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# Phase Stability Analysis and Phase Equilibrium Calculations in Reactive and Nonreactive Systems Using Charged System Search Algorithms

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## Supporting Information

**ABSTRACT:** Stochastic global optimization algorithms have shown promise in providing reliable and efficient solutions for phase stability and phase equilibrium problems in reactive and nonreactive systems. A special class of stochastic methods is Swarm Intelligence, in which search agents are allowed to interact with each other and with their environment and benefit from their peers in their collective pursuit for the global minimum, resulting in an intelligent behavior unknown to the individual agents. Of special interest are swarm intelligence methods with less tunable algorithm parameters, which allow for easy and user-friendly implementation. In particular, this study introduces the Charged System Search, a novel swarm intelligence method, as a global optimization tool to the Chemical Engineering literature via implementing it, for the first time, in solving phase stability and equilibrium problems. Two Charged System Search variants have been employed, namely, the Magnetic Charged System Search and the hybrid version with Particle Swarm Optimization. This hybrid method is coupled with chaotic maps to overcome the local optimum entrapment and to aid its exploration capability. Results indicate that these two variants generally outperformed the Charged System Search, especially the hybrid chaotic algorithm. Results of this study were also compared to those reported for other swarm intelligence methods applied in phase equilibrium calculations. In summary, this study introduces novel swarm intelligence methods for performing phase stability and equilibrium calculations in both reactive and nonreactive systems.

## 1. INTRODUCTION

Phase stability and phase equilibrium calculations are essential components of the design problems of many equipment and processes, and hence, are carried out numerous times by process simulators. These problems can be formulated as minimization problems, for which the global minimum represents the required result. These calculations are often considered as challenging problems due to the high nonlinearity of thermodynamic models used to describe the equilibrium phases, the potential nonconvexity of the objective functions, and the presence of trivial solutions in the feasible search space.<sup>1</sup> Also, these problems generally feature local minima that are comparable to the global minimum, which accentuates the need for reliable global optimizers.<sup>2</sup> The complexity of such problems are rather exacerbated for difficult mixtures and severe conditions manifested in new technologies that make use of process intensification units and models (e.g., reactive distillation). For example, the features of reactive phase equilibrium calculations increase the dimensionality and complexity of the optimization problem because the objective functions are required to satisfy the chemical equilibrium constraints.<sup>1,2</sup> The failure of finding the global minimum of these challenging problems could lead to uncertainties and numerous delays in the design stages of the processes.

Global optimization stochastic methods have emerged as a promising approach for solving challenging global optimization including those involved in thermodynamic calculations.<sup>1,2</sup> These methods, albeit probabilistic, retain high possibilities to

locate the global minimum within reasonable computational costs, and thus they offer a desirable balance between reliability and efficiency for finding the global optimum solution. Moreover, stochastic methods do not require any assumptions for the problem at hand, are more capable of addressing the nonlinearity and nonconvexity of the objective function, and are relatively easier to program and implement, among other advantages.<sup>3</sup>

The application of stochastic global optimization methods for solving phase equilibrium thermodynamic problems has grown considerably during last years and, to date, the most popular stochastic global optimization methods have been used and applied for solving phase stability and equilibrium problems in both reactive and nonreactive systems, e.g.: Simulated Annealing, Genetic Algorithms, Tabu Search, Differential Evolution, Particle Swarm Optimization, and Ant Colony Optimization.<sup>4–15</sup> These studies have analyzed the capabilities and limitations of these stochastic methods. However, there are many other metaheuristics that have not been covered in the literature of phase stability and equilibrium calculations. In particular, the field of global optimization using stochastic methods is an area of active research and it is expected that more new algorithms will emerge in the future.

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A special class of stochastic optimization techniques is Swarm Intelligence (SI). A swarm is a group of individuals that interact locally and with their environment, and which lack leadership or deterministic pattern. SI methods are inspired by numerous physical phenomena and biological colonies, with the aim of mimicking the intelligence shown by these natural swarms in their existential pursuit of food and nutrients. For example, Particle Swarm Optimization (PSO) belongs to this class and it mimics the foraging behavior of flocks of birds and schools of fish,<sup>16</sup> Ant Colony Optimization (ACO) mimics the foraging behavior of ants,<sup>17</sup> Firefly Algorithm (FA)<sup>18</sup> is based on the luminescent behavior of fireflies, and Cuckoo Search (CS) mimics the parasitic breeding of cuckoos,<sup>19</sup> to name a few. These SI methods and some variants of them, including hybrid strategies, have been employed in solving phase stability and equilibrium problems.<sup>4,6,8,20,21</sup> These studies have shown the promise of SI techniques for performing applied thermodynamic calculations.

It is important to note that each new global stochastic optimization method provides a new tool by which problems of phase stability and equilibrium can be solved. The search for the most efficient and reliable tool is still ongoing. This current study analyses the use of a new tool to fully understand its capabilities and limitations with respect to its use for solving the phase stability and equilibrium problems. In this study, a relatively new SI technique, Charged System Search (CSS),<sup>22</sup> and two of its variants namely, Magnetic Charged System Search (MCSS)<sup>23</sup> and the hybrid version with PSO<sup>24</sup> and chaotic maps (CMCSPSO) have been introduced for performing stability analysis and equilibrium calculations with and without chemical reactions. They are population-based methods, which utilize the governing laws of electrostatics and electromagnetism, coupled to Newtonian mechanics, to aid the evolution of the population and to promote the convergence to the global minimum. To the best of our knowledge, CSS has been mainly applied to civil engineering and mechanical engineering problems.<sup>25–27</sup> To date, no attempts for the evaluation of CSS algorithms in solving these thermodynamic problems have been reported in the literature. These novel SI methods have been analyzed and tested on a set of benchmark problems to determine their potential for phase equilibrium calculations related to process system engineering. Additionally, we have compared the performance of these methods with those results reported for other promising SI metaheuristics.

The remainder of this manuscript is organized as follows. The three algorithms, CSS, MCSS and CMCSPSO, are presented in section 2. A brief description of phase stability and equilibrium problems is given in section 3, including the implementation details of the three algorithms. Section 4 presents the results and discussion of the performance of CSS, MCSS and CMCSPSO on these thermodynamic calculations. Finally, the conclusions of this study are summarized in section 5.

## 2. DESCRIPTION OF CHARGED SYSTEM SEARCH (CSS) AND ITS VARIANTS

**2.1. CSS Method.** CSS is a relatively new stochastic global optimization method<sup>22</sup> which finds its inspiration in the electrostatic forces acting upon charged particles in electric fields. These forces are governed by Coulomb and Gauss's laws, which relate the electrostatic force  $F_i$  acting on a charged particle CP<sub>i</sub> linearly to the distance  $r_{ij}$  between it and other CPs inside the charged particle, and inversely proportional to the

square of the distance  $r_{ij}$  outside the CP. In the context of CSS, these forces can be defined as

$$\begin{aligned} F_i = q_i \sum_{j,j \neq i} \left( \frac{q_j}{a^3} r_{ij} i_1 + \frac{q_j}{r_{ij}^2} i_2 \right) p_{ij} (X_i - X_j) \\ j = 1, 2, \dots, N \\ i_1 = 1, i_2 = 0 \Leftrightarrow r_{ij} < a \\ i_1 = 0, i_2 = 1 \Leftrightarrow r_{ij} > a \end{aligned} \quad (1)$$

where  $N$  is the number of charged particles (or better known as the population size in a SI method),  $a$  is the radius of the charged sphere CP,  $X_i$  and  $X_j$  are the positions of CP<sub>i</sub> and CP<sub>j</sub>, respectively. Note that vectors  $X_i$  and  $X_j$  represent the decision variables of the optimization problem. The positions of the CPs in the initial population are determined randomly between the upper and lower bounds on the decision variables. According to Kaveh and Talatahari,<sup>22</sup>  $a$  can be defined using the size of the search space of the optimization problem

$$a = 0.1 \times \max(\{x_{i,\max} - x_{i,\min} | i = 1, 2, \dots, D\}) \quad (2)$$

where  $D$  is the number of decision variables. The charges  $q_j$  and  $q_i$  are defined as follows:

$$q_i = \frac{\text{fit}(i) - \text{fitworst}}{\text{fitbest} - \text{fitworst}}, \quad i = 1, 2, \dots, N \quad (3)$$

where  $\text{fit}(i)$  represents the fitness of CP<sub>i</sub>, and fitbest and fitworst represent the best (minimum) objective function value and the worst (maximum) objective function value of the current CPs, respectively. Note that  $q_i$  is normalized as follows:

$$q_i = \frac{q_i}{\sum_j q_j}, \quad i = 1, 2, \dots, N \quad (4)$$

This normalization is used to determine how close the candidate solutions are. These charges determine whether a given charged particle could affect another one or not. In the context of a binary interaction between two particles, a particle with a better fitness can create a stronger attracting force for other particle. On the other hand, a particle with lower fitness can only attract a particle with a better fitness according to a certain probability  $p_{ij}$ . Thus, the probability  $p_{ij}$  of a CP<sub>j</sub> attracts a CP<sub>i</sub> is given by

$$p_{ij} = \begin{cases} 1, & \text{fit}(j) < \text{fit}(i) \\ 1, & \frac{\text{fit}(i) - \text{fitbest}}{\text{fit}(j) - \text{fit}(i)} > \text{rand} \quad \forall \text{fit}(j) > \text{fit}(i) \\ 0, & \text{else} \end{cases} \quad (5)$$

The distance  $r_{ij}$  between two CPs is defined as

$$r_{ij} = \frac{\|X_i - X_j\|}{\left\| \frac{X_i + X_j}{2} - X_{\text{best}} \right\| + \varepsilon} \quad (6)$$

where  $X_{\text{best}}$  is the position of the best current CP, and  $\varepsilon$  is a small positive number, which is used to prevent singularities. Finally, the factor  $p_r$  is used to account for the repulsive forces and is defined as follows<sup>27</sup>

$$p_r = \begin{cases} 1 \Leftrightarrow \text{rand} < 0.8 \\ -1 \Leftrightarrow \text{else} \end{cases} \quad (7)$$

```

Step 1: Set parameters and initialize
    Randomly generate initial population of  $N$  charged particles  $X_i$ 
    Define the Charged Memory Size (CMS), Charged Memory Considering Rate
    (CMCR), and Pitch Adjusting Rate (PAR)
    Set initial velocity vector to zero

Step 2: Main evolution loop
    For  $t = 1: iter_{max}$ 
        Evaluate CPs
        Rank CPs and find the current best solution
        Update CM
        Calculate charges
        Calculate Coulomb's forces on all CPs
        Move CPs
        If (a component of the vector of new CP violates its corresponding boundary)
            Use the Harmony Search-based approach to handle constraints
        End If
        If (in the new generation of CPs, the best CP is lost)
            Replace the worst CP with the best so far CP
        End If
    End For
    Local optimization starting from the best solution found by the global search

```

**Figure 1.** Pseudocode of Charged System Search (CSS).

The optimization algorithm, after utilizing the governing laws of electrostatics to numerically compute the forces acting on pseudo charges, shifts to Newtonian mechanics to determine the motion of the charges in response to the Coulombic forces acting upon them by their peers. Hence, if the mass of a charged particle is taken to be equal to its charge, the acceleration could be defined as

$$acc_i = \frac{F_i}{q_i}, i = 1, 2, \dots, N \quad (8)$$

The position and velocity for a particle  $i$  are computed as follows

$$X_{i,new} = rand*k_a*acc_i*\Delta t^2 + rand*k_v*V_{i,old}*\Delta t + X_{i,old} \quad (9)$$

$$V_{i,new} = \frac{X_{i,new} - X_{i,old}}{\Delta t} \quad (10)$$

The initial positions of all particles are set to random values within the decision variables bounds, while the initial velocity is set to 0. Note that  $k_a$  and  $k_v$  provide a suitable balance between exploration and exploitation by defining them as follows

$$k_v = 0.5 * \left(1 - \frac{iter}{iter_{max}}\right) \quad (11)$$

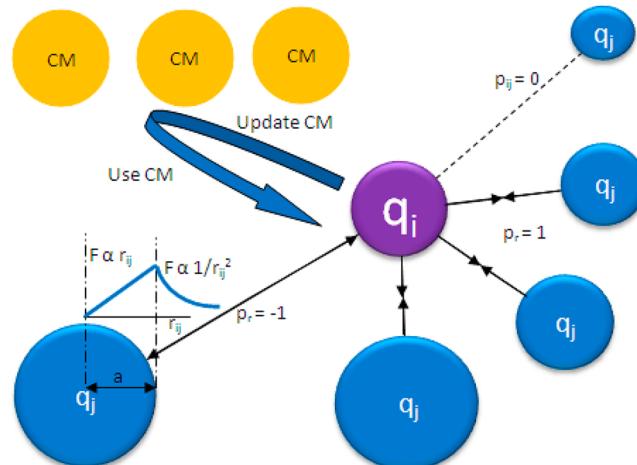
$$k_a = 0.5 * \left(1 + \frac{iter}{iter_{max}}\right) \quad (12)$$

where  $iter$  is the current iteration number and  $iter_{max}$  is the maximum number of iterations, respectively. The moving time  $\Delta t$  is equal to unity.

Finally, a charged memory CM (i.e., a vector of dimension CMS) is used to keep track of the best particles ever encountered during optimization. This parameter (CMS< $N$ ) is used to rebound particles that violate the lower and upper bounds on the decision variables. Hence, with a probability of CMCR (i.e., a Charged Memory Considering Rate), any component of the solution vector violating the lower or upper

bounds is substituted with a randomly chosen member of CM. After this, the probability PAR (i.e., Pitch Adjusting Rate) is used to decide if the value chosen from CM is perturbed to a neighboring value. If CM was not chosen to replace violating CPs, these are generated randomly between the upper and lower bounds. This mechanism has been adopted from the Harmony Search metaheuristic.<sup>28</sup> Also, if the current population does not contain the best CP ever encountered, this best solution replaces the worst member of the current population. The charged memory is updated by replacing its worst members with new CPs with better fitness. The best solution from both the CP population and CM is reported as the final solution. Figure 1 shows a simplified pseudocode for CSS algorithm, while Figure 2 depicts a conceptual view of the search space in CSS.

**2.2. MCSS Method.** MCSS is a recent variant of the CSS, which has been obtained by the inclusion of electromagnetic forces.<sup>23</sup> When a charged particle moves in a pseudo-electric field, a magnetic field is generated that adds a magnetic force

**Figure 2.** Conceptual visualization of search space in CSS.

```

Step 1: Set parameters and initialize
    Randomly generate initial population of  $N$  charged particles  $X_i$ 
    Define the Charged Memory Size (CMS), Charged Memory Considering Rate
    (CMCR), and Pitch Adjusting Rate (PAR)
    Set initial velocity and current vectors to zero

Step 2: Main evolution loop
    For  $t = 1: itermax$ 
        Evaluate CPs
        Rank CPs and find the current best solution
        Update CM
        Calculate charges and currents of all CPs
        Calculate Lorentz force on all CPs
        Move CPs
        If (a component of the vector of new CP violates its corresponding boundary)
            Use the Harmony Search-based approach to handle constraints
        End If
        If (in the new generation of CPs, the best CP is lost)
            Replace the worst CP with the best so far CP
        End If
    End For
    Local optimization starting from the best solution found by the global search

```

**Figure 3.** Pseudocode of Modified Charged System Search (MCSS).

component to all other CPs. The magnetic force is directly proportional to the charge carried by the charged particle and its speed. Hence, the total force acting upon a CP would be the superposition of the electric forces and electromagnetic forces. This total force is called Lorentz force and is defined in this algorithm as

$$F_i = q_i \sum_{j,j \neq i} \left( \frac{I_j}{r_{ij}} p_{mj} + \left( \frac{q_j}{a^3} r_{ij} i_1 + \frac{q_j}{r_{ij}^2} i_2 \right) p_{ij} p_r \right) (X_i - X_j)$$

$$j = 1, 2, \dots, N$$

$$i_1 = 1, i_2 = 0 \Leftrightarrow r_{ij} < a$$

$$i_1 = 0, i_2 = 1 \Leftrightarrow r_{ij} > a \quad (13)$$

where  $I_j$  is the current caused by the motion of CP<sub>j</sub>, which is given by

$$I_j = -\text{sign}(df_{i,k}) \times \frac{|df_{i,k}| - df_{\min,k}}{df_{\max,k} - df_{\min,k}} \quad (14)$$

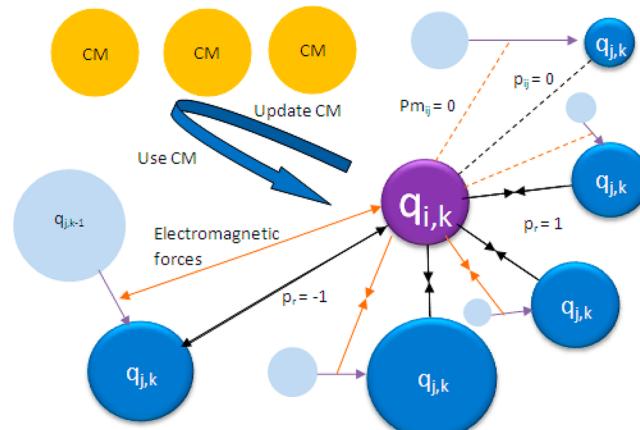
$$df_{i,k} = \text{fit}_k(i) - \text{fit}_{k-1}(i) \quad (15)$$

where  $df_{i,k}$  is the variation of the objective function value of CP<sub>i</sub> in the  $k^{\text{th}}$  iteration. Thus,  $\text{fit}_k(i)$  and  $\text{fit}_{k-1}(i)$  are the objective function values of CP<sub>i</sub> in the  $k^{\text{th}}$  and  $(k-1)^{\text{th}}$  iterations, respectively.  $df_{\min,k}$  and  $df_{\max,k}$  are the minimum and maximum absolute variations of  $f$ , respectively. The above definition of the current  $I_i$  makes possible the inclusion of informed repulsion on the CPs because the current takes a negative sign when the fitness of a CP deteriorates between two runs (i.e., its objective function value increases), providing a natural repulsion in the Lorentz force expression. On the other hand, if a CP's objective function value decreases, the current caused by its motion is positive and adds an attraction component on other CPs. By this, the MCSS stores and utilizes useful information from the previous run to direct the motion of the particles and the evolution of the population during optimization sequence. Also, the effects of parasitic currents (i.e., currents generated by

inferior CPs) are discarded by the following definition of magnetic probability

$$pm_{ij} = \begin{cases} 1 & \Leftrightarrow \text{fit}(j) < \text{fit}(i) \\ 0 & \Leftrightarrow \text{else} \end{cases} \quad (16)$$

All other features of CSS are retained in MCSS. Figures 3 and 4 provide the pseudocode of this modified method and its conceptual visualization, respectively.

**Figure 4.** Conceptual visualization of search space in MCSS.

**2.3. MCSSPSO Method.** MCSSPSO is a hybrid between MCSS and PSO.<sup>29</sup> In this hybrid, the charged memory is modified to store the so far best position encountered by each CP (i.e., the local best position). The best of these local bests is called the global best. During force determination on each CP, these terms are added to influence a CP toward the global best, its local best, and the local bests of other CPs. This stage is in addition to the usual attraction (and repulsion) forces between the current CPs. Hence, the total force acting upon CPs can be defined as follows

$$F_i = k_1(CM_{g,\text{old}} - X_i) + k_2(CM_{i,\text{old}} - X_i) \\ + \sum_{j \in S_1, j \neq i, j \notin S_2} k_j(CM_{j,\text{old}} - X_i) \\ + \sum_{j \in S_2, j \neq i, j \notin S_1} k_j(X_j - X_i) \quad (17)$$

where  $k_i$  is the main body of the Lorentz force given by

$$k_i = \left( \frac{I_i}{r_{ij}} p_{m_{ij}} + \left( \frac{q_i}{a^3} r_{ij} i_1 + \frac{q_i}{r_{ij}^2} i_2 \right) p_{ij} p_r \right) \\ i_1 = 1, i_2 = 0 \Leftrightarrow r_{ij} < a \\ i_1 = 0, i_2 = 1 \Leftrightarrow r_{ij} > a \quad (18)$$

On the other hand,  $CM_{g,\text{old}}$  indicates the global best solution obtained by all CPs so far,  $CM_{i,\text{old}}$  indicates the local best of the CP<sub>i</sub>,  $CM_{j,\text{old}}$  is the local best of all other CP<sub>j</sub> where  $j \neq i$ . It is imperative to define parallel charges and currents for the CM members. These are defined similarly to the charges of the CPs in the population and the currents caused by their motion, then

$$q_{CM,i} = \frac{CM_i - CM_{\text{worst}}}{CM_{\text{best}} - CM_{\text{worst}}} \quad (19)$$

where  $CM_i$  is the fitness of the local best of CP<sub>i</sub>,  $CM_{\text{best}}$  is the best (minimum) fitness among all CM members (i.e., the global best), and  $CM_{\text{worst}}$  is the worst (maximum) fitness among all CM members. Thus, we have that

$$q_{CM,i} = \frac{q_{CM,i}}{\sum_i q_{CM,i}}, i = 1, 2, \dots, N \quad (20)$$

while current  $I_{CM,i}$  is defined as

$$I_{CM,i} = -\text{sign}(df_{CM,i,k}) \times \frac{|df_{CM,i,k}| - df_{CM,\min,k}}{df_{CM,\max,k} - df_{CM,\min,k}} \quad (21)$$

$$df_{CM,i,k} = \text{fit}_{CM,k}(i) - \text{fit}_{CM,k-1}(i) \quad (22)$$

where  $df_{CM,i,k}$  is the variation of the objective function value of the member  $i$  of CM in the iteration  $k$ . Finally,  $\text{fit}_{CM,k}(i)$  and  $\text{fit}_{CM,k-1}(i)$  are the objective function values of the member  $i$  of CM in the iterations  $k$  and  $k - 1$ , while  $df_{CM,\min,k}$  and  $df_{CM,\max,k}$  are the corresponding minimum and maximum absolute variations of  $f_{CM}$ , respectively.

In the force expression described above, the first three terms influence a given CP to the global best, the CPs local best, and all other CPs local bests, respectively. It should be noted that the currents of the CM would often be zero, owing to the fact that this memory is only updated when a local best that is better than the current stored local best is found. In addition, when the CM current is not zero, it will always be positive, since the CM members are only expected to improve. The last two terms in the force expression apply to a specific set of CPs:  $S_1$  and  $S_2$ , respectively. In particular,  $S_1$  is made to increase with number of iterations. Hence, if  $S_2 = S - S_1$  where  $S$  is the set of all CPs, then  $S_2$  is decreasing in time. Thus, the influence of the local bests of other CPs is accentuated at later stages of the numerical search, at the expense of the current positions of other CPs. This configuration was found to be superior when compared to three other possible configurations as outlined in Kaveh and Talatahari.<sup>29</sup>

**2.4. Incorporation of Chaos into MCSSPSO.** To aid the exploration ability of MCSSPSO and to help it escape from the attraction of local minima, chaotic sequences were made to replace the random operators of MCSSPSO on different levels. Chaotic sequences generate random-like numbers, albeit in a deterministic way. It has been found that incorporation of these chaotic sequences, or chaotic maps, to replace random operators improves the overall performance of a search algorithm. To the best of our knowledge, no prior attempts to incorporate chaotic maps into the solution of any sort of thermodynamic problems have been encountered in the literature. This part of our study is inspired by a similar work to introduce chaos into CSS.<sup>30</sup> Several configurations for chaotic MCSSPSO, or better called CMCSSPSO, are studied and outlined hereafter.

**Configuration Chaotic Force Field CFF:** This configuration replaces the random operators by chaotic operators in the step for determining the type of force (attraction or repulsion) and the probability of its application among different CPs. Specifically, eqs 5 and 7 are modified and given by

$$1, \text{fit}(j) < \text{fit}(i) \\ p_{ij} = 1, \frac{\text{fit}(i) - \text{fit}_{\text{best}}}{\text{fit}(j) - \text{fit}(i)} > cm \quad \forall \text{fit}(j) > \text{fit}(i) \\ 0, \text{else} \quad (23)$$

$$p_r = 1 \Leftrightarrow cm > 0.1 * \left( 1 - \frac{\text{iter}}{\text{iter}_{\text{max}}} \right) \\ -1 \Leftrightarrow \text{else} \quad (24)$$

**Configuration Dissipative Chaotic Force Field DCFF:** In addition to the previous configuration, the chaotic numbers replace the random numbers in the step that determines the new positions of the CPs. Therefore, in addition to eqs 23 and 24, we use the following expression

$$X_{i,\text{new}} = cm * k_a * \text{acc}_i * \Delta t^2 + cm * k_v * V_{i,\text{old}} * \Delta t + X_{i,\text{old}} \quad (25)$$

**Configuration Dissipative Chaotic Force Field with Chaotic Initialization DCFFCI:** This configuration adopts eqs 23–25 and replaces the random initialization with chaotic initialization. These three configurations are tested with four one-dimensional chaotic maps, and four two-dimensional chaotic maps. Table 1 depicts the eight chaotic maps together with their initialization values,<sup>31</sup> while pseudocode of CMCSSPSO is given in Figure 5.

### 3. DESCRIPTION OF PHASE STABILITY AND PHASE EQUILIBRIUM PROBLEMS USED FOR THE EVALUATION OF CSS AND ITS VARIANTS

**3.1. Objective functions.** In this study, the phase stability and equilibrium problems are stated as a global optimization problem. Therefore, the global optimization problem to be solved is: Minimize  $F(X)$  with respect to  $D$  decision variables:  $X = (X^1, \dots, X^D)$ . The upper and lower bounds of these variables are  $(X_{\max}^1, \dots, X_{\max}^D)$  and  $(X_{\min}^1, \dots, X_{\min}^D)$ , respectively.

In particular, we have considered phase stability ( $P_S$ ), phase equilibrium ( $P_E$ ) and reactive phase equilibrium ( $P_{RE}$ ) calculations for testing the performance of CSS methods. For the sake of brevity, Table 2 shows the problem formulation, objective function, decision variables and constraints used for

**Table 1.** Chaotic Maps Used to Improve the Performance of MCSSPSO Algorithm

| type                   | name           | Chaotic Map  | initial values |
|------------------------|----------------|--|----------------|
| 1-D<br>Chaotic<br>Maps | Cubic          | $cm = 3*cm*(1 - cm^2)$   | 0.1            |
|                        | Logistic       | $cm = 4*cm*(1 - cm)$   | 0.1            |
|                        | Ricker         | $cm = 20*cm*\exp(-cm)$   | 0.1            |
|                        | Sin            | $cm = \sin(\pi*cm)$  | 0.1            |
| 2-D<br>Chaotic<br>Maps | Burgers'       | $cm1 = 0.75*cm1 - cm2^2; cm2 = 1.75*cm2 + cm1_{old}*cm2$                                 | (-0.1, 0.1)    |
|                        | Gingerbreadman | $cm1 = 1 + \text{abs}(cm1) - cm2; cm2 = cm1_{old}$                                       | (0.5, 3.7)     |
|                        | Henon          | $cm1 = 1 - 1.4*cm1^2 + 0.3*cm2; cm2 = cm1_{old}$   | (0, 0.9)       |
|                        | Tinkerbell     | $cm1 = cm1^2 - cm2^2 + 0.9*cm1 - 0.6*cm2; cm2 = 2*cm1_{old}*cm2 + 2*cm1_{old} + 0.5*cm2$ | (0, 0.5)       |

these thermodynamic calculations. Specifically, the phase stability analysis was performed using the global minimization of the tangent plane distance function (TPDF),<sup>32</sup> while the global optimization of the Gibbs free energy was used for phase equilibrium calculations with or without chemical reactions.<sup>1</sup> The mathematical formulation for phase stability and phase equilibrium calculations without chemical reactions is an unconstrained minimization of the objective function, which has been used to discard the restrictions imposed by material balances, while the constrained Gibbs free energy minimization in reactive systems was performed using the penalty function method according to the approach reported by Bonilla-Petriciolet et al.<sup>2</sup> For interested readers, several references provide a detailed description of these thermodynamic calculations.<sup>1,2,4,10,12</sup>

**3.2. Numerical Examples.** Sixteen multicomponent systems (i.e., 8 for  $P_S$  and  $P_E$  and 8 for  $P_{RE}$ ) and different thermodynamic models were used to test the CSS algorithms described in the last section. Specifically, the nonreactive mixtures used in phase stability and equilibrium calculations

are: (1) *n*-butyl acetate + water; (2) toluene + water + aniline; (3)  $N_2 + C_1 + C_2$ ; (4)  $C_1 + H_2S$ ; (5)  $C_2 + C_3 + C_4 + C_5 + C_6$ ; (6)  $C_1 + C_2 + C_3 + C_4 + C_5 + C_6 + C_{7-16} + C_{17+}$ ; (7)  $C_1 + C_2 + C_3 + iC_4 + C_4 + iC_5 + C_5 + C_6 + iC_{15}$ ; and (8)  $C_1 + C_2 + C_3 + C_4 + C_5 + C_6 + C_7 + C_8 + C_9 + C_{10}$ . For the case of reactive mixtures, the selected mixtures include: (1) ethanol + acetic acid  $\leftrightarrow$  ethyl acetate + water; (2) isobutene + methanol  $\leftrightarrow$  methyl *tert*-butyl ether with *n*-butane as inert component; (3) 2-methyl-1-butene + 2-methyl-2-butene + 2 methanol  $\leftrightarrow$  2 *tert*-amyl methyl ether; (4) acetic acid + *n*-butanol  $\leftrightarrow$  water + *n*-butylacetate; (5) an hypothetic mixture of the type A1 + A2  $\leftrightarrow$  A3; (6) 2-methyl-1-butene + 2-methyl-2-butene + 2 methanol  $\leftrightarrow$  2 *tert*-amyl methyl ether with *n*-pentane as inert component; (7) other hypothetic mixture of the type A1 + A2  $\leftrightarrow$  A3; and (8) an hypothetic mixture of the type A1 + A2  $\leftrightarrow$  A3 + A4. Operating conditions for selected examples involves a wide range of  $T$ ,  $P$  and compositions both near to and far from phase boundaries including different local composition models and EoS. These thermodynamic systems show liquid–liquid and vapor–liquid equilibrium. All problem specifications can be found in our previous studies<sup>4,20,21</sup> and Table 3 provides the global optimal solutions for these numerical examples.

### 3.3. Details of Numerical Implementation and Performance Metrics Used for Testing CSS Algorithms.

All thermodynamic problems and CSS optimization algorithms were coded in the MATLAB technical computing environment. Each problem was solved 100 times independently and with different random initial seeds to determine the reliability of CSS optimization algorithms. Calculations were performed using the traditional stopping conditions for stochastic global optimization methods. First, we have used the number of iterations (SC-1) for performing the numerical analysis. Results were obtained at milestone iterations from 10 to 1500. This analysis was complemented using an improvement-based stopping criterion (SC-2), which specifies the maximum number of iterations allowable without improvement in the objective function value of the best individual in the population. Different values of SC-

```

Step 1: Set parameters and initialize
    Randomly generate initial population of  $N$  charged particles  $X_i$ .
    Define the Charged Memory Size (CMS = N), Charged Memory Considering Rate (CMCR), and Pitch Adjusting Rate (PAR).
    Set initial velocity, charge and current vectors to zero for the population and CM members.
    Initialize chaotic sequence.

Step 2: Main evolution loop
For  $t = 1: iter_{max}$ 
    Evaluate CPs
    Rank CPs and find the current best solution
    Update CM
    Calculate charges and currents of all CPs and CM members
    Calculate Lorentz force on all CPs
    Move CPs
    If (a component of the vector of new CP violates its corresponding boundary)
        Use the Harmony Search-based approach to handle constraints
    End If
    If (in the new generation of CPs, the best CP is lost)
        Replace the worst CP with the best so far CP
    End If
End For
Local optimization starting from the best solution found by the global search

```

**Figure 5.** Pseudocode of Chaotic Modified Charged System Search - Particle Swarm Optimization (CMCSSPSO).

**Table 2.** Description of thermodynamic functions and optimization problems for phase stability analysis and equilibrium calculations in reactive and non-reactive systems

| calculation                             | description   | thermodynamic function  | optimization problem   |
|---|---|---|--|
| Phase stability analysis                | It involves the determination of whether a system will remain in one phase at the given conditions or split into two or more phases.  | Tangent plane distance function <sup>30</sup><br>$\text{TPDF} = \sum_{i=1}^c \gamma_i (\mu_{i,y} - \mu_{i,z})$  | $\min_{\beta} \text{TPDF}$<br>$0 \leq \beta_i \leq 1, i = 1, \dots, c$   |
| Phase equilibrium calculation           | It involves the determination of the number, type, and composition of the phases at equilibrium at the given operating conditions.  | Gibbs free energy of mixing ( $g$ )<br>$g = \sum_{j=1}^{\pi} \sum_{i=1}^c n_{ij} \ln(x_{ij}\theta_{ij}) = \sum_{j=1}^{\pi} \sum_{i=1}^c n_{ij} \ln\left(\frac{x_{ij}\hat{\theta}_{ij}}{\varphi_i}\right)$ | The decision variables are $\beta_{ij} \in (0, 1)$ using the following relationships:<br>$n_{ij} = \beta_{ij} n_F, i = 1, \dots, c$<br>$\gamma_i = n_{iy} / \sum_{j=1}^c n_{ij}, i = 1, \dots, c$  |
| Reactive phase equilibrium calculations | It involves the determination of the number, type and composition of the phases at equilibrium at the given operating conditions and subject to element/mass balances and chemical equilibrium constraints. | Gibbs free energy of mixing defined using reaction equilibrium constants <sup>2</sup><br>$G_K = g - \sum_{j=1}^{\pi} \ln K_{eq,j} N^{-1} \mathbf{n}_{ref,j}$  | The decision variables are $\beta_{ij} \in (0, 1)$ using the following relationships:<br>$n_{ij} = \beta_{ij} z_i n_F, i = 1, \dots, c$<br>$j = 1, \dots, \pi - 1$<br>$i = 1, \dots, c; j = 2, \dots, \pi - 1$<br>$n_{ir} = z_i n_F - \sum_{m=1}^{\pi-1} n_{im}, i = 1, \dots, c$<br>$\min_{n_{ij}} G_K$<br>subject to<br>$\sum_{j=1}^{\pi} (n_{ij} - v_j N^{-1} \mathbf{n}_{ref,j}) = n_F - v_i N^{-1} \mathbf{n}_{ref,F}$<br>$i = 1, \dots, c - r$<br>$n_{ij} > 0, i = 1, \dots, c; j = 1, \dots, \pi$ |

where  $\pi$  is the number of phases at equilibrium and  $\theta_{ij}$  denotes the composition (i.e.,  $x$  or  $n$ ) or thermodynamic property of component  $i$  in phase  $j$ .

where  $n_{iy}$  are the mole numbers of component  $i$  in phase  $y$  and  $n_F$  is the total moles in the mixture under analysis.

where  $n_{ij}$  is the initial moles of component  $i$  in the feed,  $v_j$  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.<sup>2</sup>

**Table 3.** Global Optimum Solutions of Phase Stability ( $P_s$ ), Phase Equilibrium ( $P_E$ ) and Reactive Phase Equilibrium ( $P_{RE}$ ) Problems Used in This Study

| phase stability |            | phase equilibrium |           | reactive phase equilibrium |           |
|-----------------|------------|-------------------|-----------|----------------------------|-----------|
| no.             | solution   | no.               | solution  | no.                        | solution  |
| $P_s\text{-}1$  | -0.032466  | $P_E\text{-}1$    | -0.020198 | $P_{RE}\text{-}1$          | -2.05812  |
| $P_s\text{-}2$  | -0.294540  | $P_E\text{-}2$    | -0.352957 | $P_{RE}\text{-}2$          | -1.434267 |
| $P_s\text{-}3$  | -0.015767  | $P_E\text{-}3$    | -0.547791 | $P_{RE}\text{-}3$          | -1.226367 |
| $P_s\text{-}4$  | -0.003932  | $P_E\text{-}4$    | -0.019892 | $P_{RE}\text{-}4$          | -1.10630  |
| $P_s\text{-}5$  | -0.000002  | $P_E\text{-}5$    | -1.183653 | $P_{RE}\text{-}5$          | -0.144508 |
| $P_s\text{-}6$  | -0.002688  | $P_E\text{-}6$    | -0.838783 | $P_{RE}\text{-}6$          | -0.872577 |
| $P_s\text{-}7$  | -1.486205  | $P_E\text{-}7$    | -0.769772 | $P_{RE}\text{-}7$          | -0.653756 |
| $P_s\text{-}8$  | -0.0000205 | $P_E\text{-}8$    | -1.121176 | $P_{RE}\text{-}8$          | -0.311918 |

2 were tested depending on the thermodynamic problem under analysis. In summary, Table 4 shows the values selected for the

**Table 4.** Selected Values of the Parameters Used in the Implementation of CSS, MCSS, and CMCSSPSO

| method              | parameter | selected value  |
|---------------------|-----------|---|
| CSS, MCSS, CMCSSPSO | CMCR      | 0.95  |
|                     | PAR       | 0.1   |
|                     | $n$       | 10D   |
| CSS, MCSS           | CMS       | $n/4$ , if integer<br>$n/2$ , if $n/4$ is not integer |
|                     |           |   |

parameters of the three CSS optimization algorithms. Note that most of these parameters are those of the charged memory, and this fact indicates that CSS and all its variants can be considered as user-friendly algorithms which require few tunable parameters. In our numerical analysis using both stopping criteria, the results from CSS algorithms were used as an initial guess to the local optimization algorithm SQP of MATLAB for improving the solution exactitude. If the stochastic algorithm has made it to the global minimum as judged by the specified tolerance, the intensification phase using SQP is also expected to land on the global minimum. The tolerance value for finding the global optimum was  $10^{-6}$  for  $P_s\text{-}5$  and  $P_s\text{-}8$ ,  $10^{-7}$  for  $P_E\text{-}5$  and  $10^{-5}$  for the rest of the problems.

Finally, CSS-based methods were evaluated according to the reliability and efficiency for finding the global optimum. The reliability is indicated by the Global Success Rate, GSR, defined

as the number of successful runs at landing on the global minimum out of 100 trials, and averaged over all the problems of a specific class. Specifically, it is defined as

$$\text{GSR} = \frac{\sum_{i=1}^{np} \text{SR}_i}{np} \quad (26)$$

where  $\text{SR}_i$  is the individual success rate that is given by the number of successful runs out of 100 for each problem, and  $np$  is the number of problems in the pertinent class (i.e.,  $P_s$ ,  $P_E$ , and  $P_{RE}$ ). The efficiency is determined by recording the number of function evaluations NFE for each optimization algorithm, where a low value of NFE means a higher efficiency. Note that NFE is an unbiased indicator of the computational costs required by a certain algorithm and is independent of the host hardware.

For chaos implementation on CSS methods, the eight chaotic maps were investigated versus the three chaotic configurations detailed earlier. This was only done for the most challenging  $P_{RE}$  problems. Also, these problems were only solved 50 times independently, and the number of successes at locating the global minimum up to the specified tolerance out of these 50 runs was reported for each collection of map and scheme. With illustrative purposes, Table 5 shows successes out of 50 trials at locating the global minimum for the four most challenging  $P_{RE}$  problems. These preliminary calculations showed that the combination of scheme CFF and Burgers' map is generally more reliable than other combinations. This chaos scheme was used in all calculations reported in this study.

To complete the evaluation of the CSS method with its variants, we have employed the performance profile (PP) reported by Dolan and Moré,<sup>33</sup> who introduced PP as a tool for evaluating and comparing the performance of optimization software. In particular, PP has been proposed to represent compactly and comprehensively the data collected from a set of solvers for a specified performance metric such as the computing time or the number of function evaluations. The PP plot allows visualization of the expected performance differences among several solvers and compares the quality of their solutions by eliminating the bias of failures obtained in a small number of problems.

To introduce PP, consider  $n_s$  solvers (i.e., optimization methods) to be tested over a set of  $n_p$  problems. For each problem  $p$  and solver  $s$ , the performance metric  $t_{ps}$  must be

**Table 5.** Successful Runs out of 50 Trials for the Chaotic Schemes and Chaotic Maps Used with CMCSSPSO at 1500 Iterations in Selected Reactive Phase Equilibrium Problems

|                   |        | chaotic map |          |        |     |          |                |       |            |
|-------------------|--------|-------------|----------|--------|-----|----------|----------------|-------|------------|
|                   | scheme | cubic       | logistic | Ricker | Sin | Burgers' | Gingerbreadman | Henon | Tinkerbell |
| $P_{RE}\text{-}1$ | CFF    | 22          | 2        | 0      | 0   | 11       | 0              | 0     | 11         |
|                   | DCFF   | 5           | 0        | 12     | 0   | 2        | 33             | 2     | 0          |
|                   | DCFFCI | 4           | 0        | 13     | 0   | 0        | 44             | 2     | 2          |
| $P_{RE}\text{-}3$ | CFF    | 22          | 0        | 0      | 0   | 36       | 0              | 0     | 24         |
|                   | DCFF   | 2           | 1        | 5      | 0   | 0        | 29             | 1     | 0          |
|                   | DCFFCI | 3           | 1        | 9      | 0   | 1        | 30             | 1     | 0          |
| $P_{RE}\text{-}4$ | CFF    | 0           | 0        | 0      | 0   | 8        | 0              | 0     | 4          |
|                   | DCFF   | 0           | 0        | 0      | 0   | 0        | 0              | 0     | 0          |
|                   | DCFFCI | 0           | 0        | 0      | 0   | 0        | 0              | 0     | 0          |
| $P_{RE}\text{-}8$ | CFF    | 47          | 39       | 33     | 39  | 49       | 33             | 23    | 47         |
|                   | DCFF   | 49          | 41       | 0      | 31  | 26       | 21             | 38    | 0          |
|                   | DCFFCI | 45          | 34       | 0      | 28  | 37       | 28             | 38    | 2          |

defined. In our study, reliability of the stochastic method in accurately finding the global minimum of the objective function is considered as the principal goal, and hence, the performance metric is defined as

$$t_{ps} = \hat{f}_{\text{calc}} - f^* \quad (27)$$

where  $f^*$  is the known global optimum of the objective function and  $f_{\text{calc}}$  is the mean value of that objective function calculated by the stochastic method over several runs.

For the performance metric of interest, the performance ratio,  $r_{ps}$ , is used to compare the performance on problem p by solver s with the best performance by any solver on this problem. This performance ratio is given by

$$r_{ps} = \frac{t_{ps}}{\min\{t_{ps}: 1 \leq s \leq n_p\}} \quad (28)$$

The value of  $r_{ps}$  is 1 for the solver that performs the best on a specific problem p. To obtain an overall assessment of the performance of solvers on  $n_p$  problems, the following cumulative function for  $r_{ps}$  is used:

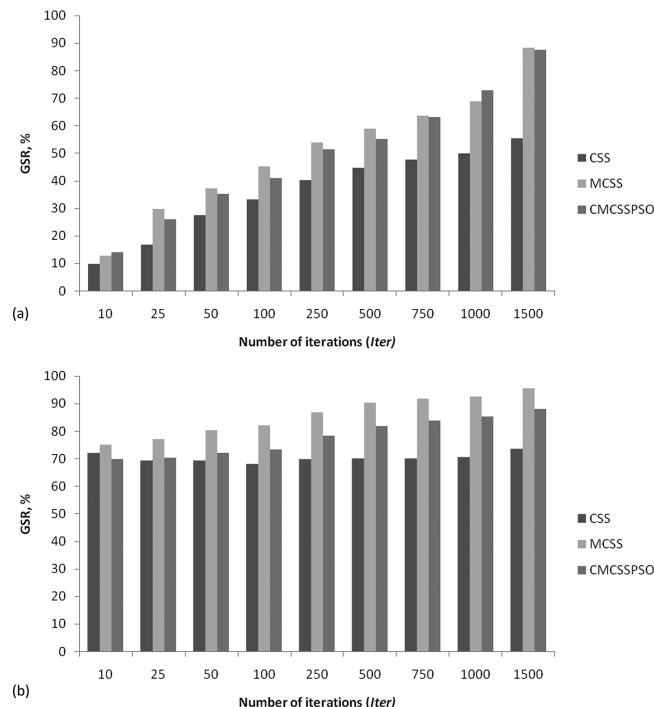
$$\rho_s(\zeta) = \frac{1}{n_p} \text{size}\{p: r_{ps} \leq \zeta\} \quad (29)$$

where  $\rho_s(\zeta)$  is the fraction of the total number of problems, for which solver s has a performance ratio  $r_{ps}$  within a factor of  $\zeta$  of the best possible ratio. The PP of a solver is a plot of  $\rho_s(\zeta)$  versus  $\zeta$ ; it is a nondecreasing, piece-wise constant function, continuous from the right at each of the breakpoints.<sup>33</sup> To identify the best solver, it is only necessary to compare the values of  $\rho_s(\zeta)$  for all solvers and to select the highest one, which is the probability that a specific solver will "win" over the rest of solvers used. In our case, the PP plot compares how accurately the stochastic methods can find the global optimum value relative to one another; thus, the term "win" refers to the stochastic method that provides the most accurate value of the global minimum in the benchmark problems used.

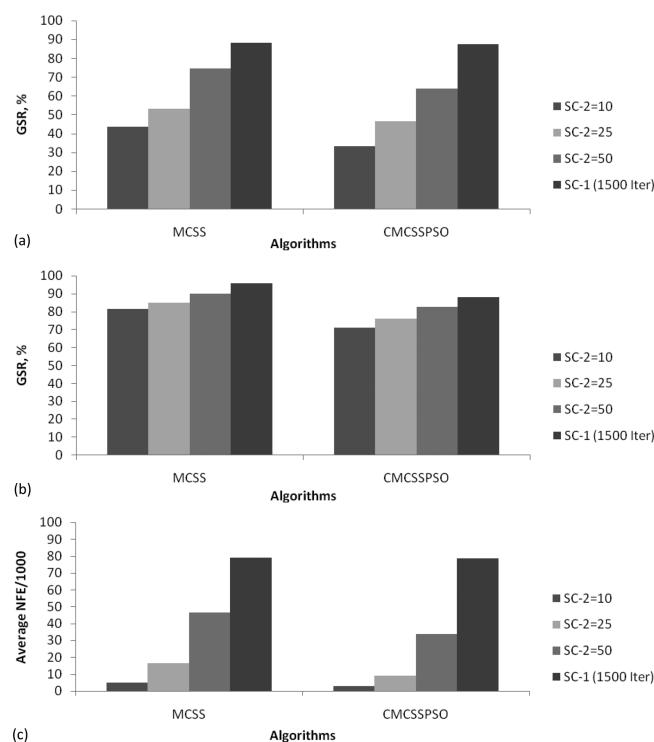
#### 4. RESULTS AND DISCUSSION

**4.1. Performance of CSS Algorithms on Phase Stability and Equilibrium Problems in Nonreactive and Reactive Systems.** Figure 6 shows the reliability of the three CSS algorithms for SC-1 with and without intensification stage for stability analysis. Both convergence schemes show a steady improvement in reliability with the increase in number of iterations. CSS generally is outperformed by its variants, with MCSS taking a small precedence over CMCSSPSO. Performance metric GSR of MCSS at SC-1 = 1500 increased from about 88% without intensification to about 95% with intensification. These performance values for CMCSSPSO were 87.5% and 88%, respectively. Note that the differences on the performance of CSS and those obtained for MCSS and CMCSSPSO are more significant as NFE increased, showing that both MCSS and CMCSSPSO are more reliable for performing phase stability in nonreactive systems.

On the other hand, Figure 7 compares the reliability and efficiency of MCSS and CMCSSPSO for convergence criterion SC-2. Both methods showed an improved GSR with increase in allowable iterations and with the use of local intensification stage. However, the performance of stochastic methods is better using SC-1 with and without local intensification. MCSS takes the lead over CMCSSPSO using both stopping



**Figure 6.** Global Success Rate (GSR) of CSS, MCSS, and CMCSSPSO without local intensification versus iterations for phase stability problems.

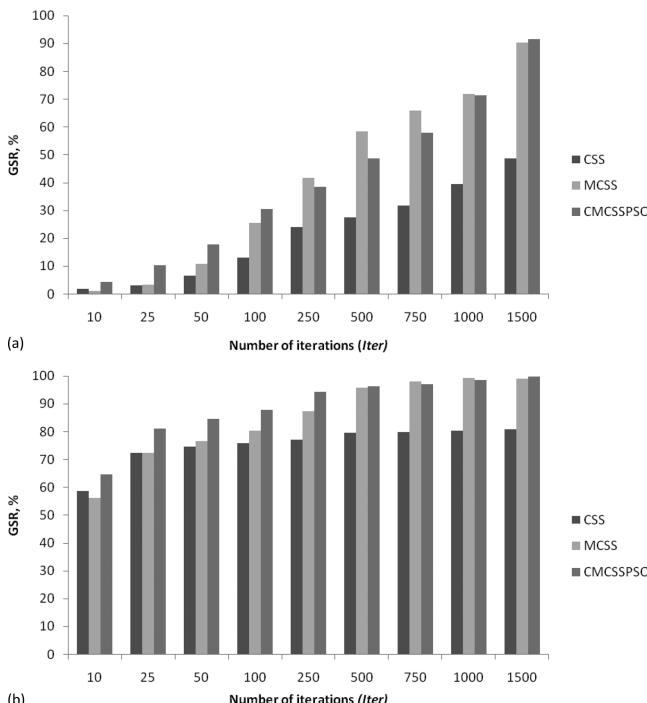


**Figure 7.** GSR of MCSS and CMCSSPSO for stopping condition SC-2. (a) Stochastic methods without intensification, (b) stochastic methods with intensification, and (c) average NFE/1000 of both approaches used for phase stability problems.

conditions. However, Figure 7c) shows that the improved reliability of MCSS is attributed to its higher NFE (with intensification) as compared to that of CMCSSPSO. This result suggests that MCSS experiences a stagnation of evolution only

at prolonged iterations, which leaves it with healthier population as compared to its counterpart. It is concluded that MCSS is slightly more reliable than CMCSSPSO in stability analysis using both stopping criteria, although this comes at a higher computational cost for SC-2; and it is clear that CSS is outperformed by these two variants in these thermodynamic calculations.

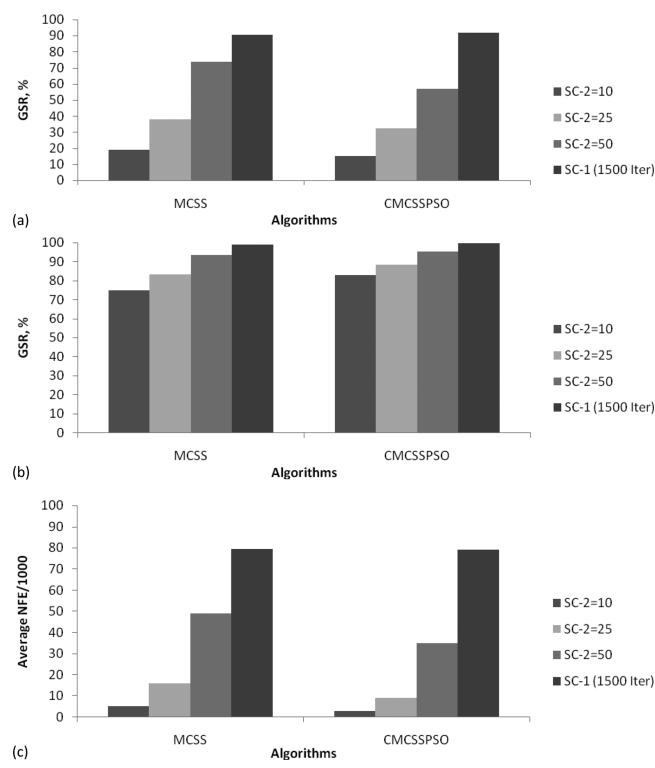
For the case of phase equilibrium calculations in nonreactive systems, Figure 8 shows the numerical performance of CSS



**Figure 8.** Global Success Rate (GSR) of CSS, MCSS, and CMCSSPSO versus iterations for phase equilibrium problems. (a) Stochastic method and (b) stochastic method with local intensification phase.

algorithms with and without a local optimization method. All algorithms are completely unreliable without intensification especially at low NFE. CSS barely reached a GSR of 50%, which increased to 80% with intensification. These results again indicate its inadequacy for performing the global minimization of Gibbs free energy if not coupled with a local optimizer. MCSS consistently outperforms CMCSSPSO for all iterations, only to slightly lag behind CMCSSPSO at the end, which exceeded a GSR of 90%. This GSR is increased to almost 100% upon application of local intensification. A similar performance trend was observed for MCSS. Therefore, CMCSSPSO is the most reliable method for performing the Gibbs free energy minimization in nonreactive problems.

For illustration, the trade-off between reliability and efficiency of MCSS and CMCSSPSO for SC-2 is reported in Figure 9. The same features observed for phase stability problems are reported for phase equilibrium problems, i.e., the reliability of both methods increased with the number of allowable iterations for reaching convergence and with the intensification stage. However, b and c of Figure 9 show an interesting feature of CMCSSPSO. In particular, this hybrid CSS shows higher reliability than MCSS at all SC-2 milestones and, at the same time, it requires less NFE. Hence,



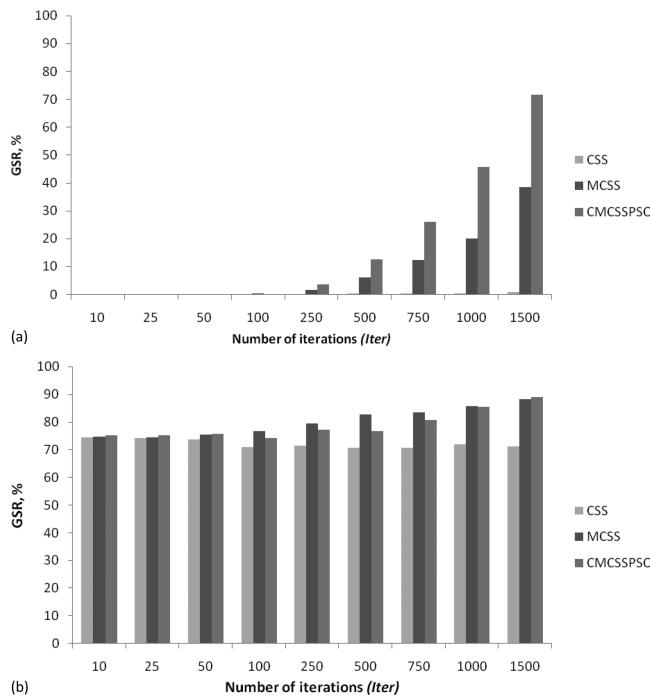
**Figure 9.** GSR of MCSS and CMCSSPSO for stopping condition SC-2. (a) Stochastic methods without intensification, (b) stochastic methods with intensification, and (c) average NFE/1000 of both approaches used for phase equilibrium problems.

CMCSSPSO has satisfied the difficult requirement of higher efficiency without compromising reliability. So, it is the best of the three CSS methods for solving phase equilibrium problems.

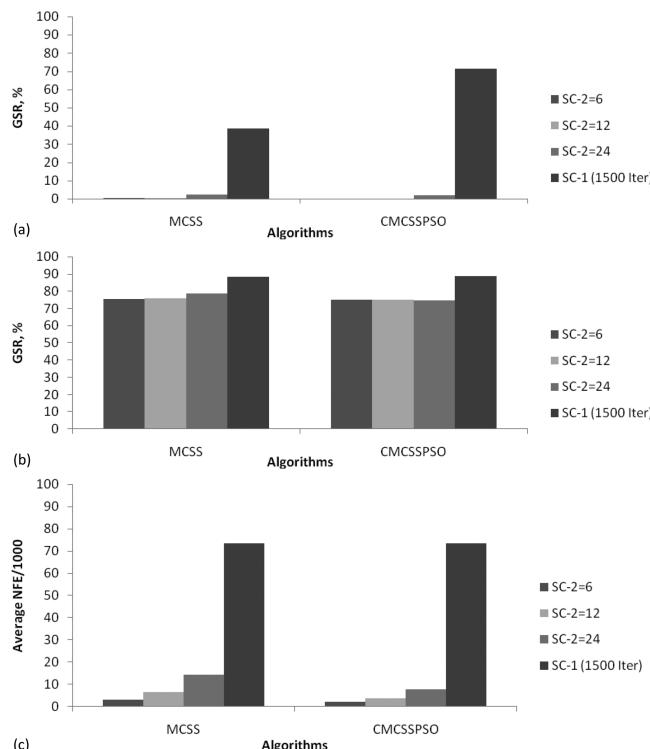
Results obtained in reactive phase equilibrium calculations are reported in Figure 10 using different levels of iterations as stopping criterion for all CSS-type algorithms. Without intensification, CSS shows negligible GSR even at prolonged iterations. In fact, all algorithms showed a poor performance until iteration 500. After iterations >500, CMCSSPSO starts to emerge as the most competitive method to finally reach a GSR of 70% at 1500 iterations, while MCSS showed a GSR < 40%. Note that CSS only reached a GSR of 70% at 1500 iterations with the intensification approach. These results confirmed the outstanding performance of CMCSSPSO over the basic CSS for reactive phase equilibrium problems. This hybrid strategy actually reached a GSR of 90% with local optimization method, with MCSS slightly behind.

Figure 11 reports the reliability and efficiency of MCSS and CMCSSPSO using the stopping condition SC-2. Overall, all three methods showed low values of GSR without the intensification method. The performance of tested stochastic methods improved significantly with SQP, where MCSS outperformed CMCSSPSO by about 4% for SC-2 = 24, but at the cost of more than 40% additional NFE. On the basis of these results, CMCSSPSO appears to be the more reliable and efficient methods for the constrained global minimization of the Gibbs free energy in reactive systems.

**4.2. Performance Comparison with Other Swarm Intelligent Methods.** Recently, Firefly Algorithm (FA),<sup>18</sup> and Cuckoo Search (CS)<sup>19</sup> were implemented to solve both phase equilibrium and stability problems. Figure 12 compares the performance of CS, FA, and MCSS for solving phase

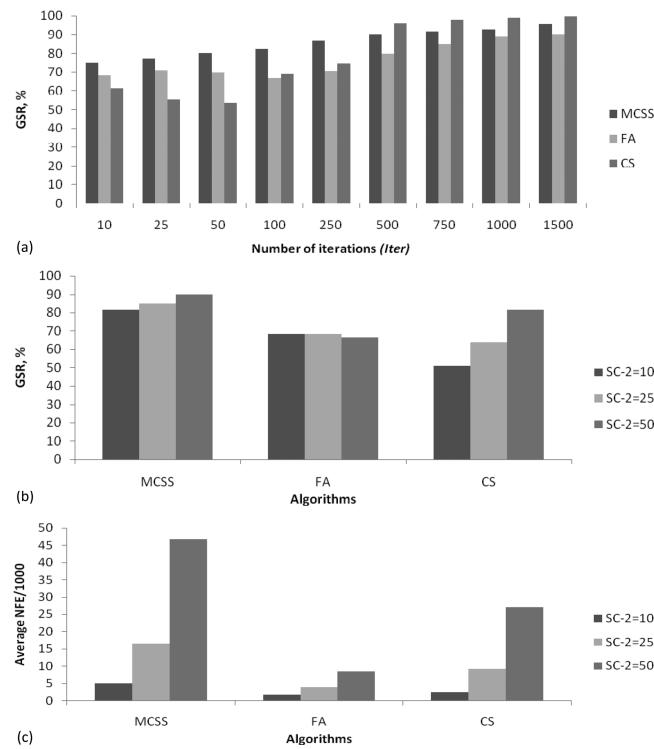


**Figure 10.** Global Success Rate (GSR) of CSS, MCSS, and CMCSSPSO versus iterations for reactive phase equilibrium problems. (a) Stochastic method and (b) stochastic method with local intensification phase.



**Figure 11.** GSR of MCSS and CMCSSPSO for stopping condition SC-2. (a) Stochastic methods without intensification, (b) stochastic methods with intensification, and (c) average NFE/1000 of both approaches used for reactive phase equilibrium problems.

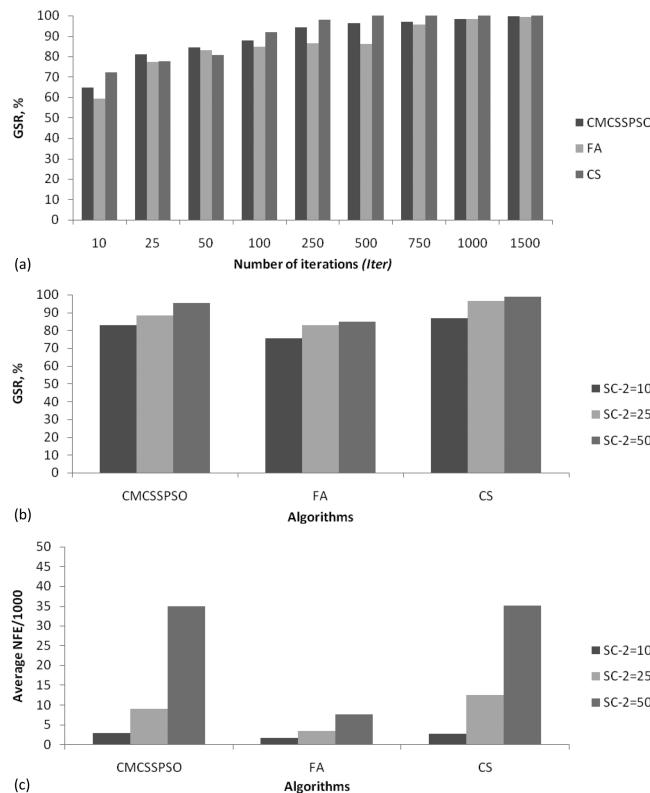
stability problems with stopping condition SC-1. It appears that MCSS is competitive to both algorithms. It takes the lead for small number of iterations, only to be slightly outperformed by



**Figure 12.** Global Success Rate (GSR) of MCSS, FA, and CS versus iterations for phase stability analysis using the stopping conditions (a) SC-1 and (b) SC-2. (c) Average NFE using intensification approach.

CS, while keeping consistent supremacy over FA. MCSS has also showed higher GSR than other stochastic methods at all milestones of SC-2, but at the expense of higher NFE (e.g., about 2 and 4 times more NFE than those required by CS and FA respectively at SC-2 = 50). This indicates that MCSS is more reliable than CS and FA for phase stability analysis using SC-2, and has comparable reliability to CS using SC-1. For illustration, the details of the performance of the three algorithms for SC-2 for each of the numerical examples used in phase stability are available in the Supporting Information. MCSS showed a better performance than other SI methods for SC-2 = 10, and it remains competitive for higher milestones of SC-2. In fact, MCSS shows the highest average GSR and needs the highest NFE as well.

Figure 13 reports the performance metrics of CMCSSPSO, FA and CS for phase equilibrium problems in nonreactive systems. Both CMCSSPSO and CS are 100% reliable at 1500 iterations, while FA showed less competitive performance for almost all of the milestones of SC-1. This is also the case for SC-2, except that CS consistently shows higher GSR than that of CMCSSPSO. The data for the performance of the three algorithms for SC-2 for each of the phase equilibrium problems are available in the Supporting Information. CMCSSPSO and FA are outperformed by CS, which showed a 94% GSR but at the expense of a higher computational cost. In fact, CS required the highest NFE among all three algorithms, with CMCSSPSO in the second place. Note that FA is the most efficient method in these calculations. For example, in phase equilibrium problem No. 7 all algorithms are 100% reliable, nevertheless FA needs only little more than third the NFE required by CMCSSPSO or sixth the NFE required by CS for SC-2 = 50. Since CS showed high reliability and low efficiency, while FA is the least reliable among all three methods, it is concluded that



**Figure 13.** Global Success Rate (GSR) of CMCSSPSO, FA, and CS versus iterations for phase equilibrium calculations using the stopping conditions (a) SC-1 and (b) SC-2. (c) Average NFE using intensification approach.

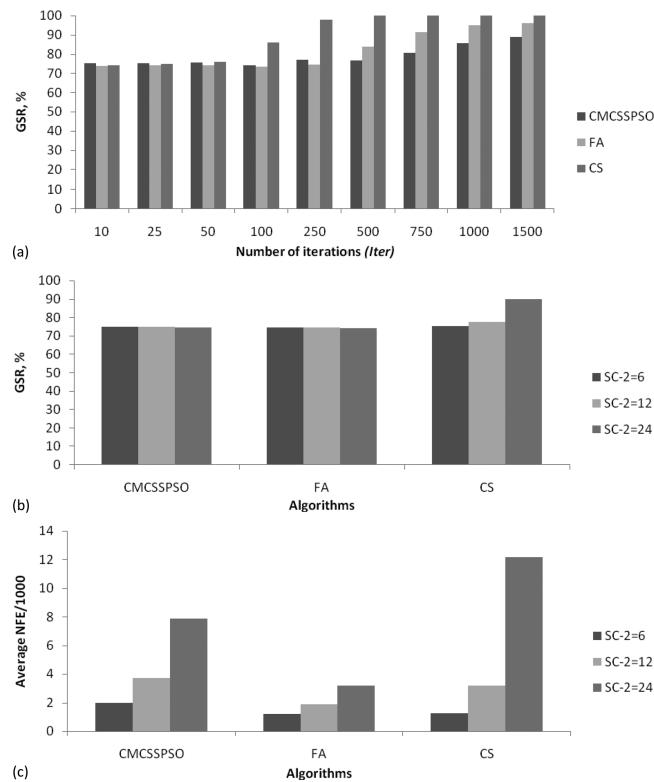
CMCSSPSO shows a suitable compromise between reliability and efficiency for phase equilibrium calculations.

Figure 14 is devoted to the comparison of CMCSSPSO, FA, and CS for phase equilibrium calculations with chemical reactions. The best of our algorithms, CMCSSPSO, performs the worst when compared to FA and CS. In fact, CS has achieved 100% reliability at a number of iterations as low as 500, which is third of the iterations that CMCSSPSO requires to reach about 89% GSR. Also, CS is more reliable than FA and CMCSSPSO using SC-2, while FA preserves its high efficiency. It is concluded that CS offers the best performance for reactive phase equilibrium problems. Detailed results for reactive phase equilibrium problems are reported in the Supporting Information. In summary, CS is the most reliable algorithm for performing the constrained minimization of Gibbs free energy in reactive systems and attempts to reduce its NFE could be promising for these calculations.

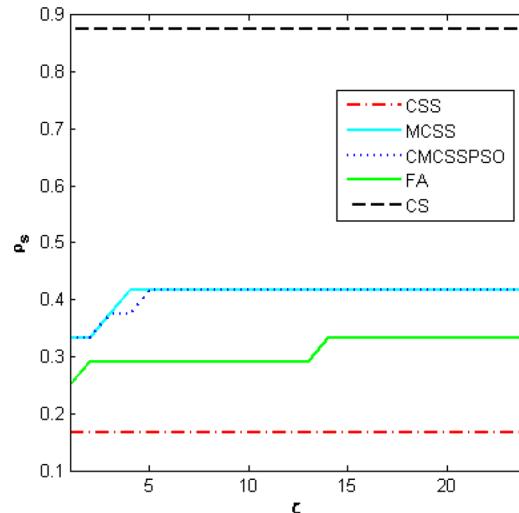
Finally, the PP plot of the stochastic algorithms without intensification, shown in Figure 15, enhances the comparison between the new methods introduced in this paper with CS and FA. The plot suggests the superiority of CMCSSPSO and MCSS at SC-1 = 1500 over the original CSS, when  $t_{ps}$  used as the performance metric. The two variants introduced in this study outperforms the FA but they may be outperformed by CS.

## 5. CONCLUSIONS

A new metaheuristic, called Charged System Search, has been introduced in Applied Thermodynamics for performing phase stability and phase equilibrium calculations in both reactive and



**Figure 14.** Global Success Rate (GSR) of CMCSSPSO, FA and CS versus iterations for reactive phase equilibrium calculations using the stopping conditions (a) SC-1 and (b) SC-2. (c) Average NFE using intensification approach.



**Figure 15.** Performance Profile (PP) of CSS, MCSS, CMCSSPSO, FA and CS for the 24 phase stability and equilibrium problems.

nonreactive systems. In particular, the Charged System Search (CSS), the Magnetic Charged System Search (MCSS), and a hybrid MCSS with Particle Swarm Optimization and chaotic maps (CMCSSPSO) have been tested and compared in the global minimization of Tangent Plane Distance Function and the Gibbs free energy with and without chemical reactions. Overall, CSS is generally found to be a modest optimization algorithm for solving these thermodynamic problems. However, MCSS is very competitive for phase stability analysis, while CMCSSPSO provides a good balance between reliability

and efficiency for performing phase equilibrium calculations in both reactive and nonreactive systems. In particular, the application of chaotic maps improves the exploration capabilities of CSS metaheuristic. Moreover, the hybrid method CMCSSPSO is found to be competitive with other reliable swarm intelligent algorithms such as Cuckoo Search. In summary, it is recommended to continue evaluating other swarm intelligence methods, while seeking to improve the performance of the already investigated techniques in applied thermodynamic calculations. In particular, the hybridization of Charged System Search and Cuckoo Search could be very promising if its NFE could be reduced to or below the level required by its counterparts.

## ■ ASSOCIATED CONTENT

### Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ NOTATION

|                     |   |
|---------------------|---|
| $a$                 | size of charged particles   |
| acc                 | acceleration of charged particles                                       |
| ACO                 | Ant Colony Optimization   |
| $c$                 | number of components  |
| CFF                 | Chaotic Force Field   |
| CM                  | Charged Memory  |
| CMCR                | Charged Memory Considering Rate   |
| CMCSSPSO            | Chaotic Magnetic Charged System Search with Particle Swarm Optimization |
| CMS                 | Charged Memory Size   |
| CP                  | Charged Particle  |
| CS                  | Cuckoo Search   |
| CSS                 | Charged System Search   |
| D                   | number of decision variables  |
| DCFF                | Dissipative Chaotic Force Field   |
| DCCFFCI             | Dissipative Chaotic Force Field with Chaotic Initialization             |
| EoS                 | Equation of State   |
| F                   | pseudoforce   |
| FA                  | Firefly Algorithm   |
| $G_K$               | $g$ Gibbs free energy of mixing   |
| GSR                 | Global Success Rate   |
| $I$                 | pseudocurrent   |
| iter                | iteration number  |
| iter <sub>max</sub> | maximum number of iterations  |
| $K_{eq}$            | chemical equilibrium constant   |
| $k_a$               | acceleration coefficient  |
| $k_v$               | velocity coefficient  |
| MCSS                | Magnetic Charged System Search  |
| MCSSPSO             | Magnetic Charged System Search with Particle Swarm Optimization         |
| N                   | population size   |
| $n$                 | moles   |
| $n_p$               | number of problems  |
| $n_s$               | number of solvers   |

NFE Number of Function Evaluations

P pressure

$p$  penalty term

$P_E$  phase equilibrium

$P_{RE}$  reactive phase equilibrium

$P_S$  phase stability

$p_{ij}$  probability of exerting force between Charged Particles

$p_r$  probability of type of force between charged particles

PAR Pitch Adjustment Rate

$p_{m_{ij}}$  magnetic probability

PSO Particle Swarm Optimization

$q$  pseudocharge

$r$  number of independent chemical reactions

$r_{ij}$  distance between charged particles

$r_{ps}$  performance ratio

SC-1, SC-2 Stopping Condition of Stochastic Method

SI Swarm Intelligence

SQP Sequential Quadratic Programming

SR Success Rate

T temperature

TPDF Tangent Plane Distance Function

$t_{ps}$  performance metric

V velocity of charged particles

X position of charged particle

$x, y, z$  mole fractions

$\beta$  decision variables

$\mu$  chemical potential

$\nu$  stoichiometric coefficients

$\varphi$  fugacity coefficient in pure state

$\hat{\varphi}$  fugacity coefficient in solution

$\gamma$  activity coefficient

$\pi$  number of phases

## ■ REFERENCES

- (1) Zhang, H.; Bonilla-Petriciolet, A.; Rangaiah, G. P. A review on global optimization methods for phase equilibrium modeling and calculations. *Open Thermodyn. J.* **2011**, *5*, 71–92.
- (2) Bonilla-Petriciolet, A.; Rangaiah, G. P.; Segovia-Hernández, J. G. Constrained and unconstrained Gibbs free energy minimization in reactive systems using genetic algorithm and differential evolution with tabu list. *Fluid Phase Equilib.* **2011**, *300*, 120–134.
- (3) Rangaiah, G. P. *Stochastic Global Optimization: Techniques and Applications in Chemical Engineering*; World Scientific Publishing Co. Inc.: River Edge, NJ; 2010; Vol. 2.
- (4) Fernández-Vargas, J. A.; Bonilla-Petriciolet, A.; Segovia-Hernández, J. G. An improved Ant Colony Optimization method and its application for the thermodynamic modeling of phase equilibrium. *Fluid Phase Equilib.* **2013**, *353*, 121–131.
- (5) Bonilla-Petriciolet, A.; Rangaiah, G. P.; Segovia-Hernández, J. G. Constrained and unconstrained Gibbs free energy minimization in reactive systems using genetic algorithm and differential evolution with tabu list. *Fluid Phase Equilib.* **2011**, *300*, 120–134.
- (6) Bonilla-Petriciolet, A.; Segovia-Hernández, J. G. A comparative study of particle swarm optimization and its variants for phase stability and equilibrium calculations in multicomponent reactive and non-reactive systems. *Fluid Phase Equilib.* **2010**, *289*, 110–121.
- (7) Rangaiah, G. P.; Segovia-Hernández, J. G.; Jaime-Leal, J. E.; Bonilla-Petriciolet, A. *Stochastic Global Optimization: Techniques and Applications in Chemical Engineering* **2010**, *2*, 413.
- (8) Rahman, I.; Das, A. K.; Mankar, R. B.; Kulkarni, B. D. Evaluation of repulsive particle swarm method for phase equilibrium and phase stability problems. *Fluid Phase Equilib.* **2009**, *282*, 65–67.
- (9) Srinivas, M.; Rangaiah, G. P. Differential evolution with tabu list for global optimization and its application to phase equilibrium and parameter estimation problems. *Ind. Eng. Chem. Res.* **2007**, *46*, 3410–3421.

- (10) Srinivas, M.; Rangaiah, G. P. A study of differential evolution and tabu search for benchmark, phase equilibrium and phase stability problems. *Comput. Chem. Eng.* **2007**, *31*, 760–772.
- (11) Teh, Y. S.; Rangaiah, G. P. Tabu search for global optimization of continuous functions with application to phase equilibrium calculations. *Comput. Chem. Eng.* **2003**, *27*, 1665–1679.
- (12) Rangaiah, G. P. Evaluation of genetic algorithms and simulated annealing for phase equilibrium and stability problems. *Fluid Phase Equilib.* **2001**, *187–188*, 83–109.
- (13) Nagatani, G.; Ferrari, J.; Cardozo Filho, L.; Rossi, C.; Guirardello, R.; Oliveira, J. V.; Corazza, M. Phase stability analysis of liquid-liquid equilibrium with stochastic methods. *Braz. J. Chem. Eng.* **2008**, *25*, 571–583.
- (14) Bonilla-Petriciolet, A.; Vázquez-Román, R.; Iglesias-Silva, G. A.; Hall, K. R. Performance of stochastic global optimization methods in the calculation of phase stability analyses for nonreactive and reactive mixtures. *Ind. Eng. Chem. Res.* **2006**, *45*, 4764–4772.
- (15) Corazza, M. L.; Cardozo Filho, L.; Vladmir Oliveira, J.; Dariva, C. A robust strategy for SVL equilibrium calculations at high pressures. *Fluid Phase Equilib.* **2004**, *221*, 113–126.
- (16) Eberhart, R.; Kennedy, J. A new optimizer using particle swarm theory. In *Proceedings of the Sixth International Symposium on Micro Machine and Human Science*; Institute of Electrical and Electronics Engineers, Inc.; Piscataway, NJ, 1995; pp 39–43.
- (17) Dorigo, M.; Maniezzo, V.; Colorni, A. Ant system: optimization by a colony of cooperating agents. *IEEE Trans. Syst., Man, Cybernet., Part B: Cybernet.* **1996**, *26*, 29–41.
- (18) Yang, X. S. Firefly Algorithm. In *Nature-Inspired Metaheuristic Algorithms*; Luniver: Bristol, U.K., 2007; pp 7990.
- (19) Yang, X. S.; Deb, S. *IEEE 2009*, 210–214.
- (20) Bhargava, V.; Fateen, S.; Bonilla-Petriciolet, A. Cuckoo Search: A new nature-inspired optimization method for phase equilibrium calculations. *Fluid Phase Equilib.* **2013**, *191*–200.
- (21) Fateen, S.-E. K.; Bonilla-Petriciolet, A.; Rangaiah, G. P. Evaluation of Covariance Matrix Adaptation Evolution Strategy, Shuffled Complex Evolution and Firefly Algorithms for phase stability, phase equilibrium and chemical equilibrium problems. *Chem. Eng. Res. Des.* **2012**, *2051*–2071.
- (22) Kaveh, A.; Talatahari, S. A novel heuristic optimization method: Charged System Search. *Acta Mechan.* **2010**, *213*, 267–289.
- (23) Kaveh, A.; Share, M. A. M.; Moslehi, M. Magnetic Charged System Search: a new meta-heuristic algorithm for optimization. *Acta Mech. Sin.* **2013**, *224*, 85–107.
- (24) Kaveh, A.; Talatahari, S. An enhanced charged system search for configuration optimization using the concept of fields of forces. *Struct. Multidiscip. Optim.* **2011**, *43*, 339–351.
- (25) Kaveh, A.; Ahmadi, B. Simultaneous analysis, design and optimization of structures using the force method and supervised charged system search algorithm. *Sci. Iran.* **2013**, *20*, 65–76.
- (26) Kaveh, A.; Talatahari, S. Charged system search for optimal design of frame structures. *Appl. Soft Comput.* **2012**, *12*, 382–393.
- (27) Kaveh, A.; Talatahari, S. Optimization of large-scale truss structures using modified charged system search. *Int. J. Optim. Civil Eng.* **2011**, *1*, 15–28.
- (28) Geem, Z. W.; Kim, J. H.; Loganathan, G. A new heuristic optimization algorithm: Harmony Search. *Simulation* **2001**, *76*, 60–68.
- (29) Kaveh, A.; Talatahari, S. Hybrid charged system search and particle swarm optimization for engineering design problems. *Eng. Comput.* **2011**, *28*, 423–440.
- (30) Talatahari, S.; Kaveh, A.; Sheikholeslami, R. An efficient charged system search using chaos for global optimization problems. *Int. J. Optim. Civil Eng.* **2011**, *2*, 305–325.
- (31) Sprott, J. C.; Sprott, J. C. *Chaos and Time-Series Analysis*; Oxford University Press: Oxford, 2003; Vol. 69.
- (32) Michelsen, M. L. The isothermal flash problem. Part I. Stability. *Fluid Phase Equilib.* **1982**, *9*, 1–19.
- (33) Dolan, E. D.; Moré, J. J. Benchmarking optimization software with performance profiles. *Math. Program.* **2002**, *91*, 201–213.