A comparative study of particle swarm optimization and its variants for phase stability and equilibrium calculations in multicomponent reactive and non-reactive systems

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Particle swarm optimization is a novel evolutionary stochastic global optimization method that has gained popularity in the chemical engineering community. This optimization strategy has been successfully used for several applications including thermodynamic calculations. To the best of our knowledge, the performance of PSO in phase stability and equilibrium calculations for both multicomponent reactive and non-reactive mixtures has not yet been reported. This study introduces the application of particle swarm optimization and several of its variants for solving phase stability and equilibrium problems in multicomponent systems with or without chemical equilibrium. The reliability and efficiency of a number of particle swarm optimization algorithms are tested and compared using multicomponent systems with vapor–liquid and liquid–liquid equilibrium. Our results indicate that the classical particle swarm optimization with constant cognitive and social parameters is a reliable method and offers the best performance for global minimization of the tangent plane distance function and the Gibbs energy function in both reactive and non-reactive systems.

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1. Introduction

Phase equilibrium calculations play a major role in the design, development, operation, optimization and control of chemical processes. These calculations involve both phase stability analysis and split computations with or without the presence of chemical reactions. For a given mixture with specified composition, temperature and pressure, the phase stability analysis is used to check if the tested phase is stable or not. If it is not stable then the phase split calculations can be performed, and the stability status of the new phases (obtained from split calculation) is again tested. The modeling of phase behavior of multicomponent reactive and non-reactive systems is a complex topic due to non-linear interactions among components, phases and reactions. Therefore, the development of reliable methods for solving phase equilibrium problems has long been a challenge and remains so [1].

Phase equilibrium calculations can be formulated as a global optimization problem where the tangent plane distance function (TPDF) is used as optimization criterion for stability analysis and the Gibbs energy function \(G\) is minimized for phase split computations [1–4]. Specifically, global optimization problems for phase and stability calculations in reactive and non-reactive systems follow the form: minimize \(f(u)\) subject to \(u \in \Omega\), where \(u\) is a continuous variable vector with domain \(\Omega \subseteq \mathbb{R}^n\), and \(f(u)\): \(\Omega \Rightarrow \mathbb{R}\) is a real-valued function. The domain \(\Omega\) is defined within upper and lower limits of each decision variable, which are generally mole numbers or mole fractions for phase equilibrium calculations. The minimization of \(G\) and TPDF (i.e., \(f(u)\)) can be performed using both equation-solving methods and direct optimization strategies [5–7]. If chemical reactions occur in the mixture, these strategies can also be classified as either stoichiometric or non-stoichiometric, depending on the formulation of material balance constraints [8]. Equation-solving methods are based on the solution of non-linear equations obtained from the stationary conditions of the optimization criterion. Local search methods with and without decoupling strategies are frequently used to solve these equations in conjunction with mass balance restrictions. However, these methods are prone to severe computational difficulties and may fail to converge when initial estimates are not suitable, especially for strongly non-ideal multicomponent and multireactive systems [5–7]. It is worth noting that the mathematical properties of the objective functions used for phase equilibrium calculations depend completely on the structure of the thermodynamic equation chosen to model each of the phases that may exist at equilibrium. Thus, TPDF and \(G\) are...
Minimization strategies are preferred by researchers in process modeling to study mixtures with complex phase behavior. Most of the available methods for minimization of TPDF and G have been proposed during recent decades, and they comprise local and global optimization approaches [5–7]. Reviews of several studies using minimization strategies for phase equilibrium calculations can be found in Teh and Rangaiah [5] and Wakeman and Stateva [7] for non-reactive systems, and in Seider and Widagdo [6] for reactive mixtures. In general, these reviews indicate that there has been a significant and increasing interest in the development of deterministic and stochastic global strategies for solving phase equilibrium problems. Studies on deterministic phase equilibrium calculations have been focused on the application of homotopy continuation methods [9–13], branch and bound global optimization [14–16] and interval analysis using an interval-Newton/generalized bisection algorithm [17–19]. Although these methods have proven to be very promising, several of them are model dependent, may require problem reformulations or significant computational time for multicomponent systems [7,20].

Alternatively, stochastic optimization techniques have often been found to be as reliable and effective as deterministic methods but may offer more advantages for phase equilibrium calculations [21]. These methods are robust numerical tools that present a reasonable computational effort in the optimization of multivariable functions (generally less time than deterministic approaches); they are applicable to ill-structure or unknown structure problems, require only calculations of the objective function and can be used with all thermodynamic models. Many thermodynamic problems that are very difficult to solve by conventional techniques can be solved by stochastic methods. To date, several stochastic global optimization methods have been studied and tested for phase equilibrium calculation in non-reactive and reactive mixtures. These methods include: the random search method of Lee et al. [22], simulated annealing [23–26], genetic algorithms [24,27], tabu search [28–30], tunneling method [1,20,31], clustering method with stochastic sampling [21], and differential evolution [29,30,32]. On the other hand, few attempts have been made in the application of stochastic methods for reactive phase equilibrium calculations, compared to those reported for non-reactive systems [22,25,26,30]. The presence of chemical equilibrium constraints increases the complexity and dimensionality of phase equilibrium problems and, as expected, these calculations are more challenging.

One of the most-promising stochastic methods is particle swarm optimization (PSO) [33–43]. This is a novel evolutionary algorithm capable of handling the difficult characteristics of global optimization problems with several decision variables. PSO is simpler, both in formulation and computer implementation, than other population-based metaheuristics. This optimization method has a flexible and well-balanced mechanism to enhance global and local exploration abilities. PSO has become a popular optimization strategy for the chemical engineering community and has been successfully applied in non-linear parameter estimation [36], process design [37,38], and thermodynamic calculations [39–43]. In the literature, there are few studies concerning the application of PSO for phase equilibrium calculations in binary and ternary non-reactive systems [40–42]. Specifically, Cheng et al. [40] reported a linear constraint PSO algorithm for the minimization of TPDF. In another study, Cheng and Chen [41] applied a hybrid PSO for Gibbs energy minimization in ternary systems. Recently, Rahman et al. [42] introduced the application of repulsive particle swarm optimization, another variant of PSO, for solving both phase equilibrium and stability problems in binary and ternary non-reactive mixtures. Unfortunately, the potential of PSO has not been demonstrated by applying it to multicomponent systems, taking into account the fact that problems with higher dimensions are expected to be more difficult to solve than those with lower dimensions, because multicomponent systems can exhibit a variety of possible phase equilibriums. Moreover, the capabilities of PSO and its variants have not yet been studied in the modeling of phase behavior for reactive systems even though preliminary results indicate that PSO may offer competitive performance for these calculations [43].

In this study, the feasibility of applying PSO-based algorithms to phase stability and equilibrium calculations in multicomponent reactive and non-reactive systems is studied. Specifically, we test and compare the performance of PSO and several of its variants using phase stability and equilibrium problems with dimension ranging from 2 to 10. This algorithm comparison is necessary to identify the relative strengths of PSO and to justify the choice of a specific algorithm. To the best of our knowledge, this comparative study has not been thoroughly done before. Our results show that the classical particle swarm optimization is a suitable alternative numerical tool for modeling phase behavior of reactive and non-reactive systems.

2. Particle swarm optimization and its variants

Particle swarm optimization is a novel and promising population-based method that belongs to the class of swarm intelligence algorithms. Kennedy and Eberhart [23] introduced this strategy for global optimization, inspired by the social behavior of flocking swarms of birds and fish schools. It exploits a population of potential solutions to identify promising areas for optimization. In this context, the population of potential solutions is called the swarm and each solution is called a particle. Particles are conceptual entities, which fly through the multi-dimensional search space. The success histories of the particles influence both their own search patterns and those of their peers. Each particle has two state variables: its current position \( \mathbf{x}_i \) and its current velocity \( \mathbf{v}_i \), which are updated using:

\[
s_i(k + 1) = s_i(k) + v_i(k + 1) \quad \text{for } i = 1, \ldots, n_p, \quad j = 1, \ldots, n_c
\]

\[
v_i(k + 1) = c_1 v_i(k) + c_2 r_1 (s^*_{i,j} - s_i(k)) + c_2 r_2 (s^*_{j,i} - s_i(k)) \quad \text{for } i = 1, \ldots, n_p, \quad j = 1, \ldots, n_c
\]

where \( r_1, r_2 \in (0, 1) \) are random numbers, \( n_p \) is the number of decision variables and \( n_c \) is the swarm size (i.e. overall number of particles). Usually, the velocity of each particle is restricted to a maximum value within the interval \([\hat{v}^{\min}, \hat{v}^{\max}]\), which is defined considering the bounds on decision variables. The lim-
optimization sequence. Therefore, we have considered a PSO over the entire search space during the early iterations and encouraged numerical experience indicates that it is advantageous to adjust the $c_1$ when multiplied by the random numbers. However, previous best position ever attained by the cognitive and social scaling parameters are fixed $c_1 = 0.5$, $c_2 = 2.0$.

The literature indicates that high values for inertia term result in straight particle trajectories with significant overshooting at the target, while lower values result in erratic particle trajectories with a reduction of overshoot, both desirable properties for a refined localized search [34]. Typically, an intermediate value of $w$ is selected. This version of PSO is referred to as PSO-I.

Recently, Shi and Eberhart [44] proposed a significant variation on the original PSO by introducing the inertia term $w$ into the original velocity rule. The inertia weight factor is used to control the impact of the previous velocities on the current velocity. It also influences the trade-off between the global and local exploration abilities of the particles. The velocity is updated using $w$ as follows:

$$V_{i,j}(k+1) = wV_{i,j}(k) + c_1 R_1(s_i - s_{i,j}(k)) + c_2 R_2(s_{best} - s_{i,j}(k))$$

for $i = 1, \ldots, n_q$, $j = 1, \ldots, n_p$.

The literature indicates that high values for inertia term result in straight particle trajectories with significant overshooting at the target, while lower values result in erratic particle trajectories with a reduction of overshoot, both desirable properties for a refined localized search [34]. Typically, an intermediate value of $w$ is selected. This version of PSO is referred to as PSO-D. In a recent study, Clerc and Kennedy [45] introduced constriction factor ($\kappa$) into the velocity rule. This parameter also has the effect of reducing particle velocity as the search progresses, thereby contracting the overall swarm diameter and resulting in a progressively smaller search area. Constriction factor is obtained from $c_1$ and $c_2$ as follows:

$$\kappa = \frac{2}{|2 - \sqrt{4 - 4l}|}$$

where $l = c_1 + c_2$ and $l > 4$. Then, the swarm velocity is updated using:

$$V_{i,j}(k+1) = \kappa(V_{i,j}(k) + c_1 R_1(s_i - s_{i,j}(k)) + c_2 R_2(s_{best} - s_{i,j}(k)))$$

for $i = 1, \ldots, n_q$, $j = 1, \ldots, n_p$.

The literature indicates that high values for inertia term result in straight particle trajectories with significant overshooting at the target, while lower values result in erratic particle trajectories with a reduction of overshoot, both desirable properties for a refined localized search [34]. In this version of PSO (PSO-DI), $w$ decreases linearly from $w_0$ to 0.4 over the entire run by using:

$$w = (0.4 - w_0) \left( \frac{k}{Iter_{max}} \right) + w_0$$

In PSO-DI, the swarm velocity is updated using Eqs. (4) and (5). In a recent study, Clerc and Kennedy [45] introduced constriction factor ($\kappa$) into the velocity rule. This parameter also has the effect of reducing particle velocity as the search progresses, thereby contracting the overall swarm diameter and resulting in a progressively smaller search area. Constriction factor is obtained from $c_1$ and $c_2$ as follows:

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$$V_{i,j}(k+1) = \kappa(V_{i,j}(k) + c_1 R_1(s_i - s_{i,j}(k)) + c_2 R_2(s_{best} - s_{i,j}(k)))$$

for $i = 1, \ldots, n_q$, $j = 1, \ldots, n_p$.

In the literature, many modifications have been proposed to improve the convergence performance of the original PSO [34,35,44,45]. These modifications are generally based on introducing new algorithm parameters (e.g., constriction factor or inertia weight) to modify the velocity rule. Other studies have examined the hybridization of PSO with both local and global search strategies [35]. Below, typical PSO variants are described.

In the original version of PSO, Kennedy and Eberhart [33] suggested that the cognitive and social scaling parameters are fixed constant and multiplied by the random numbers. However, previous numerical experience indicates that it is advantageous to adjust the cognitive/social ratio to favor cognitive learning. In particular, the dynamic values of these parameters may improve the global search over the entire search space during the early iterations and encourage the particles to converge to global optimum at the end of the optimization sequence [34]. Therefore, we have considered a PSO with dynamic $c_1$ and $c_2$ (referred to as PSO-D) where $c_1$ decreases linearly from $c_{1,0}$ to 0.5 using:

$$c_1 = (0.5 - c_{1,0}) \left( \frac{k}{Iter_{max}} \right) + c_{1,0}$$

where $c_{1,0}$ is the initial value for cognitive parameter, $k$ is the iteration counter and $Iter_{max}$ is the maximum number of iterations allowed for PSO. Note that $c_2 = l - c_1$ where $l$ is defined by the user and is usually $\geq 4$ [34].

![Flowchart of particle swarm optimization](image-url)
methods including PSO [1]. In the literature, mainly two stopping criteria are applied for global optimization using stochastic methods [1,28,29,32]: (a) a maximum number of iterations (Iter max) and (b) a maximum number of successive iterations (Smax) without improvement in the best function value. Thus, these criteria are used in this study for the assessment of PSO-based algorithms.

3. Formulation of phase stability and equilibrium problems in non-reactive and reactive mixtures

3.1. Phase stability

Stability analysis is a fundamental stage in phase equilibrium calculations and allows identification of the thermodynamic state that corresponds to the global minimum of Gibbs free energy. 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 mixture composition [3,4]. This statement is a necessary and sufficient condition for global stability. Stability analysis can be performed using the tangent plane distance function (TPDF). Specifically, phase stability of a non-reactive mixture with c components and a global composition \( z = (z_1, \ldots, z_c) \) in mole fraction units, at constant P and T, is analyzed by the global minimization of TPDF [3,4]:

\[
TPDF = \sum_{i=1}^{c} y_i (\mu_i |y\rangle - \mu_i |z\rangle) 
\]

where \( \mu_i |y\rangle \) and \( \mu_i |z\rangle \) are the chemical potentials of component \( i \) calculated at compositions \( y \) and \( z \), respectively. TPDF is the distance between the Gibbs free energy surface at \( y \) and the tangent plane constructed to this surface at \( z \) [4]. To perform a stability analysis, TPDF must be globally minimized with respect to composition of a trial phase \( y \). If the global minimum of TPDF < 0, the mixture under analysis is considered unstable; otherwise it is a globally stable system.

For reactive systems, the stability criterion can be employed in exactly the same way as in phase equilibrium calculations under non-reactive conditions, but for mixtures that are both physically and chemically equilibrated [4,8,13,19]. However, Wasylkiwicz and Ung [12] have proposed an extension of TPDF in terms of the reaction-invariant composition variables of Ung and Doherty [46,47]. This alternative stability criterion retains all characteristics and advantages of the classical TPDF equation, including a significant reduction in problem dimensionality, and it appears to be more suitable for the modeling of multireactive mixtures [12].

In particular, Ung and Doherty [46,47] proposed the reaction-invariant composition variables for modeling the phase behavior of reactive systems. These variables depend only on the initial composition of each independent chemical species. They also restrict the solution space to the compositions that satisfy stoichiometry requirements and reduce the dimension of the composition space by the number of independent reactions. These features allow all of the procedures used to obtain thermodynamic properties of non-reactive mixtures to be extended to systems subject to chemical equilibrium, and, consequently, non-reactive phase equilibrium algorithms can be easily modified to account for chemical reactions [46,47]. In this study, this thermodynamic framework has been used in the formulation of phase stability and equilibrium problems for systems subject to chemical equilibrium.

For a system of \( c \) components that undergoes \( r \) independent chemical reactions, the transformed mole fractions \( x_i \) are defined selecting \( r \) reference components:

\[
x_i = \frac{x_i - v_i N^{-1} x_{ref}}{1 - v_i N^{-1} x_{ref}} \quad \text{for } i = 1, \ldots, c - r
\]

where \( x_i \) is the mole fraction of component \( i \), \( x_{ref} \) is a column vector of mole fractions for \( r \) reference components, \( v_i \) is the row vector of stoichiometric coefficients of component \( i \) for each of the \( r \) reactions. \( N \) is an invertible and square matrix formed from the stoichiometric coefficients of the reference components in the \( r \) reactions, and \( v_i \) is a row vector where each element corresponds to the sum of stoichiometric coefficients for all components that participate in each of the \( r \) reactions, respectively. The transformed mole fractions in reactive systems are similar to the mole fractions in non-reactive mixtures and the sum of all transformed mole fractions must equal unity, or \( \sum_{i=1}^{c-r} x_i = 1 \), but a transformed mole fraction can be negative or positive depending on the reference components, number and type of reactions. Note that \( x \) are related to \( x \) using the reaction equilibrium constants \( K_{eq,k} \):

\[
K_{eq,k} = \prod_{i=1}^{c} q_i^{a_i} \quad k = 1, \ldots, r
\]

where \( \alpha_i \) is the stoichiometric coefficient of component \( i \) in reaction \( k \), and \( q_i \) is the activity of component \( i \), respectively. To evaluate thermodynamic properties in reactive systems using this approach, the mole fractions \( x_i \) are obtained from the transformation procedure \( X \rightarrow x \) using Eqs. (9) and (10). These mole fractions \( x \) satisfy the stoichiometry requirements and are chemically equilibrated.

In this study, the bisection method is used for variable transformation \( X \rightarrow x \) in single reactive systems, while the Newton method is applied for multireactive systems. As indicated by Ung and Doherty [47], it is not possible to find multiple solutions for \( x_{ref} \) during variable transformation \( X \rightarrow x \) because only one solution set of \( x \) simultaneously satisfies the chemical equilibrium equations and corresponds to the specified values of the transformed composition variables.

Then, the reactive tangent plane distance function (RTPDF) for a \( c \) multicomponent and \( r \) multireactive system with transformed global composition \( Z = (z_1, \ldots, z_c) \) is defined as:

\[
RTPDF = \sum_{i=1}^{c-r} y_i (\mu_i |y\rangle - \mu_i |z\rangle)
\]

where \( \mu_i |y\rangle \) and \( \mu_i |z\rangle \) are the chemical potentials of component \( i \) calculated at the transformed mole compositions \( Y \) and \( Z \), respectively. RTPDF represents the displacement from the tangent plane at a composition \( Z \) to the transformed molar Gibbs free energy surface at composition \( Y \) [12]. The necessary and sufficient condition for global phase stability is given by \( RTPDF \geq 0 \) for any transformed composition \( Y \) from the whole transformed composition space. Thus, RTPDF must be globally optimized with respect to the transformed composition of a trial phase \( Y \) for solving the phase stability problem in reacting mixtures.

### Table 1

Characteristics of PSO variants used for phase stability and equilibrium calculations in reactive and non-reactive systems.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>PSO-C</td>
<td>Particle swarm optimization with constant ( c_1 ) and ( c_2 ). Swarm position and velocity are given by Eqs. (1) and (2).</td>
</tr>
<tr>
<td>PSO-D</td>
<td>Particle swarm optimization with dynamic ( c_1 ) and ( c_2 ) (Eq. 3). Swarm position and velocity are given by Eqs. (1) and (2).</td>
</tr>
<tr>
<td>PSO-I</td>
<td>Particle swarm optimization with constant inertia weight ( w ) and constant ( c_1 ) and ( c_2 ). Swarm position and velocity are given by Eqs. (1) and (2).</td>
</tr>
<tr>
<td>PSO-DI</td>
<td>Particle swarm optimization with dynamic inertia weight ( w ) (Eq. (5)) and constant ( c_1 ) and ( c_2 ). Swarm position and velocity are given by Eqs. (1) and (2).</td>
</tr>
<tr>
<td>PSO-CF</td>
<td>Particle swarm optimization with constant ( c_1 ) and ( c_2 ) and constriction factor. Swarm position and velocity are given by Eqs. (1), (6) and (7).</td>
</tr>
</tbody>
</table>
The global minimization of TPDF and RTPDF is difficult and requires robust numerical methods since these functions are multivariable, non-convex and highly non-linear. For the case of TPDF, several deterministic [9–11,13–19] and stochastic [21,23–25,27,29,31,32,40,42] optimization methods have been reported. On the other hand, few studies have dealt with the global solution of RTPDF using a homotopy continuation method [22], simulated annealing [29], differential evolution and tabu search [30]. Thus, PSO and its variant have not been applied to solve the phase stability problem of multicomponent reactive and non-reactive mixtures.

The decision variables in phase stability problems are \(c - 1\) mole fractions \(y_i\) for non-reactive systems and \(c - r - 1\) transformed mole fractions \(Y_i\) for reactive systems, taking into account that \(y_c = 1 - \sum_{i=1}^{c-1} y_i\) and \(Y_c = 1 - \sum_{i=1}^{c-1} Y_i\), Following previous studies [24,29,32], the constrained global optimization of TPDF or RTPDF can be transformed into an unconstrained problem by using new decision variables \(\hat{\beta}_i\) instead of \(y_i\) and \(Y_i\). The decision variables \(\hat{\beta}_i \in (0, 1)\) are related to composition variables \(y\) and \(Y\) by:

\[
\hat{\beta}_i = \frac{z_i}{\sum_j z_j} n_{ij} \quad i = 1, \ldots, c
\]

(12)

and

\[
\hat{Y}_i = \frac{\hat{\beta}_i Z_i}{\sum_j \hat{\beta}_j Z_j} \quad i = 1, \ldots, c - r
\]

(13)

where

\[
y_i = \frac{n_{ij}}{\sum_{j=1}^c n_{ij}} \quad i = 1, \ldots, c
\]

(14)

\[
Y_i = \frac{\hat{\beta}_i Y_i}{\sum_j \hat{\beta}_j Y_j} \quad i = 1, \ldots, c - r
\]

(15)

where \(n_{ij} = \sum_{j=1}^c n_{ij}\) and \(\hat{\beta}_i = \sum_{j=1}^{c-1} \hat{\beta}_j\) are the total amount of conventional and transformed moles in the feed composition used for stability analysis, and \(n_{ij}\) and \(\hat{\beta}_i\) are the conventional and transformed mole number of component \(i\) in trial phase \(y\) and \(Y\), respectively. Note that the transformed mole numbers \(\hat{\beta}_i\) are given as:

\[
\hat{\beta}_i = n_i - n_{ref} \quad i = 1, \ldots, c - r
\]

(16)

where \(n_i\) is the number of moles of component \(i\) and \(n_{ref}\) is a column vector of dimension \(r\) of the moles of each of the reference components, respectively. The mole fractions \(z_i\) and \(Z_i\) are obtained from \(z_i = \hat{\beta}_i n_{ij}\) and \(Z_i = \hat{\beta}_i N_{ij}\). Eqs. (12)–(15) have been used for all stability calculations performed in this study. Finally, the calculation of TPDF and RTPDF is straightforward with almost any thermodynamic model because:

\[
\frac{\mu_i - \mu^0_i}{R_k T} = \ln \left( \frac{x_i v_i}{\phi_i} \right) = \ln(x_i y_i)
\]

(17)

where \(R_k\) is the universal gas constant, \(\mu^0_i\) is the chemical potential of pure component \(i\), \(\hat{\beta}_i\) is the fugacity coefficient of component \(i\) in the mixture, \(\phi_i\) is the fugacity coefficient of pure component, \(\gamma_i\) is the activity coefficient of component \(i\) in the mixture, and \(x_i\) is the mole fraction of component \(i\) in the mixture.

3.2. Phase split calculations

In phase split problems, the main objectives are to correctly establish the number and types of phases existing at equilibrium as well as the composition and quantity of each phase such that the Gibbs free energy of the system is a minimum [7]. At constant temperature and pressure, a \(c\) multicomponent and \(\pi\) multiphase non-reactive system achieves equilibrium when its molar Gibbs free energy of mixing \((g)\) is at the global minimum. The corresponding objective function is given by:

\[
g = \sum_{j=1}^{\pi} \sum_{i=1}^c n_{ij} \ln(x_{ij} y_{ij}) = \sum_{j=1}^{\pi} \sum_{i=1}^c n_{ij} \ln \left( \frac{x_{ij} y_{ij}}{\phi_i} \right)\]

(18)

where \(n_{ij}\) is the mole number of component \(i\) in phase \(j\), \(y_{ij}\) is the activity coefficient of component \(i\) in phase \(j\), and \(\phi_i\) is the fugacity coefficient of component \(i\) in phase \(j\), respectively. The Gibbs free energy of mixing \((g)\) is used to avoid the calculation of the pure component free energies, which do not influence equilibrium and stability results [46]. For a non-reactive system, \(g\) must be minimized with respect to \(n_{ij}\) taking into account the following mass balance constraints:

\[
\sum_{j=1}^{\pi} n_{ij} = z_i n_{ref} \quad i = 1, \ldots, c
\]

(19)

where \(z_i\) is the mole fraction of component \(i\) in the feed. In reactive mixtures, the Gibbs free energy minimization is subject to chemical equilibrium restrictions [7]. However, this difficult thermodynamic problem can be readily solved if the Gibbs energy function is expressed in terms of transformed composition variables \((X)\) [46,47]. For these conditions, minimizing the Gibbs free energy is equivalent to the optimization of transformed Gibbs free energy. Then, the transformed Gibbs free energy of mixing \((\hat{g})\) for a multiphase reactive system is defined as:

\[
\hat{g} = \sum_{j=1}^{\pi} \sum_{i=1}^{c-1} \hat{n}_{ij} \ln(x_{ij} y_{ij}) = \sum_{j=1}^{\pi} \sum_{i=1}^{c-1} \hat{n}_{ij} \ln \left( \frac{x_{ij} y_{ij}}{\phi_i} \right)
\]

(21)

where \(\hat{n}_{ij}\) is the transformed mole number of component \(i\) in phase \(j\). Assuming a reactive system where all transformed composition variables are positive, the material balances are described as follows:

\[
\sum_{j=1}^{\pi} \hat{n}_{ij} = Z_i \hat{n}_{ref} \quad i = 1, \ldots, c - r
\]

(22)

where \(Z_i\) is the transformed mole fraction of component \(i\) in the feed.

For phase equilibrium calculations in non-reactive and reactive systems, \(g\) and \(\hat{g}\) are the objective functions which, due to the non-linear nature of thermodynamic models, are generally multivariable and non-convex. As indicated, simulated annealing and genetic algorithms [24], tabu search [28], tunneling method [20], differential evolution [29,32] and particle swarm optimization [41,42] have been used for performing Gibbs energy minimization in non-reactive systems. To date, PSO has been applied in binary and ternary systems. In contrast, few stochastic methods have been tested and applied for phase equilibrium calculations in reactive systems, especially using reaction-invariant composition variables [26,30], and preliminary results [43] have suggested that PSO appears to be a robust strategy for the global minimization of \(\hat{g}\). To the best of our knowledge, no one has reported a detailed evaluation and comparison of PSO and its variants for Gibbs energy minimization in both multicomponent reactive and non-reactive systems.

To perform an unconstrained minimization of \(g\) and \(\hat{g}\), we can again use a set of new variables instead of \(n_{ij}\) and \(\hat{n}_{ij}\) as optimization targets. The introduction of these variables eliminates the restrictions imposed by material balances, reduces problem dimensionality, and the optimization problem is transformed to an
unconstrained one [24,29,30,32]. For multiphase non-reactive systems, real variables $\beta_i \in (0, 1)$ are defined and employed as decision variables by using the following expressions:

\[
\begin{align*}
    n_{i1} &= \beta_i z_{i1} n_{iF} & i &= 1, \ldots, c \\
    n_{ij} &= \beta_i z_{ij} \left( z_{iF} - \sum_{m=1}^{\pi-1} n_{jm} \right) & i &= 1, \ldots, c, \quad j = 2, \ldots, \pi - 1 \\
    n_{ic} &= z_{iF} - \sum_{j=1}^{\pi-1} n_{ij} & i &= 1, \ldots, c
\end{align*}
\]

while for systems subject to chemical equilibrium, we have

\[
\begin{align*}
    \tilde{n}_{i1} &= \beta_i z_{iF} & i &= 1, \ldots, c - r \\
    \tilde{n}_{ij} &= \beta_i z_{iF} - \sum_{m=1}^{\pi-1} \tilde{n}_{jm} & i &= 1, \ldots, c - r, \quad j = 2, \ldots, \pi - 1 \\
    \tilde{n}_{ic} &= z_{iF} - \sum_{j=1}^{\pi-1} \tilde{n}_{ij} & i &= 1, \ldots, c - r
\end{align*}
\]

Using this formulation, all trial compositions will satisfy the material balances allowing the easy application of optimization strategies [24,29,32]. For Gibbs energy minimization, the number of phases existing at the equilibrium is assumed to be known a priori and the number of decision variables is $c(\pi - 1)$ for non-reactive and $(c - r)(\pi - 1)$ for reactive systems, respectively.

4. Results and discussion

4.1. Description of phase equilibrium problems

We have tested and compared the performance of PSO and its variants using reactive and non-reactive systems with dimension ranging from 2 to 10. Several systems are multicomponent (i.e., $c \geq 3$) and their thermodynamic properties are represented with equation of state, solution model and ideality. Our collection of test problems includes systems with vapor–liquid and liquid–liquid equilibrium. A brief description of all examples are given in Tables 2–4 and detailed global solutions of all phase equilibrium problems can be found in Refs. [14,16,24–26,30]. The objective functions (i.e., $TPDF$, $RTPDF$, $g$ and $h$) have at least one local minimum, which corresponds to a trivial solution, for all tested conditions. In addition, the selected conditions involve feed compositions near phase boundaries, which are generally challenging for any algorithm. Most of the selected phase equilibrium problems have been used for testing other deterministic and stochastic optimization strategies, e.g. [9,12,14–16,21,22,24–26,29–31].

4.2. Parameter tuning of PSO-based methods

The key parameters of PSO and its variants have been tuned by finding the global minimum of several phase stability and equilibrium problems. For this purpose, we have considered systems with different degrees of difficulty: example nos. 3 and 5 for non-reactive systems and example nos. 4 and 8 for reactive mixtures. Parameter tuning was performed by varying one parameter at a time while the rest are fixed at nominal values, which were established using values reported in the literature and results of preliminary calculations (not reported in this paper). The tested and suggested parameter values for each PSO-based method are presented in Table 5. For calculations performed in this study, we set $n_p = 10n_{max}$ (i.e., swarm size) and $n_r = 0.25n_p$ (i.e., neighborhood size) in all PSO variants because our preliminary calculations suggest that these parameter values are a reasonable compromise between numerical effort and reliability. All numerical experiments were performed on an Intel Pentium M 1.73 GHz processor with 504 MB of RAM. This computer performs 254 million floating point operations per second (MFlops) for the LINPACK benchmark program (available at http://www.netlib.org/) for a matrix of order 500.

4.3. Comparison of PSO and its variants in phase stability and equilibrium calculations

Having performed parameter tuning, we now compare the performance of PSO-based methods. In order to facilitate understanding and to make the performance difference between

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>Feed</th>
<th>Thermodynamic models</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-Butyl acetate + water</td>
<td>$z(0.5, \ldots, 0.5)$ at 298 K and 101.325 kPa</td>
<td>NRTL model. Model parameters reported by Rangaiah [24].</td>
<td>[14,15,24,29,42]</td>
</tr>
<tr>
<td>2</td>
<td>Toluene + water + aniline</td>
<td>$z(0.29998, 0.00006, 0.00005)$ at 298 K and 101.325 kPa</td>
<td>NRTL model. Model parameters reported by McDonald and Floudas [14].</td>
<td>[14,24,29,42]</td>
</tr>
<tr>
<td>3</td>
<td>N$_2$ + C$_1$ + C$_2$</td>
<td>$z(0.3, 0.1, 0.6)$ at 270 K and 7600 kPa</td>
<td>SRK EoS with classical mixing rules. Model parameters reported by Bonilla-Petriciolet et al. [25].</td>
<td>[16,25,31]</td>
</tr>
<tr>
<td>4</td>
<td>C$_1$ + H$_2$S</td>
<td>$z(0.9813, 0.0187)$ at 190 K and 4053 kPa</td>
<td>SRK EoS with classical mixing rules. Model parameters reported by Rangaiah [24].</td>
<td>[4,9,16,21,24,29,31]</td>
</tr>
<tr>
<td>5</td>
<td>H$_2$O + CO$_2$ + 2-propanol + ethanol</td>
<td>$z(0.99758, 0.00003, 0.00013, 0.00022)$ at 350 K and 2250 kPa</td>
<td>SRK EoS with classical mixing rules. Model parameters reported by Harding and Floudas [16].</td>
<td>[16,25]</td>
</tr>
<tr>
<td>6</td>
<td>C$_2$ + C$_1$ + C$_4$ + C$_6$</td>
<td>$z(0.401, 0.293, 0.199, 0.070, 0.0363)$ at 390 K and 5583 kPa</td>
<td>SRK EoS with classical mixing rules. Model parameters reported by Bonilla-Petriciolet et al. [25].</td>
<td>[25]</td>
</tr>
<tr>
<td>7</td>
<td>C$_1$ + C$_4$ + C$<em>6$ + C$<em>8$ + C$</em>{10}$ + C$</em>{17}$</td>
<td>$z(0.7212, 0.09205, 0.00445, 0.003123, 0.01273, 0.01361, 0.007215, 0.01248)$ at 353 K and 38500 kPa</td>
<td>SRK EoS with classical mixing rules. Model parameters reported by Harding and Floudas [16].</td>
<td>[16,25]</td>
</tr>
<tr>
<td>8</td>
<td>C$_1$ + C$<em>4$ + C$<em>6$ + C$<em>9$ + C$</em>{12}$ + C$</em>{20}$ + C$</em>{15}$</td>
<td>$z(0.614, 0.10259, 0.04985, 0.008989, 0.02116, 0.00722, 0.01187, 0.01435, 0.01273, 0.01361, 0.007215, 0.01248)$ at 314 K and 2010.288 kPa</td>
<td>SRK EoS with classical mixing rules. Model parameters reported by Rangaiah [24].</td>
<td>[22,24,25,29]</td>
</tr>
<tr>
<td>9</td>
<td>C$_1$ + C$_4$ + C$_6$ + C$<em>8$ + C$</em>{10}$</td>
<td>$z(0.6436, 0.0752, 0.0474, 0.0412, 0.0297, 0.0138, 0.0303, 0.0371, 0.0415, 0.0402)$ at 435.35 K and 19150 kPa</td>
<td>SRK EoS with classical mixing rules. Model parameters reported by Bonilla-Petriciolet et al. [25].</td>
<td>[25]</td>
</tr>
</tbody>
</table>
Table 3
Examples selected for phase stability and equilibrium calculations in reactive systems using particle swarm optimization and its variants.

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>Feed and transformed variables</th>
<th>Thermodynamic models</th>
<th>Reference</th>
</tr>
</thead>
</table>
| 1   | $A_1 + A_2 \rightarrow A_3$
     | $2A_1 \rightarrow 2A_4 + A_2$ | $Z (0.445, 0.555)$ at 101.325 kPa and 310 K
     | $X_1 = (x_1 + x_2 + 2x_4)/(1 + x_2 + 2x_4)$
     | $X_2 = (x_2 + x_4)/(1 + x_2 + 2x_4) = 1 - X_1$ | Ideal solution and ideal gas.
     | Reference components: $A_3, A_4$ | $K^c_{A_3} = \exp \left( -(-22.57 \pm (7388/T)) \right)$
     | | $K^c_{A_4} = \exp \left( -(-2.0265 \pm (6844.1/T) - (1.391, 790)/T) \right)$ |
|     |        |                                 |                      | [26,47]   |
| 2   | $A_1 + A_2 \rightarrow A_3$, and $A_4$ as an inert component.
     | (1) Isobutene | $Z (0.3, 0.3, 0.4)$ at 373.15 K and 1013.25 kPa
     | $X_1 = (x_1 + x_2)/(1 + x_2 + x_3)$
     | $X_2 = (x_2 + x_4)/(1 + x_2 + 2x_4) = 1 - X_1 - X_2$ | Wilson model and ideal gas.
     | Reference component: $A_3$ | $\Delta G^o_{A_3}/R = -4205.05 - 10.0982T - 0.26677 \ln T$
     | | In $K_{eq} = (-\Delta G^o_{A_3}/RT)$, where $T$ is in K.
     | | Model parameters are taken from Bonilla-Petriolet et al. [26].
| 3   | $A_1 + A_2 + 2A_4 \rightarrow 2A_4$
     | (1) 2-Methyl-1-butene | $Z (0.354, 0.183, 0.463)$ at 335 K and 151.9875 kPa
     | $X_1 = (x_1 + x_3)/(1 + x_2)$
     | $X_3 = (2x_2 + 0.5x_4)/(1 + x_4)$ | Wilson model and ideal gas.
     | (2) 2-Methyl-2-butene | $X_1 = (x_1 + x_3)/(1 + x_4) = 1 - X_1 - X_2$ | [26]
     | Reference component: $A_4$ | $K_{eq} = 1.057 \times 10^{-94} e^{(717.5/T)}$, where $T$ is in K.
     | | Model parameters are taken from Bonilla-Petriolet et al. [26].
| 4   | $A_1 + A_2 \rightarrow A_3 + A_4$
     | (1) Acetic acid | $Z (0.05, 0.2, 0.75)$ at 298.15 K and 101.325 kPa
     | $X_1 = x_1 + x_3$
     | $X_2 = x_2 + x_4$ | UNIQUAC model.
     | (2) n-Butanol | $X_1 = x_1 - x_3 - x_4$ | [12,26]
     | (3) Water | $X_2 = x_2$ | In $K_{eq} = (450/T) + 0.8$, where $T$ is in K.
     | Reference component: $A_4$ | Model parameters are taken from Wasylikiewicz and Ung [12].
| 5   | $A_1 \rightarrow A_4$
     | (1) Acetic acid | $Z (0.6305, 0.00355, 0.36595)$ at 101.325 kPa and 333.15 K
     | $X_1 = x_1$
     | $X_2 = x_2 + x_4$ | Ideal solution and ideal gas.
     | (2) n-Butanol | $X_1 = x_1 - x_4 + x_5 + x_6 = 1 - X_1 - X_3$ | [30,49]
     | Reference components: $A_3, A_4, A_5$
     | with $A_1$ and as $A_2$ inert components. | $K_{eq,1} = 1.5$
     | | $K_{eq,2} = 0.15$
     | | $K_{eq,3} = 0.35$
     | | Model parameters are taken from Bonilla-Petriolet et al. [30].
| 6   | $A_1 + A_2 + 2A_4 \rightarrow 2A_4$ with $A_3, A_6, A_7, A_8$, and $A_9$ as inert components.
     | (1) 2-Methyl-1-butene | $Z (0.16, 0.169, 0.119, 0.02339, 0.213, 0.177, 0.13861)$ at 310 K and 100 kPa.
     | $X_1 = (x_1 + 0.5x_4)/(1 + x_4)$
     | $X_3 = (x_4)/(1 + x_4)$ | Model parameters are taken from Bonilla-Petriolet et al. [50].
     | (2) 2-Methyl-2-butene | $X_1 = (x_1 + x_3)/(1 + x_4)$
     | $X_3 = (x_3)/(1 + x_4)$ | In $K_{eq,1} = (450/T) + 0.8$, where $T$ is in K.
     | Reference component: $A_4$ | Model parameters are taken from Luyben [50].
|     | (3) Methanol
     | (4) Tert-amy methyl ether
     | (5) n-Pentane
     | (6) Isopentane
     | (7) T-Pentene
     | (8) 2-Pentene | | | | |
| 7   | $A_1 + A_2 \rightarrow A_3$
     | (1) Propene | $Z (0.6, 0.4)$
     | $X_1 = (x_1 + x_3)/(1 + x_1)$
     | $X_2 = (x_2 + x_4)/(1 + x_2) = 1 - X_1$ | Margules solution model.
     | Reference component: $A_3$ | $(g^a/T_2g) = 3.6 a x_2 + 2.4 a x_1 x_2 + 2.3 x_1 x_3$ |
|     |        |                                 |                      | [26]      |
| 8   | $A_1 + A_2 + 2A_4 \rightarrow 2A_4$ with $A_3$ as inert component
     | (1) 2-Methyl-1-butene | $Z (0.1, 0.1, 0.1, 0.6, 0.2)$ at 335 K and 151.9875 kPa
     | $X_1 = (x_1 + 0.5x_4)/(1 + x_4)$
     | $X_3 = (x_4)/(1 + x_4)$ | Wilson model and ideal gas.
     | (2) 2-Methyl-2-butene | $X_1 = (x_1 + x_3)/(1 + x_4)$
     | $X_3 = (x_3)/(1 + x_4)$ | $K_{eq,1} = 1.057 \times 10^{-94} e^{(717.5/T)}$, where $T$ is in K.
     | Reference component: $A_4$ | Model parameters are taken from Bonilla-Petriolet et al. [26].
|     | (3) Methanol
     | (4) Tert-amy methyl ether
     | (5) n-Pentane | | | | | | |
| 9   | $A_1 + A_2 \rightarrow A_3$
     | (1) Propene | $Z (0.37, 0.63)$ at 353.15 K and 100 kPa
     | $X_1 = (x_1 + x_3)/(1 + x_1)$
     | $X_2 = (x_2 + x_4)/(1 + x_2) = 1 - X_1$ | SRK EoS with conventional mixing rules and all interaction parameters equal to zero.
     | Reference component: $A_3$ | $K_{eq} = 23$
     | | Model parameters are taken from Bonilla-Petriolet et al. [26].
|     | (2) Water | | | | | | | | |
|     | (3) 2-Propanol | | | | | | | | |
PSO-based methods more explicit, we have employed the performance profile (PP) reported by Dolan and More [48]. PP is an alternative tool for evaluating and comparing the performance of several solvers on a set of test problems. The results of PP allow us to identify the expected performance differences among several solvers and to compare the quality of their solutions by eliminating the bias of failures obtained in a small number of problems. We will give a brief overview of PP, and a detailed description is provided by Dolan and More [48]. Suppose that, for a set of \( N_{\text{prob}} \) problems (in our case, the collection of phase equilibrium problems reported in Tables 2 and 3) and a set of \( S \) solvers (in our case, PSO and its variants tested), we obtain a performance metric \( t_{ij} \geq 0 \) for every solver \( i \in S \) and problem \( j \in N_{\text{prob}} \). This performance metric should give information on solver reliability, efficiency or another performance measure useful to characterize the capabilities of the solver under evaluation. For each problem \( j \in N_{\text{prob}} \), we calculate:

\[
t_j = \min(t_{ij} / \text{solver } i \in S)
\]

which indicates the best possible performance for problem \( j \) among all the solvers tested. For a particular solver \( i \), the set of performance ratios \( \sigma_j \) is determined by:

\[
\sigma_j = \frac{t_{ij}}{t_j} \quad j \in N_{\text{prob}}
\]

The performance ratio \( \sigma_j \) of method \( i \) for problem \( j \) is simply the ratio of the method's performance to the best performance value over all solvers for the same problem. The value of \( \sigma_j \) is 1 for the solver that performs best on a specific problem \( j \). For every solver \( i \in S \), let \( \rho_j(\xi) \) be the fraction of problems for which \( \sigma_j \leq \xi \) where \( \xi \geq 1 \). Specifically, we have:

\[
\rho_j(\xi) = \frac{1}{N_{\text{prob}}} \sum_{j \in N_{\text{prob}} : \sigma_{ij} \leq \xi}
\]

where the “size” is the number of problems such that the performance ratio \( \sigma_j \) is less than or equal to \( \xi \) for solver \( j \). The parameter \( \rho_j(\xi) \) indicates the fraction of problems for which solver \( i \) is within a factor of \( \xi \) of the best solver (according to the performance metric chosen for solver comparison). Thus, the performance profile of a solver represents the cumulative distribution function of its performance ratios and is a plot of \( \rho_j(\xi) \) versus \( \xi \). Note that \( \rho_j(1) \) indicates the probability (i.e., fraction of problems tested) for which solver \( i \) was the best solver overall. To identify the best solver using PP, it is only necessary to compare the values of \( \rho_j(1) \) for all solvers and to select the highest one.

Our study compares how well the PSO-based methods can estimate the global optimum relative to one another in phase stability and equilibrium calculations. So, we have used the following performance metric for a systematic assessment of PSO reliability:

\[
t_j = f_{\text{calc}}^j - f_j^*
\]

where \( f_j^* \) is the known global optimum of the objective function for problem \( j \) and \( f_{\text{calc}}^j \) is the mean value of the objective function calculated by the stochastic method for solver \( i \) over 100 runs performed with random initial values for problem \( j \). This performance metric is useful to identify the algorithm that provides the most accurate value of the global minimum in phase equilibrium problems and we consider that it is suitable for comparison of PSO-based methods. In this study, performance profiles are calculated at different levels of efficiency, which are obtained by varying the stopping conditions \( \text{Iter}_{\text{max}} \) and \( \text{Sc}_{\text{max}} \), to investigate the behavior of PSO algorithms.

First we assess the effect of stopping criterion \( \text{Iter}_{\text{max}} \) on performance of PSO-based methods. To directly compare the reliability of PSO and its variants, we keep the number of function evaluations (\( \text{NEF}_{\text{calc}} \)) constant using \( \text{Iter}_{\text{max}} \) alone as stopping condition and evaluate the quality of the results obtained. Note that fair algorithm comparisons can only occur if all solvers have a uniform stopping condition. Fig. 2a shows the results of \( \rho_j(1) \) versus \( \text{Iter}_{\text{max}} \) for PSO and its variants in phase stability and equilibrium calculations of both reactive and non-reactive systems using Eq. (33) as performance metric. Our results indicate that PSO-C offers the best performance and shows the highest probability for finding the best solutions in the collection of phase equilibrium problems used in the present study. It is clear from Fig. 2a that the probability \( \rho_j(1) \) of PSO-C increases as \( \text{Iter}_{\text{max}} \) increases. In fact, PSO-C dominates the other PSO variants and is the best method throughout the range of \( \text{Iter}_{\text{max}} \) tested. On the other hand, PSO-CF appears to be the second best algorithm for this stopping criterion especially at early iterations. But, its probability \( \rho_j(1) \) decreases when \( \text{Iter}_{\text{max}} \) increases. Overall, results of PP indicate that the best solutions found by PSO-D, PSO-I and PSO-DI are worse than the best solution found by PSO-C and PSO-CF in the global optimization of \( \text{TPDF} \), \( \text{RTPDF} \), \( g \) and \( \hat{g} \).

The results of PP using \( \text{Sc}_{\text{max}} \) alone as stopping condition are reported in Fig. 2b. At low values of \( \text{Sc}_{\text{max}} \), PSO-CF has the high-

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Global minimum of selected reactive and non-reactive examples.</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Non-reactive</td>
</tr>
<tr>
<td></td>
<td>TPDF</td>
</tr>
<tr>
<td></td>
<td>( g )</td>
</tr>
<tr>
<td>1</td>
<td>-0.032466</td>
</tr>
<tr>
<td>2</td>
<td>-0.294540</td>
</tr>
<tr>
<td>3</td>
<td>-0.015767</td>
</tr>
<tr>
<td>4</td>
<td>-0.009352</td>
</tr>
<tr>
<td>5</td>
<td>-0.012650</td>
</tr>
<tr>
<td>6</td>
<td>-0.000002</td>
</tr>
<tr>
<td>7</td>
<td>-0.002688</td>
</tr>
<tr>
<td>8</td>
<td>-0.1486205</td>
</tr>
<tr>
<td>9</td>
<td>-0.000020</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Suggested values of parameters in PSO and its variants for phase stability and equilibrium calculations in multicomponent reactive and non-reactive mixtures.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSO method</td>
<td>Parameter</td>
</tr>
<tr>
<td>PSO-C</td>
<td>( c_1 )</td>
</tr>
<tr>
<td></td>
<td>( c_2 )</td>
</tr>
<tr>
<td>PSO-D</td>
<td>( c_{1p} )</td>
</tr>
<tr>
<td></td>
<td>( l )</td>
</tr>
<tr>
<td>PSO-I</td>
<td>( c_1 )</td>
</tr>
<tr>
<td></td>
<td>( c_2 )</td>
</tr>
<tr>
<td></td>
<td>( w )</td>
</tr>
<tr>
<td>PSO-DI</td>
<td>( c_1 )</td>
</tr>
<tr>
<td></td>
<td>( c_2 )</td>
</tr>
<tr>
<td></td>
<td>( w_0 )</td>
</tr>
<tr>
<td>PSO-CF</td>
<td>( c_1 )</td>
</tr>
<tr>
<td></td>
<td>( c_2 )</td>
</tr>
</tbody>
</table>
Results of performance profiles for the comparison of PSO and its variants in phase stability and equilibrium calculations of reactive and non-reactive mixtures. Performance metric \( t_i = \hat{f}_{\text{calc}} - f_\ast \). Stopping condition of PSO: (a) a maximum number of iterations and (b) a maximum number of successive iterations without improvement in the best function value. Note that missing bars indicate that the probability \( p_i(1) \) for solver \( i \) is 0.0.

As indicated by Ali and Kaelo [35], the usual variants to the original PSO have been proposed to make it faster. Unfortunately, these variants improve the convergence rate of PSO but compromise reliability in reactive and non-reactive phase stability and equilibrium calculations.

In conclusion, the order of reliability of the PSO algorithms in finding the global minimum for phase equilibrium problems is PSO-C > PSO-CF > PSO-D > PSO-DI ≈ PSO-I using either \( \text{Iter}_{\text{max}} \) or \( \text{Sc}_{\text{max}} \) as stopping condition. Among the PSO variants tested in this study, PSO-C is the best from the standpoint of algorithm reliability and its selection is therefore clearly justified for solving phase stability and equilibrium problems in reactive and non-reactive systems.

4.4. Numerical study of the best PSO algorithm in combination with a local optimization method

After selecting the best PSO algorithm, we now perform a comparative study using PSO in combination with a local optimization technique for finding the global minimum accurately and efficiently. Specifically, the point identified by the best PSO algorithm is used as initial guess for a local optimization technique. Note that stochastic optimization methods may require a significant computational effort to improve the accuracy of global solution because they explore the search space of decision variables by creating random movements instead of determining a logical optimization trajectory. This convergence behavior is illustrated in Fig. 4 for some reactive and non-reactive phase equilibrium problems. Therefore, the intensification step is needed for rapid convergence and for improving the accuracy of final solutions once the particles of PSO are clustered around the global optimum especially in multicomponent systems. For local optimization, we have applied and compared two strategies, namely: (a) a quasi-Newton (QN) method implemented in the subroutine DBCONF from IMSL library and (b) a Nelder–Mead (NM) simplex method implemented in the subroutine DBCPOL from IMSL library. The former is an efficient gradient-based method that calculates the gradient via finite differences and approximates the Hessian matrix according to the BFGS formula, whereas the latter is a direct search method not requiring derivatives. The default values of both DBCONF and DCPOL parameters in the IMSL library were used in our calculations. The performance of the best PSO with local optimization is studied from the standpoints of reliability and efficiency. All algorithms were run 100 times, with random initial values for decision variables and random number seed, on each of the test problems to
determine the success rate (SR, measured in terms of number of times the algorithm located the global minimum out of 100 trials and reported as percentage) and computational efficiency (measured in terms of average number of function evaluations NFE and CPU time). The average NFE and CPU time were calculated using successful trials only. A trial is considered successful if the global optimum is obtained with an absolute error of $10^{-5}$ or lower in the objective function value, i.e., $|f^* - f_{cal}| \leq 10^{-5}$. One exception is the non-reactive example no. 5 where an absolute error of $10^{-7}$ in the objective function $g$ was used to avoid counting local minima as the global optimum. NFE includes both the function calls for evaluating the objective function using the stochastic method ($NFE_{stoc}$) and the function calls for the local optimization ($NFE_{loc}$).

The performance of PSO-C implemented with DBCONF and DCPOL subroutines is given in Fig. 5 and Tables 6 and 7. The PSO methods consisting of PSO-C followed by QN or NM are denoted as PSO-CQN and PSO-CNM, respectively. For the sake of brevity, algorithm reliability results are summarized through the global success rate (GSR, %). Specifically, GSR is defined as the total number of successes out of all calculations performed on the collection of phase equilibrium problems tested:

$$GSR = \sum_{i=1}^{nb} \frac{SR_i}{N_{prob}}$$

where $SR_i$ is the success rate in the problem $i$. Overall, the GSR of PSO-CNM is slightly higher than that obtained for PSO-CQN using $Iter_{max}$ and $Sc_{max}$. As expected, the GSR of both PSO-CNM and PSO-CQN improves as $Iter_{max}$ or $Sc_{max}$ increases (see Fig. 5). Our results show that there is an improvement in the reliability of both PSO-CQN and PSO-CNM using $Iter_{max}$ compared to that of $Sc_{max}$. This could be because PSO algorithms require several iterations to improve objective function values after getting stuck at some local optima especially in challenging optimization problems. It is important to note that PSO-CNM offers better performance in reactive phase equilibrium problems than PSO-CQN. This could be because the objective functions $RTPDF$ and $\hat{g}$ appear to be flat near the global solution, affecting the numerical behavior of gradient-based methods. In general, the SR of PSO-CNM is around 100% in the global optimization of $TPDF$ for examples 1–4 and $\hat{g}$ whereas the global optimum of $RTPDF$ is found with a high SR in all reactive examples if proper values of $Iter_{max}$ and $Sc_{max}$ are used. PSO-CNM failed several times to find the global optimum of $TPDF$ in non-reactive example nos. 5–7 and 9. In particular, non-reactive example no. 5 is very challenging and useful for testing new global optimization strategies due to the presence of comparable minima [16]. With respect to phase split calculations, PSO-CNM is also very reliable in the global optimization of $g$ for all non-reactive examples with the exception of example no. 5, where performance is very poor (i.e., 0% SR). For the case of $\hat{g}$, the reliability of PSO-CNM is close to 100% SR for reactive example nos. 2, 4–8, while this method showed failures in the global optimization of reactive example nos. 1, 3 and 9. On the other hand, PSO-CQN requires a slightly lower NFE than PSO-CNM using $Iter_{max}$ and $Sc_{max}$ (see results reported in Tables 6 and 7). The CPU time ranged from 0.01 to 5.88 s for non-reactive examples and from 0.16 to 101.1 s in reactive examples in all calculations performed using PSO-CNM. Note that the CPU time in reactive systems is higher due to the variable transformation procedure $X \rightarrow x$ involved in the calculation of thermodynamic properties especially when EoS models and high values of $Iter_{max}$ ($>1000$) are used.

Finally, the performance of PSO-CNM is compared with results reported by Rahman et al. [42] for repulsive particle swarm opti-
CNM can find the global optimum of both phase equilibrium compositions. Our results indicate that PSO-CNM required to complete the stability test is only 1057 and the SR but using a lower NFE than RPSO. Specifically, the NFE of PSO-CNM 5871 11,24 26,190 51.258 76,298 101,317 151,330 NC 7226 10,237

5. Conclusions

This paper reports on a comparative study of particle swarm optimization and several of its variants for performing phase stability and equilibrium calculations in both reactive and non-reactive systems. We have shown and compared the effect that the stopping condition has on the reliability and efficiency of PSO-based methods for solving phase equilibrium problems. Overall, classical particle swarm optimization with constant cognitive and social parameters offers the best performance from the standpoint of algorithm reliability, whereas the classical variants of particle swarm optimization are effective but not reliable methods to perform the global optimization of TPDF, RTPDF, g and h. The results clearly demonstrate that the incorporation of constriction factor or inertia term in the velocity update rule does not provide a significant improvement in PSO performance in terms of the reliability for finding the global optimum. Furthermore, the Nelder–Mead simplex method is more robust than a quasi–Newton method for the intensification step of PSO especially for reactive phase equilibrium calculations. In summary, our results indicate that PSO–CNM is a suitable alternative method for reliably performing phase stability and equilibrium calculations in reactive and non-reactive systems. Further research is underway for development of an efficient and robust hybrid PSO algorithm using other metaheuristics such as simulated annealing or differential evolution.

List of symbols

- $a_i$: activity of component $i$
- $c$: number of components
- $c_1$: cognitive parameter in PSO
- $c_2$: social parameter in PSO
- $f$: objective function value

Table 6

NFE of PSO–CNM and PSO–CQN in phase stability and equilibrium calculations in selected non-reactive examples.

<table>
<thead>
<tr>
<th>Example</th>
<th>$f$</th>
<th>$n_{var}$</th>
<th>Method</th>
<th>NFE for $\hat{a}$</th>
<th>$\hat{a}_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TPDF</td>
<td>2</td>
<td>PSO–CQN</td>
<td>1029 2.026 5.023 10.019 15.019 20.018 30.018 481 1027 1.958</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>1057 2.055 5.052 10.050 15.049 20.048 30.047 536 1030 1.905</td>
<td></td>
</tr>
<tr>
<td></td>
<td>g</td>
<td></td>
<td>PSO–CQN</td>
<td>1051 2.048 5.045 10.040 15.038 20.037 30.036 553 1248 2.313</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>1074 2.073 5.071 10.071 15.070 20.069 30.068 623 1259 2.354</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>TPDF</td>
<td>5</td>
<td>PSO–CQN</td>
<td>2718 5.219 12.722 25.223 37.722 50.220 75.223 1.915 3013 5.506</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>2769 5.281 12.769 25.264 37.758 50.266 75.271 1.830 2972 5.349</td>
<td></td>
</tr>
<tr>
<td></td>
<td>g</td>
<td></td>
<td>PSO–CQN</td>
<td>2677 5.169 12.666 25.162 37.661 50.162 75.159 1.477 2680 4.680</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>2788 5.293 12.787 25.283 37.783 50.285 75.284 1.896 2790 4.850</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>TPDF</td>
<td>8</td>
<td>PSO–CQN</td>
<td>4652 8.766 20.748 40.771 60.762 80.763 120.757 4.216 5806 9.387</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>4573 8.707 20.692 40.724 60.735 80.712 120.678 3.752 5653 9.366</td>
<td></td>
</tr>
<tr>
<td></td>
<td>g</td>
<td></td>
<td>PSO–CQN</td>
<td>4728 8.718 20.713 40.711 60.712 80.706 120.700 2.411 4371 7.852</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>TPDF</td>
<td>10</td>
<td>PSO–CQN</td>
<td>5861 10.925 25.959 51.008 76.019 101.044 151.072 5.877 7340 11.420</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>5752 10.858 25.908 50.969 75.929 100.922 150.968 4.105 7360 12.024</td>
<td></td>
</tr>
</tbody>
</table>

Table 7

NFE of PSO–CNM and PSO–CQN in phase stability and equilibrium calculations in selected reactive examples.

<table>
<thead>
<tr>
<th>Example</th>
<th>$f$</th>
<th>$n_{var}$</th>
<th>Method</th>
<th>NFE for $\hat{a}$</th>
<th>$\hat{a}_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>RTPDF</td>
<td>3</td>
<td>PSO–CQN</td>
<td>1564 3063 7.562 15.062 22.562 30.063 45.063 744 1625 2909</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>1611 3109 7.607 15.106 22.605 30.105 45.104 914 1673 2956</td>
<td></td>
</tr>
<tr>
<td></td>
<td>g</td>
<td></td>
<td>PSO–CQN</td>
<td>1559 3073 7.586 15.089 22.585 30.083 45.080 681 1471 2928</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>1648 3164 7.671 15.174 22.670 30.169 45.165 1008 1558 3017</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>RTPDF</td>
<td>7</td>
<td>PSO–CQN</td>
<td>3861 7471 17.987 35.542 52.970 70.473 105.546 2162 3761 6834</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>4020 7518 18.015 35.508 53.005 70.504 105.501 3436 4330 6900</td>
<td></td>
</tr>
<tr>
<td></td>
<td>g</td>
<td></td>
<td>PSO–CQN</td>
<td>3849 7414 17.881 35.372 52.832 70.336 105.353 1915 3726 6686</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>4091 7623 18.127 35.619 53.123 70.620 105.623 3518 4639 6893</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>RTPDF</td>
<td>2</td>
<td>PSO–CQN</td>
<td>1053 2051 5.047 10.047 15.046 20.047 30.047 492 1011 1930</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>1101 2059 5.057 10.056 15.056 20.057 30.057 537 1020 1938</td>
<td></td>
</tr>
<tr>
<td></td>
<td>g</td>
<td></td>
<td>PSO–CQN</td>
<td>1070 2070 5.068 10.066 15.064 20.067 30.066 600 1141 2121</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PSO–CNM</td>
<td>1074 2074 5.072 10.071 15.070 20.070 30.069 648 1140 2124</td>
<td></td>
</tr>
</tbody>
</table>
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