of solutions (i.e., population-based methods) at each iteration or objective function evaluation. They include random search, simulated annealing, particle swarm optimization, tabu search, genetic algorithms, differential evolution, ant colony optimization and harmony search. In the following sections, we describe the general characteristics of several stochastic methods used in phase equilibrium modeling and calculations.

3.2.1. Random Search

The original random search method is pure random search (PRS) which was first defined by Brooks [32]. It is the simplest algorithm among the random search methods, and consists of generating a sequence of uniformly distributed points in the feasible region, while keeping track of the best point that was already found. PRS offers a probabilistic asymptotic guarantee that the global minimum will be found with probability one as the sample size grows to infinity. Among the random search methods, a direct search algorithm (also called adaptive random search, ARS) proposed by Luus and Jaakola has found many applications in chemical engineering; it uses random search points and systematic region reduction for locating the global optimum [33].

The ARS algorithm begins with a feasible initial point and region size vector r. Then, it generates a number of random points R around the initial point. The feasibility of each randomly chosen point is checked. The objective function values of such feasible points are found, and the best point is recorded. In the next iteration, R random points are generated around the best point found so far and the same procedure is repeated. After each iteration, the region size is reduced by a certain factor. Iterations are continued until the termination criterion is satisfied. Pseudo-code of ARS is shown in Algorithm 1, and details of this optimization procedure can be found in [34, 35]. There are several versions of ARS, which have been applied to different chemical engineering application problems [36-39].

Algorithm 1 Pseudo-code of Adaptive Random Search

```
Set region size vector r and x_best = Ø
Give a feasible initial point x_0 within the search space
While the stopping criterion is not satisfied
    Randomly generate R points, x_i around x_0
    Check the feasibility of each x_i
    For i = 1 to R
        If x_i is feasible then
            Evaluate x_i
        End if
    End for
    Update x_best based on the objective function value and let x_0 = x_best
        Reduce the region size by a certain factor
End while
```

3.2.2. Simulated Annealing

Simulated annealing (SA), which was developed by Kirkpatrick *et al*. [40], is a stochastic method inspired by the analogy to annealing of metals. In the physical process of annealing, a metal is first heated to its molten state and then slowly cooled to solid state in order to reach thermal equilibrium with minimum energy. This process of slow, controlled cooling scheme of the melted metal to obtain the desired crystalline structure is simulated in SA. It starts from an initial point in the search space and a given high temperature T. A new point is randomly created in the neighborhood of the initial point, and its energy (objective function) is evaluated. If this new point has lower energy than the previous one, it is accepted; otherwise, the new point is accepted with probability, $P = \exp(-\Delta E/K_B T)$ where ΔE is the difference in the energy of these two points, K_B is the Boltzmann constant. Generation of new points and their evaluation/acceptance are repeated N time at the same temperature to ensure the system is in thermal equilibrium at this T. After that, T is reduced according to the cooling schedule and the same procedure is repeated until the termination criterion is satisfied. The probability of acceptance, P decreases as the search progresses because of lower T.

From mathematical point of view, SA can be viewed as a randomization device that allows wrong-way movements during the search for the optimum through an adaptive acceptance/rejection criterion. Based on this concept, SA not only accepts the point with better value but also accepts a point with worse value with some probability, which decreases as search progresses. The main control parameter in the cooling schedule is the temperature, T. The main role of T is to let the probability of accepting a new move be close to 1 in the earlier stage of the search and to make it almost zero in the final stage of the search. Convergence to an optimal solution can theoretically be guaranteed after an infinite number of iterations controlled by the procedure of cooling schedule. Pseudo-code of SA is shown in Algorithm 2, and more details of this optimization method are available in Chibante [41]. Various versions of SA have been proposed and applied to chemical engineering problems [42-45].

Algorithm 2 Pseudo-code of Simulated Annealing

```
Choose an initial point x_o
While the stopping criterion is not satisfied
    For i = 1 to N
        Randomly generate x_new around x_0
        ΔE = f(x_new) − f(x_o)
        If ΔE < 0 then
            x_o = x_new
        Else
            If random(0,1) < exp (-ΔE/K_B T) then
                x_0 = x_new
            End if
        End if
    End for
    Reduce T according to cooling schedule
End While
```

3.2.3. Genetic Algorithm

Genetic algorithm (GA), developed by Holland [46], is inspired by the evolutionary process occurring in nature. The main ideas of this algorithm are the 'survival of the fittest', and crossover and mutation operations for generating a new solution. GA starts with initializing a population of individuals or trial solutions, which are generated randomly within the feasible region. Objective function value of these individuals is evaluated. The individuals undergo three main operations, namely, reproduction, crossover and mutation. Reproduction creates a mating pool in which the individuals with good fitness will have more copies than the ones with lower fitness value. Crossover is an operation which allows the algorithm to explore the entire search space and to escape from the local minima. In this operation, new strings

(individuals) are formed by exchanging the information among parents of the mating pool. Mutation operation involves making changes in each individual directly. Mutation is exploitative; it can create random small diversions, thereby staying near the parent. After the mutation, the new population is created.

The new population enters into the next generation and the same process of reproduction, crossover and mutation is repeated until the stopping criteria are satisfied. Since the selection of the population for the mating pool is based on the survival of the fittest, the solutions will converge towards its optimal point. GA is probably the most widely known stochastic algorithm, and has found many applications in chemical engineering [5, 10, 47, 48]. Pseudo-code of GA is shown in Algorithm 3, and more details of this stochastic method can be found in Younes *et al*. [49].

Algorithm 3 Pseudo-code of Genetic Algorithm

Initialization:

Randomly generate *NP* individuals within the search space

Evaluate objective function of each of the individuals generated

While the termination criterion is not satisfied

Reproduction: Create a mating pool of parents

Crossover: New individuals formed from parents

Mutation: Randomly modify the new individuals

Selection: Offspring created by crossover and mutation replaces the original parent population based on its fitness

End While

3.2.4. Tabu Search

Tabu (or taboo) Search (TS) was developed by Glover in 1989 [50]. Tabu means that the things must be left alone and should not be visited or touched. Accordingly, the main idea of TS is that the points searched by the algorithm should not be re-visited. This procedure enhances the searching capability of the solution space economically and effectively. Initially, a set of candidate solutions is evaluated and then stored in a taboo list. Then, each new solution generated is compared with the solutions in the taboo list. If the new solution is near to any point in the taboo list, then it will not be evaluated and discarded right away. The length of taboo list is defined by the user. If a new solution enters into the taboo list, the oldest solution in the taboo list will be removed to keep the specified length of the taboo list. After a number of iterations, several promising areas containing the global optimum solution will be found. Then the intensive search is carried out from these areas to find the global optimum. See the pseudo-code of TS is given in Algorithm 4. For more details on this stochastic optimization method, see the book by Glover and Laguna [50] and the book chapter by Sim *et al*. [51]. TS has been successfully applied to a wide range of optimization problems [6, 52-55].

Algorithm 4 Pseudo-code of Tabu Search

Randomly generate N initial points, X_i within the search space

Evaluate objective function of all these points, and send them to tabu list

While the termination criterion is not satisfied

For i =1 to N

Generate a new point $X_{i,new}$

If $X_{i,new}$ is near any point in the tabu list then

Discard $X_{i,new}$

End if

End for

Evaluate the objective function at all the remaining points $X_{i,new}$

Update tabu list

End while

3.2.5. Differential Evolution

Differential evolution (DE) was proposed by Storn and Price in 1997 [56]. The main idea behind it is taking the difference between two individuals and adding it to another individual to produce a new individual. It contains four steps similar to GA, namely, initialization of population, mutation, crossover and selection (see the pseudo-code in Algorithm 5). The main difference between DE and GA is that the search is guided by mutation in the former whereas it is governed by the crossover in the latter. DE algorithm starts with a randomly generated initial population within the search region. For each (target) individual in the population, three other individuals are randomly selected, and the weighted difference between two of them is added to the third individual in order to produce a mutant individual. This operation is called as mutation. Elements of the mutant individual thus obtained are copied to the target individual using crossover constant/probability to produce a trial individual, in the crossover operation. In the selection operation, the better one between the trial and target individuals is selected based on the objective function values, for the next generation. This selection of the fittest individual causes the individuals to improve over the generations, finally converging to an optimum. DE has been successfully applied to a wide range of optimization problems [6, 57]. More details of DE can be found in Price *et al*. [58].

Algorithm 5 Pseudo-code of Differential Evolution

Initialization:

Randomly generated N individuals (x_i) within the search space

Evaluate the objective function of all these individuals, and find the best, X_{Best}

While the termination criterion is not satisfied

For i =1 to N

Randomly choose 3 individuals ($x_{r1} \neq x_{r2} \neq x_{r3}$) from the current population

Mutation to find mutant individual: $v_i = x_{r1} + F\,(x_{r2} - x_{r3})$
Crossover: For $j = 1$ to D

If rand(0,1) $\geq$ Cr then

$u_{i,j} = v_{i,j}$

Else

$u_{i,j} = x_{i,j}$

End If

End For

Find the objective function of the new (trial) individual

Between u_i and x_i, the better one goes to next generation

Update X_{Best}

End For

End While

3.2.6. Particle Swarm Optimization

Particle swarm optimization (PSO), developed by Eberhart and Kennedy in 1995 [59], exploits swarm intelligence (i.e., the behavior of a biological social system like a flock of birds or a school of fish) for finding the global optimum. This search algorithm is also a population-based stochastic optimization technique. The swarm in PSO consists of a number of particles, each of which represents a potential solution in the search space. Each particle moves to a new position according to certain velocity and the previous position of the particle.

PSO algorithm starts with a randomly generated initial population of particles in the search space. Unlike other evolutionary optimization methods, particles in PSO do not recombine genetic material directly between individuals during the search, but work according to the social behavior of swarms instead. Therefore, PSO finds the global best solution by simply adjusting the moving vector of each individual according to the personal best and the global best positions of particles in the entire swarm at each time step (generation). In other words, the search process allows particles to stochastically return toward previously successful regions in the search space. Recent developments and applications of PSO can be found in [60-63]. Pseudo-code PSO is presented in Algorithm 6, and more details of this method can be found in Kennedy *et al*. [64].

Algorithm 6 Pseudo-code of Particle Swarm Optimization

Initialization:

Randomly generate N particles (x_i), velocities (v_i) and positions ($pbest_i$)

Evaluate objective function of all the particles

Set global best particle to *gbest*

While the termination criterion is not satisfied

For $i = 1$ to N

$v_i = w v_i + c_1 \text{rand}(0,1)(pbest_i - x_i) + c_2 \text{rand}(0,1)(gbest - x_i)$

$x_i = x_i + v_i$

Evaluate the objective function of the new particle

If x_i better than $pbest_i$

$pbest_i = x_i$

End if

If x_i better than *gbest*

$gbest = x_i$

End if

End for

End While

3.2.7. Random Tunneling Algorithm

The tunneling method was first introduced by Levy and Montalvo [65]. It is composed of a sequence of cycles, where each cycle has two phases: a local minimization phase and a tunneling phase. In the first phase, a minimization algorithm such as gradient descent or Newton's method is used to minimize the given objective function, $f(x)$ to locate the first local minimum, x^*. In the second phase, the method searches for the zeros of the tunneling function such that $x^0 \neq x^*$ but $f(x^0) = f(x^*)$ Then, the zero point is used as the starting point of the next cycle, and the two phases are repeated sequentially until a stopping criterion such as failure to find a zero within the prescribed CPU time is met.

One of the tunneling algorithms, namely, random tunneling algorithm (RTA) was developed by Jiang *et al*. [66]. It is a stochastic algorithm based on the concepts of sub-energy transformation and terminal repeller in the terminal repeller and unconstrained sub-energy tunneling (TRUST) algorithm of Cetin *et al*. [67]. RTA consists of two phases: a global search phase and a local optimization phase. The global phase perturbs the system randomly from the last local minimum and solves a system of differential equations from the perturbed point to explore new regions of attraction. Then, the local phase employs a local optimization method (e.g., Quasi-Newton method) to find an improved point in the new region.

Srinivas and Rangaiah [68] implemented RTA differently, as in Algorithm 7; it starts with setting parameter values and randomly generating an initial point within the search space. A local optimization is performed from this point to find the local optimum in this area. Then, tunneling phase is started from this local minimum which comprises of three steps. The first step is random perturbation from the current local minimum, and the second step involves tunneling from the perturbed point in a random direction using uniform grid search until it hits the boundary. The third step consists of 1D tunneling from the perturbed point along each

Algorithm 7 Pseudo-code of Random Tunneling Algorithm

```
Initialization:
    Randomly generate a point, x, within the search space
While termination criterion is not satisfied
    Local phase: Local search starts from x and optimum found is x*
    Tunneling: Do
        Random perturbation from the best local minimum x*
        Perform tunneling from perturbed point along a random direction
        1D tunneling from perturbed point along each coordinate axis
        If any point is better than x* then
            Exit Do and go to Local phase
        End if
    Until maximum number of perturbations exceed
        Set last perturbed point as new initial guess x
End while
Local search starts from x and optimum found is x*
```

coordinate axis. The three steps of tunneling phase are repeated until the number of perturbations reaches the maximum number or a better point is found. If any better point is found, the tunneling phase will be terminated, and this better point will be the new initial guess for the local minimization phase; else, the last perturbed point will be the new initial guess. In the local minimization step, a new local minimum is found and compared with the previous local minima, and the best minimum is taken as the current local minimum for the subsequent tunneling phase. The cycle of local minimization and tunneling is repeated until the number of tunneling phases reaches the maximum specified number. The algorithm then terminates declaring the last/best local minimum as the global minimum. More details about this RTA algorithm can be founded in Srinivas and Rangaiah [68].

3.2.8. Ant Colony Optimization

Ant colony optimization (ACO) is a novel meta-heuristic that mimics foraging behavior of real ant colonies. The first ant algorithm was developed by Dorigo *et al*. in 1996 [69], and since then several improvements of the ant system have been proposed [70]. It is an evolutionary approach where several generations of artificial ants search for good solutions in a co-operative way. These ants deposit pheromone on the ground for making some favorable paths that should be followed by other members of the colony. Note that the indirect communication between the ants is performed by means of pheromone trails which enable them to find short paths between their nest and food sources. This characteristic of real ant colonies is exploited in ACO algorithms in order to solve optimization problems. On the other hand, pheromone evaporation is a process of decreasing the intensities of pheromone trails over time. This process is used to avoid local convergence and to explore more in the search space. The meta-heuristic of classical ACO consists of three basic components, and its pseudo-code is given by:

```
While termination conditions not met, do
    Schedule activities
        Ants generation and activity
        Pheromone evaporation
        Daemon actions
    end Schedule activities
End while
```

Ants find solutions, starting from an initial value and moving to feasible neighbor regions, in the step of *Ants generation and activity*. During this step, information collected by ants is stored in the so-called pheromone trails. An agent-decision rule, made up of the pheromone and heuristic information, guides the ant's search toward neighbor regions stochastically. Objective function values of candidate solutions are usually used to modify the pheromone values in a way that is deemed to bias future sampling towards high quality solutions. However, due to *pheromone evaporation*, later generations of ants have smaller influence of the pheromone values than earlier or more recent ones. Ants use this information and make their decisions according to the probability distribution determined by the relative size of the pheromone values corresponding to the possible outcomes of the decision variables. Finally, *Daemon actions* are optional for ACO, and they can be used to implement centralized actions which cannot be performed by single ants. Examples are the application of local search methods to the constructed solutions, or the collection of global information that can be used to decide whether it is useful or not to deposit additional pheromone to bias the search process from a non-local perspective. Details of this stochastic optimization method can be found in [70].

3.2.9. Harmony Search

Harmony search (HS) is a music-inspired meta-heuristic algorithm, which has been introduced by Geem *et al*. in 2001 [71]. This stochastic optimization method was developed in an analogy with music improvisation process where music players improvise the pitches of their instruments to obtain better harmony. Specifically, when musicians improvise they may perform the following steps: playing an existing score from memory, performing variations on an existing piece, or creating an entirely new composition. In the optimization context, each musician is replaced with a decision variable, and the possible notes in the musical instruments correspond to the possible values for the decision variables. So, the harmony in music is analogous to the vector of decision variables, and the musician's improvisations are analogous to local and global search schemes in optimization techniques. HS combines heuristic rules and randomness to imitate this music improvisation process.

Briefly, HS involves three stochastic operators to perform both diversification and intensification stages: a) memory consideration, b) pitch adjustment, and c) random selection. Pseudo-code of HS is given by:

While termination conditions not met, do

Perform Improvisation (i.e., generate a new solution)

Memory consideration

Pitch adjustment

Random selection

end Improvisation

End while

The diversification is controlled by the pitch adjustment and random selection operators, while memory consideration is generally associated with the intensification. The proper combination of these operators is important to favor the performance of HS in global optimization. This iterative procedure is repeated until a proper convergence criterion is satisfied. Recently, some modifications have been proposed in the literature to improve the convergence performance of the original HS. According to Geem [72], variations proposed for HS may involve: a) mechanisms for the proper initialization of HS parameters, b) mechanisms for the dynamic adaptation of HS parameters during optimization, and c) the application of new or modified HS operators that include hybrid methods using other meta-heuristics such as simulated annealing or differential evolution. For example, two typical and promising variants of HS are the Improved HS and the Global-Best HS. For more details on this meta-heuristic, consult the book by Geem [72].

3.2.10. Hybrid Methods

In recent years, many hybrid methods have been proposed and studied. A judicious combination of effective concepts of different meta-heuristics can provide a better algorithm for dealing with real world and large scale problems [73]. The hybrid algorithm usually provides several advantages such as better solution using less computational time and handle large or difficult problems [7, 74-77]. We focus here on hybrid algorithms that have been applied to phase equilibrium modeling and calculations.

Srinivas and Rangaiah [7] proposed a hybrid method which combines DE and tabu list of TS. The tabu list used in DE can avoid re-visiting the same area, increase the diversity of the population, avoid unnecessary function evolutions, enhance global exploration and prevent premature convergence. The proposed method was shown to be more reliable and efficient compare to many other stochastic algorithms [10, 20]. Chaikunchuensakun *et al*. [78] presented a combined algorithm based on nonlinear parametric optimization (NLQPB) routines. It solves the Kuhn-Tucker conditions by minimizing a quadratic sub-problem with linearized equality and inequality constraints. The solution vector of the quadratic sub-problem is used as a search direction until sufficient decrease of a merit function is found. The approximate Hessian matrix is updated for each quadratic sub-problem by the quasi-Newton algorithm. Mitsos and Barton [79] proposed a hybrid method which combines CPLEX and BARON solvers in GAMS. The upper bound of the problem is solved with CPLEX, and lower bound of the problem is solved through BARON in order to enhance its reliability. Pereira *et al*. [80] combined three solvers in GAMS, where BARON is used for global optimization, MINOS is used as a nonlinear solver and CPLEX is used for linear problems. The proposed algorithm can solve challenging optimization problems.

Srinivas and Rangaiah [81] proposed two versions of DE with tabu list, referred as DETL-G (wherein the tabu list is implemented in the generation step) and DETL-E (wherein the tabu list is implemented in the evaluation step). These two algorithms combine the good reliability of DE with the computational efficiency of TS. Recently, Zhang *et al*. [63] proposed a novel bare-bones particle swarm optimization for parameter estimation of vapor-liquid data modeling problems. The proposed method combines the mutation strategy of differential evolution with bare-bones particle swarm optimization for a good balance between the exploration and exploitation to enhance the global search ability.

Besides the above hybrid methods, one common approach is to use stochastic algorithm for global search followed by a local optimizer for intensifying search. Accordingly, a local optimizer has been combined with stochastic optimization algorithms such as GA, SA, PSO, DE and HS [5, 6, 45, 62, 82-86].

4. APPLICATIONS OF GLOBAL OPTIMIZATION METHODS TO PHASE EQUILIBRIUM MODELING AND CALCULATIONS

The following sections summarize studies, mainly from the year 2000, on application and evaluation of deterministic and/or stochastic global optimization methods to phase equilibrium modeling (in Section 4.1), phase stability analysis (in Section 4.2) and/or phase equilibrium calculations (in Section 4.3), and prediction of critical points and azeotropes (in Section 4.4).

4.1. Applications to Phase Equilibrium Modeling

Deterministic and stochastic global optimization methods have been applied to parameter estimation in VLE modeling, which are summarized in Table **1**. In comparison to phase equilibrium calculations, there are fewer studies on the solution of parameter estimation problems for phase equilibrium modeling using global optimization methods. Specifically, Esposito and Floudas [87] have reformulated the optimization problem in terms of convex under-estimating functions and then used a branch-and-bound procedure to solve parameter estimation problems using vapor-liquid equilibrium equations. This method provides a mathematical guarantee of global optimality but, in general, it may be necessary to perform problem reformulation and develop convex under-estimators specific to each new application. Gau *et al*. [18] and Dominguez *et al*. [88] have used an interval analysis approach and classical least square formulation for modeling vapor-liquid equilibrium data. These studies indicated that several sets of parameter values of local composition models published in the DECHEMA VLE Data Collection correspond to local optima. These authors also showed that these locally optimal parameters

Table 1. Application of Global Optimization Methods to Modeling Vapor-Liquid Equilibrium Data

Method (Reference)	Problem Formulation	Thermodynamic Models
Branch and Bound (Esposito and Floudas, 1998) [87]	Error-in-variable	Local composition model and ideal gas
Interval Analysis (Gau *et al*., 2000; Dominguez *et al*., 2002) [18,88]	Least squares	Local composition models and ideal gas
Interval Analysis (Gau and Stadtherr, 2002) [89]	Error-in-variable	Local composition model and ideal gas
Simulated Annealing (Costa *et al*., 2000) [90]	Least squares	Equation of state
Simulated Annealing (Bonilla-Petriciolet *et al*., 2007) [45]	Least squares and Error-in-variable	Local composition model and ideal gas
Random Tunneling (Srinivas and Rangaiah, 2006) [68]	Error-in-variable	Local composition model and ideal gas
Genetic Algorithm (Alvarez *et al*., 2008) [47]	Least squares	Local composition and EoS models
Differential Evolution (Kundu *et al*., 2008) [92]	Least squares	Equation of state
Particle Swarm Optimization, Differential evolution, Simulated Annealing, Genetic Algorithm, Differential Evolution with tabu list (Bonilla-Petriciolet *et al*., 2010) [20]	Least squares and Error-in-variable	Local composition model and ideal gas
Particle Swarm Optimization (Lazzus, 2010) [93]	Least squares	Local composition model and ideal gas
Bare bone particle swarm optimization (Zhang *et al*., 2011) [63]	Least squares and Error-in-variable	Local composition model and ideal gas
Harmony Search (Bonilla-Petriciolet *et al*., 2010) [85]	Least squares	Local composition model and ideal gas
Ant Colony Optimization (Fernandez-Vargas, 2011) [86]	Least squares and Error-in-variable	Local composition model and ideal gas

affect the predictive capability of thermodynamic models for phase equilibrium modeling. Later, Gau and Stadtherr [89] applied an interval-Newton approach for the reliable solution of EIV parameter estimation problems in vapor-liquid equilibrium modeling of binary systems. Note that this approach can be used for both parameter estimation and data reconciliation.

With respect to stochastic methods, several meta-heuristics have been used to solve the parameter estimation problems in phase equilibrium modeling, and they include: simulated annealing (SA), genetic algorithm (GA), random tunneling algorithm (RTA), differential evolution (DE), differential evolution with tabu list (DETL), particle swarm optimization (PSO), harmony search (HS), bare-bones particle swarm optimization (BBPSO) and ant colony optimization (ACO). Specifically, Costa *et al*. [90] reported the application of SA for parameter estimation in the modeling of vapor-solid equilibrium with supercritical carbon dioxide as the solvent. Results of data fitting using SA were compared with those obtained using the Powell method, and the authors concluded that SA may offer a better performance. Steyer and Sundmacher [91] used an evolutionary optimization strategy for the simultaneous fitting of VLE and liquid-liquid equilibrium (LLE) data for ternary systems. Bonilla-Petriciolet *et al*. [45] also studied the performance of SA for parameter estimation in VLE modeling using both least squares and maximum likelihood formulations. This study concluded that SA is a robust method for non-linear parameter estimation in thermodynamic models. However, in difficult problems (e.g., EIV problems with several decision variables), it still can converge to a local optimum of the objective function. Srinivas and Rangaiah [68] used a RTA for VLE modeling using the error-in-variable approach. This method was able to solve reliably the two modeling problems having 18 and 34 decision variables, and with a global minimum not comparable to a local minimum. Alvarez *et al*. [47] applied and compared two versions of GA for VLE modeling using local composition models and equations of state and LS approach. DE was successfully applied to modeling the equilibrium solubility of CO_2 in aqueous alkanolamines [92].

Recently, the performance of SA, GA, DE, DETL and PSO has been compared for VLE modeling using experimental data for binary systems and both least squares and maximum likelihood criteria [20]. This comparison shows that DE and DETL perform better than other algorithms tested in terms of reliability for parameter estimation in VLE data modeling. Further, DETL offers a significant reduction in the computational time. Lazzus [93] also reported the application of PSO to modeling vapor-liquid equilibrium in binary systems using UNIQUAC and NRTL local composition models. Zhang *et al*. [63] studied the performance of PSO and variants of BBPSO algorithms for parameter estimation in VLE modeling problems based on LS and EIV approaches. The reliability of BBPSO proposed by Zhang *et al*. [63] is shown to be better than or comparable to other stochastic global optimization methods tested; in addition, it has less parameters to be tuned. Preliminary studies have also been performed for parameter estimation in VLE modeling using both HS and ACO [85, 86]. In particular, HS is reliable for solving parameter estimation problems using LS approach but its performance is poor for finding the global optimum using EIV formulation. On the other hand, ACO appears to be a competitive stochastic method for VLE modeling especially using EIV formulation.

The above review indicates that several researchers have studied the parameter estimation in VLE modeling problems using stochastic optimization methods instead of deterministic methods. In particular, stochastic optimization methods may offer reduced computational time and easier numerical implementation than the deterministic approaches. The former methods usually show robust performance for solving parameter estimation problems but, in some challenging problems, they may fail to locate the global optimum especially using fewer function evaluations and for

optimization problems with many decision variables (e.g., EIV problems). In addition, the performance of many stochastic methods is significantly dependent on the stopping condition used.

4.2. Applications to Phase Stability Analysis

With the introduction of the tangent plane criterion for phase stability analysis, many researchers have studied the solution of this optimization problem using different computational methods. These studies using deterministic and stochastic optimization methods are summarized in Tables **2a** and **2b** respectively. Sun and Seider [94] introduced homotopy continuation method for phase stability problem, in order to locate all stationary points of the tangent plane distance function (TPDF). However, their technique requires several initial estimations for finding all stationary points of TPDF. Harding and Floudas [95] studied the

Table 2a. Application of Deterministic Optimization Methods to Phase Stability Analysis

Method (Reference)	Problem Formulation	Thermodynamic Models
Homotopy Continuation (Sun and Seider, 1995) [94]	Tangent plane distance function	SRK and PR
Branch and Bound (Harding and Floudas, 2000) [95]	Tangent plane distance function	SRK, PR and van der Waals
Interval Newton/Generalized Bisection (Tessier *et al*., 2000)[96]	Excess Gibbs energy	NRTL and UNIQUAC
Branch and Bound (Zhu and Inoue, 2001) [97]	Tangent plane distance function	NRTL activity coefficient equation
Interval Newton/Generalized Bisection (Xu *et al*., 2002) [98]	Volume-based formulation using the Helmholtz energy	Statistical associating fluid theory
Tunneling Method (Nichita *et al*., 2002) [99]	Tangent plane distance function	SRK and PR
Terrain Method (Lucia *et al*., 2005) [100]	Projected Gibbs energy and the norm of chemical potentials	PR
Interval Newton method (Gecegormez and Demirel, 2005) [101]	Tangent plane distance function	NRTL
Tunneling Method (Nichita *et al*., 2008) [102]	Tangent plane distance function in terms of Helmholtz free energy	SRK and PR
CPLEX and BARON (Mitsos and Barton, 2007) [79]	Tangent plane distance function	NRTL and UNIQUAC
Homotopy Continuation (Jalali *et al*., 2008) [26]	Michelsen criteria [92]	NRTL
Tunneling Method (Nichita *et al*., 2008) [103]	Tangent plane distance function	Perturbed-chain statistical association fluid theory
Dividing Rectangles (Saber and Shaw, 2008) [104]	Tangent plane distance function	PR and SRK
Tunneling Method (Nichita and Gomez, 2009) [105]	Tangent plane distance function	PR and SRK

Table 2b. Application of Stochastic Optimization Methods to Phase Stability Analysis

Method (Reference)	Problem Formulation	Thermodynamic Models
Genetic Algorithm and Simulated Annealing (Rangaiah, 2001) [5]	Tangent plane distance function	NRTL, UNIQUAC and SRK
Stochastic Sampling and Clustering Method (Balogh *et al*., 2003) [106]	Modified tangent plane distance function	SRK
Simulated Annealing (Henderson *et al*., 2004) [107]	Modified tangent plane distance function	SRK and PR
Simulated Annealing, very fast SA, a modified direct search SA and stochastic differential equations (Bonilla-Petriciolet *et al*., 2006) [82]	Tangent plane distance function	SRK
Differential Evolution and Tabu Search (Srinivas and Rangaiah, 2007a) [6]	Tangent plane distance function	NRTL, UNIQUAC and SRK
Adaptive Random Search (Junior *et al*., 2009) [108]	Tangent plane distance function	SRK, PR and Perturbed Chain – Statistical associating fluid theory
Repulsive Particle Swarm Optimization (Rahman *et al*., 2009) [109]	Tangent plane distance function	NRTL and UNIQUAC
Particle Swarm Optimization and its Variants (Bonilla-Petriciolet and Segovia-Hernandez, 2010) [62]	Tangent plane distance function	NRTL, SRK, Wilson, UNIQUAC, ideal solution and gas
Differential Evolution, Simulated Annealing and Tabu Search (Bonilla-Petriciolet *et al*. 2010) [111]	Tangent plane distance function with reaction	NRTL, Wilson and UNIQUAC

phase stability of three cubic equations of state: SRK, Peng-Robinson and van der Waals, based on analytical findings and the principles of the αBB (branch and bound) global optimization framework. In this study, stability problems with several decision variables (i.e., ≤ 8) have been analyzed.

Tessier *et al*. [96] introduced an interval Newton/ generalized bisection technique for solving phase stability problems involving excess Gibbs energy models. The proposed technique is independent of initialization, immune to rounding errors, and provides both mathematical and computational guarantees that all stationary points of TPDF are enclosed. Zhu and Inoue [97] developed a general quadratic under-estimating function based on branch and bound algorithm by the construction of a rigorous under-estimator for TPDF involving NRTL model, and showed its effectiveness for phase stability analysis of three ternary mixtures with up to 2-3 phases. Xu *et al*. [98] studied the phase stability criterion involving the statistical associating fluid theory equation of state model. They introduced an interval Newton/generalized bisection algorithm and a volume-based formulation for the Helmholtz energy, and then applied them successfully to non-associating, self-associating, and cross-associating systems.

Nichita *et al*. [99] proposed the tunneling method for phase stability analysis with cubic equations of state by minimization of the TPDF on a variety of representative systems. Their results show that the proposed method is very robust even for the very difficult systems. Lucia *et al*. [100] incorporated some new ideas within the terrain methods and applied them to phase stability and equilibrium of n-alkanes mixtures. This method provides global knowledge for understanding the solution structure, saddle points and other information. Gecegormez and Demirel [101] introduced interval Newton method for phase stability analysis of binary systems and ternary systems modeled by NRTL, to locate all the stationary points. Their results confirm that the interval Newton method is able to locate all the stationary points of TPDF. Nichita *et al*. [102] used the tunneling method to solve the non-convex optimization problem that results from the TPDF in terms of the Helmholtz free energy. Mitsos and Barton [79] reinterpreted the Gibbs tangent plane stability criterion *via* a Lagrangian duality approach, as the solution of the dual problem of a primal problem that minimizes Gibbs free energy subject to material balances. Then, this optimization problem was solved using CPLEX and BARON in GAMS.

Jalali *et al*. [26] studied homotopy continuation method for phase stability analysis in the complex domain using Michelsen criteria [4]. However, this approach is not possible if the equations cannot be converted into complex variables. Nichita *et al*. [103] applied the tunneling method to solve the phase stability problem for more complex equation of state like perturbed-chain statistical association fluid theory. Calculations were performed for several benchmark problems and for (binary and multi-component) mixtures of non-associating molecules. Saber and Shaw [104] tested dividing rectangles (DIRECT) global optimization algorithm for optimizing TPDF with SRK equation of state for multi-component mixtures and near critical points systems, and showed that this algorithm has better robustness and efficiency compared to Lipschitz method, interval Newton method, tunneling method, very fast simulated annealing, stochastic differential equations and/or modified direct search annealing. Nichita and Gomez [105] applied the tunneling method to perform stability analysis of various systems modeled by PR and SRK equation of state.

Besides the application of deterministic methods outlined in the above paragraphs, stochastic methods have been studied by many researchers for phase stability problems. Rangaiah [5] applied genetic algorithm and simulated annealing to phase stability problems of various systems. The results show that the former is more efficient and reliable than the latter. Balogh *et al*. [106] introduced a stochastic sampling and clustering method, and applied it to a modified TPDF with an equation of state as the thermodynamic model. This method was able to solve small to moderate size problems efficiently and reliably. Henderson *et al*. [107] formulated the phase stability optimization problem with a slight modification of the Gibbs tangent plane criterion, and used simulated annealing to solve it. Bonilla-Petriciolet *et al*. [82] compared four algorithms: simulated annealing, very fast simulated annealing, a modified direct search simulated annealing and stochastic differential equations, on several phase stability problems. Their results show that simulated annealing is the most reliable among the methods tested for minimization of TPDF for both reactive and non-reactive mixtures.

Srinivas and Rangaiah [6] investigated solution of phase stability problems with differential evolution and tabu search, and reported that the former has better reliability but less computational efficiency compared to the latter. Junior *et al*. [108] applied a hybrid adaptive random search method to solve the phase stability problems for three different equation of state model. Their results show that the proposed method outperforms the classical adaptive random search, quasi-Newton and DIRECT methods. Rahman *et al*. [109] tested a repulsive particle swarm optimization for phase stability problems. This optimization algorithm uses the propagation mechanism to determine new velocity for a particle. Consequently, it can prevent the swarm from being trapped in a local minimum. Ferrari *et al*. [110] used simulated annealing and particle swarm optimization for modeling liquid-liquid phase equilibrium data of binary and multi-component systems. They concluded that both algorithms are robust for estimating the model parameters in these applications. Bonilla-Petriciolet and Segovia-Hernandez [62] performed a comparative study of different variants of particle swarm optimization algorithms for phase stability of multi-component mixtures. Their results indicate that the classical particle swarm optimization with constant cognitive and social parameters is reliable and offers the best performance for global minimization of TPDF in both reactive and non-reactive systems.

Srinivas and Rangaiah [81] proposed two versions of DE with tabu list, referred as DETL-G and DETL-D, and applied to phase stability problems. The results show that the overall performance of DETL-G and DETL-D is better than that of DE and TS. Bonilla-Petriciolet *et al*. [111] studied phase

stability and equilibrium calculations in reactive systems using differential evolution, simulated annealing and tabu search, and showed that differential evolution and tabu search are better than simulated annealing in terms of efficiency but not so in terms of reliability. In these and our other studies [5, 6, 62, 81], a local optimization technique was used after the global search for efficiently and accurately finding the (global) minimum. And, among the many stochastic methods tested and compared for solving the phase stability problems, DETL has shown better performance.

It is clear that both stochastic and deterministic methods can be used for reliably solving phase stability problems in multi-component system. Overall, finding all stationary points of TPDF is not an easy task because a search over the entire composition space is required and the number of these stationary points is also an unknown. Hence, it is better to find the global optimum of TPDF during phase stability analysis. Several studies indicate that optimization methods tested may fail to find the global optimum in phase stability analysis when there are comparable minima (i.e., the difference in function values at the global minimum and at a local minimum is very small). The reduction of CPU time of global optimization methods is one of the major challenges in phase stability analysis of multi-component systems. This improvement would allow us to extend the application of these strategies for performing phase equilibrium calculations in more complex systems.

4.3. Applications to Phase Equilibrium Calculations

Both deterministic and stochastic global optimization methods have been applied for phase equilibrium calculations of different systems with and without chemical reactions; these investigations are summarized in Tables **3a** and **3b**. For example, Lucia *et al*. [112] introduced unique initialization strategies and successive quadratic programming for phase equilibrium calculations. The overall algorithmic framework is based on using a combination of binary tangent plane analyses, bubble point calculations and dimensionless Gibbs free energy minimization approach for solving a sequence of sub problems (i.e., VLE, LLE, and VLLE). Chaikunchuensakun *et al*. [78] applied a combined algorithm, NLQPB stated in Section 3.2.10, for the calculation of multi-phase equilibrium conditions at fixed temperature, pressure and overall composition. Although global solutions cannot be guaranteed, NLQPB can find equilibrium compositions accurately for multi-phase mixtures by the minimization of the Gibbs free energy of the system. Cheung *et al*. [113] developed a branch-and-bound algorithm, which incorporates tight convex under-estimators and bounds on the dependent variables approach, and applied it to determine the global minimum potential energy for the solvent-solute interactions in phase equilibrium. Nichita *et al*. [24] tested the tunneling method for multi-phase equilibrium calculation by direct minimization of Gibbs free energy of a variety of multi-component systems. Their results suggest that tunneling method is a robust and efficient tool for solving phase equilibrium problems even for extremely difficult cases. However, it requires feasible and improved initial estimates for reliability and computational efficiency respectively. Scurto *et al*. [114] applied interval analysis methodology to predict the behavior of high-pressure solid-multiphase equilibrium systems using cubic equations of state with cosolvents, where the likelihood of formation of more than two phases is great. Nichita *et al*. [115] too used the tunneling method to directly minimize the Gibbs free energy in multi-phase equilibrium calculations. Rossi *et al*. [116] applied convex analysis method to chemical and phase equilibrium of closed multi-component reactive systems. This method employs the CONOPT solver in GAMS (General Algebraic Modeling System). The optimization is by minimizing the Gibbs free energy of systems at constant pressure and temperature, and constant pressure and enthalpy. The proposed method can solve the phase equilibrium problems with high efficiency and reliability but it requires the convexity of the model. Pereira *et al*. [80] proposed a duality based optimization for phase equilibrium where the volume-composition space is converted from the Gibbs free energy to the Helmholtz free energy. They used BARON for global optimization, MINOS as the nonlinear local solver and CPLEX for linear problems. The method is applicable to the calculation of any kind of fluid phase behavior (e.g., VLE, LLE and VLLE). The method proposed by Pereira *et al*. [80] can guarantee the global optimum but it requires a differentiable objective function.

Beside deterministic methods for solving the phase equilibrium problems reviewed above, many stochastic methods have been used to solve this thermodynamic problem. Specifically, Zhu *et al*. [44] introduced enhanced simulated annealing for phase equilibrium calculations of multi-component systems at high pressure, which include ternary, quaternary and five component mixtures. Although the proposed algorithm requires slightly more computational time compared to two algorithms in the literature (MULPRG and HOMPEQ), it provides comparable reliability, is self-starting and simple. Rangaiah [5] evaluated the performance of genetic algorithm, simulated annealing and hybrid genetic algorithm for phase equilibrium problems of several mixtures. The results show that genetic algorithm is more efficient and reliable than simulated annealing, and that hybrid genetic algorithm outperforms both genetic algorithm and simulated annealing in terms of reliability but its main limitation is the significant increase in the CPU time. Teh and Rangaiah [52] tested enhanced continuous tabu search for phase equilibrium calculations *via* Gibbs free energy minimization, of VLE, LLE and VLLE systems. The results indicate that tabu search is more efficient than genetic algorithm but both require further improvement for 100% reliability.

Srinivas and Rangaiah [68] evaluated the random tunneling algorithm on a number of medium sized problems including VL, LL and VLL equilibrium problems. The random tunneling algorithm can locate the global optimum for most of the examples tested but its reliability is low for problems having a local minimum comparable to the global minimum. Srinivas and Rangaiah [6] compared differential evolution and tabu search algorithms for phase equilibrium calculations of various VLE, LLE and VLLE systems. Subsequently, Srinivas and Rangaiah [7] introduced differential evolution with tabu list algorithm to phase equilibrium calculation. The results show that this hybrid algorithm performs better than both differential evolution

Table 3a. Application of Deterministic Optimization Methods to Phase Equilibrium Calculation

Method (Reference)	Problem Formulation	Thermodynamic Models
Successive Quadratic Programming (Lucia *et al*. 2000) [112]	Gibbs free energy	NRTL, UNIQUAC, UNIFAC, RK, PolyNRTL, HOC, SRK and PolySRK
Nonlinear parametric optimization (NLQPB) (Chaikunchuensakun *et al*., 2000) [78]	Gibbs free energy	UNIQUAC, PR and van der Waals
Branch and Bound (Cheung *et al*., 2002) [113]	Potential energy	van der Waals and Coulombic
Tunneling Method (Nichita *et al*., 2002) [24]	Gibbs free energy	SRK and PR
Interval Analysis (Scurto *et al*., 2003) [114]	Gibbs energy surface	PR and van der Waals
Tunneling method (Nichina *et al*., 2004) [115]	Gibbs free energy	SRK and PR
CONOPT in GAMS (Rossi *et al*., 2010) [116]	Gibbs free energy	NRTL and Wilson
Duality based optimization (BARON, MINOS and CPLEX) (Pereira *et al*., 2010) [80]	Helmholtz free energy	Augmented van der Waals

Table 3b. Application of Stochastic Optimization Methods to Phase Equilibrium Calculations

Method (Reference)	Problem Formulation	Thermodynamic Models
Enhanced Simulated Annealing (Zhu *et al*. 2000) [44]	Gibbs free energy	PR and SRK
Genetic Algorithm, Simulated Annealing and hybrid GA (Teh and Rangaiah, 2001) [5]	Gibbs free energy	SRK, PR, NRTL and UNIFAC
Enhanced Tabu Search (Teh and Rangaiah, 2003) [52]	Gibbs free energy	SRK, PR, NRTL and UNIFAC
Random Tunneling Algorithm (Srinivas and Rangaiah, 2006) [68]	Gibbs free energy	SRK, PR, NRTL and ideal gas
Differential Evolution and Tabu Search (Srinivas and Rangaiah, 2007a) [6]	Gibbs free energy	SRK, PR, NRTL and UNIFAC
Differential Evolution with Tabu List (Srinivas and Rangaiah, 2007b) [7]	Gibbs free energy	SRK, PR, NRTL and UNIFAC
Hybrid Artificial Immune System (Lin and Chen, 2007) [83]	Gibbs free energy with reaction	NRTL and UNIQUAC
Simulated Annealing (Bonilla-Petriciolet *et al*, 2009) [14]	Gibbs free energy with its orthogonal derivatives	NRTL, Wilson and ideal gas
Hybrid Genetic Algorithm with Interior Point Method (Staudt and Soares, 2009) [84]	Gibbs free energy	NRTL, SRK and PR
Genetic Algorithm and Differential Evolution with Tabu List (Bonilla-Petriciolet *et al*, 2011) [10]	Gibbs free energy with reaction	NRTL, Wilson, UNIQUAC and Margules solution

and tabu search. Lin and Chen [83] proposed a hybrid method for chemical reaction and phase equilibrium calculation. The hybrid method was constructed by making use of the advantages of artificial immune system and sequential quadratic programming. The results show that the hybrid method is better than the artificial immune system method alone.

Staudt and Soares [84] proposed a hybrid global optimization method for the minimization of Gibbs free energy for multi-phase equilibrium calculation. The proposed method uses genetic algorithm for the global search and interior point method for refinement after the global search. Bonilla-Petriciolet *et al*. [10] applied GA and DETL for phase equilibrium calculations in reactive systems by Gibbs free energy minimization; two approaches – constrained and unconstrained, were tried for solving these problems. The results show that unconstrained free energy minimization involving transformed composition variables requires more computational time compared to constrained minimization, and that DETL has generally better performance for free energy minimization in reactive systems. Among the stochastic methods, hybrid methods often provide better performance in terms of reliability and efficiency.

In summary, the literature indicates that the major difficulties of Gibbs free energy minimization using both deterministic and stochastic methods arise in phase equilibrium calculations for highly non-ideal mixtures and, particularly, in the vicinity of critical points and phase boundaries. At these conditions, the difference of function value at the global minimum and at a local optimum (i.e., at trivial solutions and unstable phase equilibria) is also very small. In fact, trivial solutions present a significant region of attraction for numerical strategies that may cause convergence problems. Note that many of the studies and tests assume that the correct number of phases at equilibrium is known *a priori*. However, the number and type of phases, at which Gibbs free energy function achieves the global

minimum, are unknown in phase equilibrium problems and, as a consequence, several calculations must be performed using different phase configurations (adding or removing phases) to identify the stable equilibrium state. Hence, it is desirable to develop more effective deterministic and stochastic methods for the global Gibbs free energy minimization in both reactive and non-reactive systems.

4.4. Applications to Critical Points and Azeotropes Calculations

In contrast to other phase equilibrium calculations, fewer stochastic and deterministic global optimization methods have been applied to critical points and azeotrope calculations (see Table **4**). Specifically, homotopy continuation methods have been used to locate all the homogeneous azeotropes [117], to study the sensitivity of azeotropic states to operating conditions using both local composition and (equation of state) EoS models [118,119], to locate reactive and kinetic azeotropes [120, 121], and to calculate critical loci of binary mixtures [122]. Branch and bound global optimization has been used for the calculation of all reactive and non-reactive homogeneous azeotropes of multicomponent systems [123, 124]. This method offers a theoretical guarantee for finding all azeotropes; but, depending on the thermodynamic model, it is necessary to reformulate the problem and the success of this technique depends upon proper construction of the convex functions for the thermodynamic equations to perform a global minimization.

Interval analysis has also been used to calculate both azeotropes and critical points. For example, Maier *et al*. [125] used an interval-Newton/generalized-bisection (IN/GB) algorithm to locate all solutions of the thermodynamic conditions for homogeneous azeotropy using solution models and ideal gas behavior. Later, Salomone and Espinosa [126] combined this IN/GB algorithm with Zharov-Serafimov topological index theory to reduce the total computation time for the calculation of homogeneous azeotropes. In another study, Maier *et al*. [127] extended their IN/GB algorithm to locate all homogeneous reactive azeotropes using solution models and ideal gas behavior. Stradi *et al*. [128] employed interval analysis for locating all the critical points of a given mixture using cubic EoS models; they claim a computational guarantee for the convergence of interval analysis method. Finally, Nichita *et al*. [129] reported application of the tunneling method for finding all critical points of several mixtures from binaries to multi-component petroleum reservoir fluids using cubic EoS models.

With respect to stochastic optimization methods, simulated annealing (SA) and differential evolution (DE) have been applied in the calculation of critical points and azeotropes. Freitas *et al*. [130, 131] introduced the application of stochastic global optimization using SA for the calculation of critical points and criticality conditions obtained from a slight modification of the Gibbs tangent plane criterion. Sanchez-Mares and Bonilla-Petriciolet [132] tested SA for solving the Heidemann and Khalil's formulation for the prediction of critical point in multi-component systems. These authors concluded that SA is generally robust for these calculations, but the computational time is still significant for multi-component systems. Later, Justo-García *et al*. [133] have also applied SA for the calculation of critical points of multi-component systems; here, criticality conditions were evaluated using a formulation based on the tangent plane distance in terms of the Helmholtz energy where temperature and volume are the independent variables.

Table 4. Application of Global Optimization Methods to the Calculation of Critical Points and Azeotropes

Method (Reference)	Problem Formulation	Thermodynamic Models
Homotopy continuation method (Fidkowski *et al*., 1993; Aslam and Sunol, 2006; Aslam and Sunol, 2004) [117, 118,119]	Homogeneous azeotropy	Local composition and EoS models
Homotopy continuation method (Okasinski and Doherty, 1997; Qi and Sundmacher, 2005) [120, 121]	Homogeneous reactive azeotropy	Local composition models
Homotopy continuation method (Wang *et al*., 1999) [122]	Critical point	EoS
Branch and bound method (Harding *et al*., 1997; Harding and Floudas, 124) [123, 124]	Homogeneous azeotropy and reactive azeotropy	Local composition models
Interval analysis (Maier *et al*., 1998 ; Salomone and Espinosa, 2001 ; Maier *et al*., 2000) [125, 126, 127]	Homogeneous azeotropy and reactive azeotropy	Local composition models
Interval analysis (Stradi *et al*., 2001) [128]	Critical point	EoS
Tunneling algorithm (Nichita *et al*., 2010) [129]	Critical point	EoS
Simulated annealing (Henderson *et al*., 2004; Freitas *et al*., 2004; Sanchez-Mares and Bonilla-Petriciolet, 2006; Justo-García *et al*., 2008) [130, 131, 132, 133]	Critical point	EoS
Simulated annealing (Bonilla-Petriciolet *et al*., 2009) [14]	Homogeneous azeotropy and reactive azeotropy	Local composition models
Differential evolution (Henderson *et al*., 2010) [134]	Critical point	EoS

Recently, Henderson *et al*. [134] reported the prediction of critical points of thermodynamic mixture using four different versions of DE. They tested the performance of DE algorithms in multi-component petroleum fluids. Finally, Bonilla-Petriciolet *et al*. [14] studied the calculations of homogeneous azeotropes in reactive and nonreactive mixtures where SA is used to robustly solve the system of non-linear equations that results from the equalities of the orthogonal derivatives of the Gibbs energy and the Gibbs energy of mixing in the vapor and the liquid phases. To best of our knowledge, this study is the first and unique application of a stochastic optimization method for the prediction of both reactive and non-reactive homogeneous azeotropes.

CONCLUDING REMARKS

Optimization problems involved in phase equilibrium modeling and calculations are complex and difficult to solve using traditional local optimization methods due to (a) the presence of several local minima, (b) the objective function may be flat and/or with discontinuities in some regions of solution domain, (c) wide range of decision variables in modeling problems, and (d) presence of trivial solutions in some problems. In fact, these optimization problems are generally non-convex, constrained, and highly non-linear with many decision variables. Hence, solution of these important and common problems requires reliable and efficient global optimization methods able to handle different problem characteristics. To date, a number of deterministic and stochastic global optimization methods have been developed and evaluated for solving phase equilibrium modeling and calculation problems. In particular, deterministic and stochastic global methods have been widely applied to solve phase stability and Gibbs free energy minimization problems in non-reactive systems including the prediction of critical points and azeotropes; however, fewer attempts have been made in the application of these methods to reactive phase equilibrium calculations and modeling, compared to those reported for non-reactive systems.

Even though research in the application of global optimization methods for phase equilibrium modeling and calculations has grown significantly over the last decade, results reported in the literature indicate that both deterministic and stochastic global optimization methods require further improvement for solving, robustly and efficiently, these application problems. One of the major limitations of deterministic global optimization methods is the significant computational time required for solving high dimensional problems, which grows exponentially with the number of decision variables. This aspect limits the application of these strategies to model multi-component and multi-phase systems and the use of complex thermodynamic models for predicting mixture properties. Therefore, further research should be performed to improve the performance of available optimization algorithms and to develop general purpose and effective deterministic methods for solving phase equilibrium problems in multi-component systems.

Compared to deterministic optimization methods, stochastic optimization techniques involve simple concepts, do not require any assumptions and can be used for any type of problem. Hybridization to synergize selected features of different stochastic algorithms is a promising approach for developing highly effective algorithms since reported results show that the performance of pure algorithms is almost always inferior to that of hybrid algorithms. In particular, further studies should be focused on the development of hybrid strategies to improve the reliability of stochastic optimization methods using fewer NFE. In addition, alternative termination criteria should be studied and tested for reliably determining the global convergence of stochastic optimization methods for phase equilibrium modeling and calculations. It is also desirable that these methods should have no or fewer tuning parameters. We believe these research directions for stochastic methods offer many possibilities for developing robust and efficient optimization strategies.

Despite the many advances in this area, research in global optimization for phase equilibrium modeling and calculations will continue to be an active field in chemical engineering, in order to develop and evaluate effective global optimization methods, in the foreseeable future. Further, promising deterministic and stochastic methods need to be compared carefully and comprehensively for solving phase equilibrium modeling and calculation problems.

CONFLICT OF INTEREST

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