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Performance of Stochastic Global Optimization Methods in the Calculation of Phase Stability Analyses for Nonreactive and Reactive Mixtures

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In this paper, we perform a comparative study of four stochastic optimization methods for calculating the phase stability of reactive and nonreactive mixtures. We have compared the algorithms: simulated annealing, very fast simulated annealing, a modified version of direct search simulated annealing, and stochastic differential equations. We test the numerical performance and reliability of these methods using several stability problems. From our results, the simulated annealing algorithm appears to be the most reliable method for minimization of the tangent plane distance function for both reactive and nonreactive mixtures.

Introduction

Phase stability analyses are fundamental procedures in phase equilibria calculations for multicomponent and multiphase systems with or without chemical reactions. Gibbs proved that any nonreactive mixture at a given temperature, pressure, and overall composition is globally stable if the tangent to the Gibbs free energy surface at its composition does not intersect the surface. Baker et al. and Michelsen have established the necessary and sufficient conditions for phase stability analyses of nonreactive mixtures. They minimize the vertical distance from the tangent hyperplane (TPDF, tangent plane distance function) on a molar Gibbs energy surface at a composition to the energy surface at composition . An equivalent approach to minimization of the TPDF is to find all its stationary points. Recently, Wasykiewicz and Ung have proposed an extension of the stability criterion for reactive equilibrium systems (RTPDF, reactive tangent plane distance function). Global minimization of the TPDF and the RTPDF and location of the stationary points are difficult tasks and require robust numerical methods because these functions are multivariable, nonconvex, and highly nonlinear.

For nonreactive systems, several procedures purport to solve, robustly and efficiently, the phase stability problem. The traditional approach uses different initial estimations and local search methods to locate the stationary points. However, these methods do not necessarily find all stationary points of the TPDF using different initial values. Sun and Seider have applied a homotopy method to locate all stationary points of the TPDF. Their method requires different initial points to establish the homotopy paths, and because the thermodynamic models are highly nonlinear, they frequently cannot find all the solutions. To solve this problem, McDonald and Floudas used the global optimization (GOP) algorithm and a bound and branch method to solve the stability problem with the nonrandom two-liquid (NRTL) and UNIQUAC equations, respectively. Their methods guarantee global minimization of the TPDF, but it is necessary to develop appropriate convex underestimating functions for each thermodynamic model. Later, Hua et al. applied an interval Newton/generalized bisection algorithm to locate all the stationary points of the TPDF. For multicomponent mixtures, the algorithm requires a significant computational effort. Zhu and Xu and Zhu and Inoue proposed different deterministic global optimization methods for phase stability calculations. Recently, stochastic techniques for global optimization have appeared for phase stability analyses of nonreactive mixtures. In general, these methods are reliable strategies and require a reasonable computational effort to optimize multivariable functions. The simulated annealing (SA) and genetic (G) algorithms are the most prevalent stochastic optimization methods. Rangaiah has compared the SA and G algorithms for stability and equilibrium calculations. Henderson et al. have tested the SA algorithm in flash calculations for multicomponent mixtures. Nichita et al. have applied the tunneling algorithm and the theorem of variables reduction to phase stability calculations with cubic equations of state. Recently, Balogh et al. have used a stochastic sampling and a clustering method to find all stationary points of the TPDF. Zhu and Xu and Zhu et al. reported applications of the SA algorithm in the phase stability problem. For reactive mixtures, a few studies have attempted to solve the phase stability problem. Wasykiewicz and Ung introduced the RTPDF, and they applied a homotopy continuation approach to locate all stationary points of this function. To the best of our knowledge, their work is the only one related to the global solution of an RTPDF.

In this work, we examine the performance of several optimization methods in phase stability calculations. According to several studies, simulated annealing algorithms are robust and efficient methods for global minimization of continuous multivariable functions. The objective of this work is to assess and compare the numerical performance of four SA-type stochastic optimization methods in phase stability analyses for both nonreactive and reactive mixtures. We have tested the simulated annealing algorithm of Corana et al. the very fast simulated annealing reported by Sharma and Kaikkonen, our modified version of the direct search simulated annealing proposed by Ali et al., and the stochastic differential equations optimization algorithm of Aluffi-Pentini et al. To the best of our knowledge, this is the initial use of these stochastic

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optimization methods in the solution of phase stability problems for reactive systems.

**Description of the Stochastic Global Optimization Methods**

**Simulated Annealing (SA).** The simulated annealing optimization technique reflects the thermodynamic process of cooling molten metals to achieve the lowest free energy state.25 We have used the algorithm proposed by Corana et al. 20 because of its reliability and efficiency in thermodynamic calculations. In this algorithm, a randomly chosen trial point chosen within the step length VM (a vector of length n variables) is the starting point. The function evaluated at this trial point is compared to its value at the initial point. The Metropolis criterion,26 with a parameter termed the “annealing temperature” T, is used to accept or reject the trial point. If the trial point is accepted, the algorithm moves on from that point. If the trial is rejected, another point is chosen for a trial evaluation. After having adjusted each element of VM periodically, half of all function evaluations in that direction are acceptable. Rf, the temperature reduction factor, imposes a drop in T using

$$T_{j+1} = R_T \times T_j$$  \hspace{1cm} (1)

where j is the iteration counter. Thus, as T declines, downhill moves are less likely to be accepted and the percentage of rejections rises. Given the scheme for the selection for VM, VM falls. As T declines, VM falls and the method focuses upon the most promising area for optimization. Corana et al. 26 provide a full description of this algorithm. We use the subroutine implemented by Goffe et al.27

**Very Fast Simulated Annealing (VFSA).** In this algorithm, each variable of the objective function is perturbed using the Cauchy probability distribution28 and each new variable is

$$x_i^{j+1} = x_i^j + \text{sgn}(u_i - 0.5)T_j \left[ 1 + \frac{1}{T_j} \left( 2u_i - 1 \right) \right] (x_i^{\text{max}} - x_i^{\text{min}})$$ \hspace{1cm} (2)

where $u_i$ is a random number varying between 0 and 1, $T_j$ is the annealing temperature which may be the same or different for various variables depending upon the nature of the problem, and $x_i^{\text{max}}$ and $x_i^{\text{min}}$ are the upper and lower bound for the variable $i$.

At the same annealing temperature, each variable is perturbed numerous times and a new configuration is selected or rejected according to the Metropolis criterion. The number of perturbations for each variable (Np) at each annealing temperature level is constant and generally depends on the number of unknowns. After completing the desired number of moves at a particular annealing temperature, the annealing temperature is reduced exponentially to a lower level using

$$T_j(k) = T_{ao} \exp(-c_k K^c)$$ \hspace{1cm} (3)

where k is the iteration number, $c_1$ is a constant, $T_{ao}$ is the initial annealing temperature, and $c_k$ is an algorithm parameter used to control the cooling of the annealing temperature. In this work, we have set $c_1 = 1$ and used the same annealing temperature for all the variables. This method has not been used to solve the phase stability problem of reactive and nonreactive mixtures.

**Stochastic Differential Equations (SDE).** Aluffi-Pentini et al.23,24 have proposed an optimization method that associates a stochastic differential equation with the function whose global minimum we seek. A global minimizer of $f(x)$ is sought by monitoring the values of $f(x)$ along trajectories generated by a discretization of the stochastic differential equation

$$d\xi = -\nabla f(\xi) \, dt + \epsilon(t) \, dw$$ \hspace{1cm} (4)

with the initial condition

$$\xi(0) = x_0$$ \hspace{1cm} (5)

and

$$\lim_{t \to \infty} \epsilon(t) = 0$$ \hspace{1cm} (6)

where $\nabla f$ is the gradient of $f(x)$, $\xi(t)$ is the solution trajectory, $\omega(t)$ is an N-dimensional standard Wiener process, and $\epsilon(t)$ is the noise coefficient. The authors use the Euler method to discretize eq 4:

$$\xi_{k+1} = \xi_k - h_k \hat{\gamma}(\xi_k) + \epsilon(t_k) \sqrt{h_k} u_k; \hspace{1cm} k = 0, 1, 2, \ldots$$ \hspace{1cm} (7)

$$\xi_{0} = x_0$$ \hspace{1cm} (8)

where $h_k$ is the time-integration step length, $\hat{\gamma}(\xi_k)/N$ is a numerical approximation of the directional derivative of $f$ and $u_i$ is a random sample from a N-dimensional standard Gaussian distribution. The algorithm considers the simultaneous evolution of $N_{\text{traj}}$ trajectories during an observation period with $N_{\text{HP}}$ time-integration steps. During this observation, the noise coefficient of each trajectory is a constant positive value equal to $\epsilon_p$ and the step length, and the spatial increments for computing $\hat{\gamma}(\xi_k)$ are adjusted automatically for each trajectory by the algorithm. The duration of the observation period is

$$N_{\text{HP}} = 1 + \lfloor \log_2(K_p) \rfloor \text{ for short duration}$$ \hspace{1cm} (9)

$$N_{\text{HP}} = \lfloor K_p^{1/2} \rfloor \text{ for medium duration}$$ \hspace{1cm} (10)

$$N_{\text{HP}} = K_p \text{ for long duration}$$ \hspace{1cm} (11)

where $K_p = 1, 2, \cdots$ and $[x]$ is the largest integer not greater than x. A comparison is made among the trajectories in which only one is discarded at the end of every observation period. One of the trajectories replaces the discarded one and generates a second continuation trajectory with different values of $\epsilon_p$. The complete algorithm is a set of repeated trials in which a trial is a set of simultaneous trajectories. A single trial is stopped, at the end of an observation period, having reached the maximum given number of observation periods or when the final values of accepted $f(x)$ equal a minimal value $f_{\text{TRIAL}}$. The complete algorithm ceases at the end of a trial when the number of successful trials $N_{\text{TRIAL}}$ or when the maximum number of trials $N_{\text{TRIAL}}$ has been reached. The algorithm claims success if the current count $K_{\text{TRIAL}}$ of successful trials is at least one and if such trials are currently valid. In the algorithm, a valid successful trial occurs when $f_{\text{TRIAL}}$ and the best current minimal values are equal. Aluffi-Pentini et al.23,24 provide a full description of the algorithm.

**Modified Direct Search Simulated Annealing (MDSA).** Ali et al.25 proposed a memory-based simulated annealing algorithm that associates a set of points with a Markov chain and uses a probabilistic point generation mechanism. Their algorithm starts with N random points, and their functions stored in an array A and a single starting point of the initial Markov chain. The trial points are generated in a Markov chain using the configuration of $n_p + 1$ points stored in A with a user-defined probability $P_w$.
or using a random point generation mechanism with probability 1 - \( P_w \) similar to that of Corana et al.\(^{20} \)

\[
x_{\text{new}} = x_{\text{old}} + ((2u) - 1)\text{VM}
\]  

(12)

where \( u \) is a random number between 0 and 1 and VM is a step length. The generation mechanism of probability \( P_w \) starts with the random selection of \( n_p \) points, \( x_1, x_2, ..., x_{n_p+1} \), from \( A \) excluding the best point of \( A \) with function \( f_i \). The centroid \( G \) is calculated from \( x_1, x_2, ..., x_{n_p} \) where \( x_1 \) is the best point in \( A \) and the trial point is

\[
x_{\text{new}} = 2G - x_{n_p+1}
\]  

(13)

We use four random points selected from \( A \) to calculate \( G(n_p = 4) \). If \( x_{\text{new}} \) falls outside the search space, the random selection process of \( n_p \) points and the calculation of \( x_{\text{new}} \) are repeated until \( x_{\text{new}} \) satisfies the restrictions. If, after seven trials calculating \( x_{\text{new}} \) using \( G \), we do not find a \( x_{\text{new}} \) that falls inside the search space, we calculate the new point using the mechanism provided in eq 12. The new point is accepted or rejected using a modified Metropolis criterion\(^{22} \)

\[
M(T) = \min\{1, \exp(-f_{\text{new}} - f_i)/T)\}
\]  

(14)

where the trial function value \( f_{\text{new}} \) is compared with the worst function value in \( A \) (\( f_i \)). The accepted point replaces the worst point in \( A \) and the new best and worst points are in \( A \) before the process continues. This process continues until the Markov chain ends. The length of the Markov chain is

\[
L_i = N_T + [N_T F]
\]  

(15)

where \( L_i \) is the length of the Markov chain and \( N_T \) is the iteration number before annealing temperature reduction proposed by the user. The function \( F \) is

\[
F = 1 - \exp(-f_{\text{new}} - f_i)]
\]  

(16)

According to Ali et al.,\(^{22} \) this strategy allows increasing the number of function evaluations at a given annealing temperature if the difference between \( f_i \) and \( f_i \) increases. They propose that generating a point whose function value is less than \( f_i \) ends the current Markov chain. We have tested this strategy in preliminary calculations, and we have found that it converges prematurely to a local optimum of the objective function. In this work, we use a full Markov chain and the cooling schedule is defined by eq 1 in which the annealing temperature reduction factor is 0.85. This algorithm (MDSA) stops when the difference between \( f_i \) and \( f_i \) is less than a specified tolerance. We have implemented the method in a FORTRAN subroutine, which is available upon request.

**Phase Stability Problem**

The phase stability of a nonreactive mixture with \( c \) components and a global composition \( z_1, z_2, ..., z_c \), at constant pressure and temperature, results from global minimization of the tangent plane distance function (TPDF):

\[
F(y) = \sum_{i=1}^{c} y_i (\mu|_y - \mu|_z)
\]  

(17)

where \( \mu|_y \) and \( \mu|_z \) are the chemical potentials of component \( i \) calculated at compositions \( y \) and \( z \), respectively. Also, the phase stability of the mixture can be determined by finding all solutions (stationary points of the TPDF) of

\[
\mu|_y - \mu|_z - \mu|_y + \mu|_z = 0; \quad i = 1, ..., c - 1
\]  

(18)

For a chemical reaction in equilibrium, Wasylikiewicz and Ung\(^4 \) use the transformed composition variables of Ung and Doherty\(^{29,30} \) to define the reactive tangent plane distance function (RTPDF):

\[
\hat{F}(y) = \sum_{i=1}^{c-R} y_i (\hat{\mu}|_y - \hat{\mu}|_z)
\]  

(19)

where \( \hat{\mu}|_y \) and \( \hat{\mu}|_z \) are the transformed chemical potentials of component \( i \) calculated at the transformed composition \( Y \) and \( Z \), respectively. The transformed composition variable is

\[
X_i = \frac{x_i - N_v^{-1} \hat{\mu}|_y}{1 - N_{v}^{-1} \hat{\mu}|_z}
\]  

(20)

where \( x_i \) is the mole fraction of component \( i \), \( \hat{\mu}|_y \) is the column vector of \( R \) reference component mole fractions, \( v_i \) is the row vector of stoichiometric coefficients of component \( i \) for each reaction, \( v_{i,j} \) is a row vector in which each element corresponds to reaction \( r \) and is the sum of the stoichiometric coefficients for all components that participate in reaction \( r \), and \( N \) is a square matrix formed from the stoichiometric coefficients of the reference components in the \( R \) reactions. Wasylikiewicz and Ung\(^4 \) calculate the transformed compositions that globally minimize eq 19 for a reactive mixture with \( c \) components and \( R \) independent chemical reactions. Obviously, these compositions result from solving for the stationary points of

\[
\hat{\mu}|_y - \hat{\mu}|_z - \hat{\mu}|_{Y} - \hat{\mu}|_{Z} = 0; \quad i = 1, ..., c - R - 1
\]  

(21)

The solution of the phase stability for a reactive and nonreactive mixture is straightforward with an equations of state (EoS) or a solution model because the chemical potential is

\[
\frac{\mu_i(x) - \mu_i^0}{RT} = \ln \left( \frac{x_i \hat{\mu}_i(x)}{q_i} \right) = \ln (x_i \gamma_i(x))
\]  

(22)

and

\[
\frac{\hat{\mu}_i(X) - \mu_i^0}{RT} = \ln \left( \frac{x_i \hat{\mu}_i(X)}{q_i} \right) = \ln (x_i \gamma_i(x))
\]  

(23)

respectively. In eqs 22 and 23, \( \mu_i^0 \) is the chemical potential of pure component, \( q_i \) is the fugacity coefficient of component \( i \) in the mixture, and \( \gamma_i \) is the activity coefficient of component \( i \). For vapor–liquid equilibrium at low pressures (ideal gas), the condition for the chemical potential is

\[
\frac{\mu_i(x) - \mu_i^0}{RT} = \ln \left( \frac{x_i \hat{\mu}_i(x)}{p_i^m} \right) \quad \text{if} \quad \frac{\Delta g^V}{RT} < \frac{\Delta g^L}{RT}
\]

else \( \frac{\mu_i(x) - \mu_i^0}{RT} = \ln (x_i \gamma_i(x)) \)

(24)

for a nonreactive mixture and, for a reactive system, the condition is
\[
\frac{\mu_i^0(X) - \mu_i^0}{RT} = \ln\left(\frac{x_i P}{P^i_{sat}}\right)
\]

if \( \frac{\Delta g^V}{RT} < \frac{\Delta g^L}{RT} \),

else \( \frac{\mu_i^0(X) - \mu_i^0}{RT} = \ln(x_i \gamma_i(X)) \) \( \quad (25) \)

The dimensionless molar Gibbs free energy expressions of mixing for vapor and liquid without chemical reactions are

\[
\frac{\Delta g^V}{RT} = \sum_{i=1}^{c} x_i \ln\left(\frac{x_i P}{P^i_{sat}}\right)
\]

and

\[
\frac{\Delta g^L}{RT} = \sum_{i=1}^{c} x_i \ln(x_i \gamma_i)
\]

respectively. For reactive mixtures,

\[
\frac{\Delta g^V}{RT} = \sum_{i=1}^{c} x_i \ln\left(\frac{x_i P}{P^i_{sat}}\right)
\]

and

\[
\frac{\Delta g^L}{RT} = \sum_{i=1}^{c} x_i \ln(x_i \gamma_i)
\]

are the dimensionless transformed molar Gibbs free energy of mixing for the vapor and liquid phases evaluated at the transformed mole fraction \( X \).

**Results and Discussion**

**Solution Approach and Minimization Procedure.** We have applied the optimization methods in the global minimization of the TPDF and the RTPDF. The tolerance value for each algorithm is \( 1 \times 10^{-6} \). We have considered that the global minimization of the TPDF and the RTPDF is successful upon satisfying the following condition:

\[
|OBJ_{calc} - OBJ_{min}| < |OBJ_{min}| \cdot 10^{-4} + 10^{-6}
\]

where \( OBJ_{min} \) is the known global minimum of the TPDF or the RTPDF and \( OBJ_{calc} \) is the calculated value for the objective function with the optimization method, respectively. This criterion has been used by Teh and Rangaiah,\(^{31}\) Hedar and Fukushima,\(^{32}\) and Chelouah and Siarry\(^{33}\) to judge the success of a trial in the context of global optimization using stochastic methods. In all nonreactive examples, the TPDF is minimized with respect to mole numbers. The admissible region for all mole numbers is \( n_i \in \{0,1\} \). At each evaluation of the objective function, the mole numbers are used to calculate the corresponding mole fractions. For reactive mixtures, we use the transformed mole fractions or the transformed mole numbers depending upon the problem characteristics.

The reliability and efficiency of the optimization methods is evaluated based upon the following: (1) the success rate \( (S_R) \) of finding the global minimum given as percent of calculations performed that satisfies eq 30; (2) the mean total number of function evaluations (NFEV) during the optimization procedure; (3) the mean absolute percentage deviation of the calculated variables from the known variables at global minimum

\[
\text{AAD} = 100 \sum_{j=1}^{n_{opt}} \frac{|x_j^\text{min} - x_j^\text{Calc}|}{x_j^\text{min}}
\]

where \( x_j^{\text{min}} \) is the known global optimum value for the \( j \) variable, \( x_j^{\text{Calc}} \) is the calculated global optimum value \( j \) variable using the stochastic method, and \( n_{opt} \) is the overall number of optimization variables. Equation 31 is an indication of how close the method converges to the solution since we are not using an intensification procedure to refine the solution obtained from the stochastic optimization method.

Teh and Rangaiah\(^{31}\) have used these criteria before with the exception of the last one in which we use a percentage deviation. We solve all examples 100 times (each time with different random initial values and random number seeds).

**Tuning Parameters.** Stochastic optimization methods require several parameters defined by the user. We tune these parameters by finding the global minimum of the TPDF and the RTPDF of two reactive and two nonreactive systems. We include systems with different degrees of difficulty in Table 1. The systems are multicomponent, and their thermodynamic behavior is represented with an equation of state, solution model, and ideality. In Table 2, we show the tested and the suggested parameters values for each algorithm. For algorithm parameters not considered here, we use default values proposed by Corana et al.,\(^{20}\) Sharma and Kaikkonen,\(^{21}\) Aluffi-Pentini et al.,\(^{23,24}\) and Ali et al.,\(^{22}\) respectively.

During the selection process, all the algorithms find the global minimum of the TPDF and the RTPDF with different efficiency and reliability depending upon the chosen parameters values. Of all methods, only the SDE method has problems in the minimization of the TPDF for the twelve-component mixture. Having selected the parameters, we compare the performance of the methods with eight test problems of nonreactive and reactive mixtures from the literature.

**Test Problems for Nonreactive Mixtures.** In these problems, we model equilibrium using the Soave–Redlich–Kwong (SRK) equation of state with conventional mixing rules, and we take the physical constants for the pure components from Reid et al.\(^{34}\)

**Problem 1** \( N_2-C_1-C_2 \) at 270 K and 7600 KPa. Hua et al.\(^{3}\) and Harding and Floudas\(^{35}\) have analyzed this system. We use the interaction parameters, \( k_{N_2C_1} = 0.038, k_{N_2C_2} = 0.08, \) and \( k_{C_2C_2} = 0.021, \) with five different global compositions. In all cases, all optimization methods predict the compositions of the phase stability condition correctly. However, the numerical effort of each optimization method is different. We observe in Table 3 that the mean total number of function evaluations in each method varies as \( \text{SDE} > \text{SA} > \text{MDSA} > \text{VFSA} \). In all cases, the mean absolute percentage deviation of the variables is less than 0.05%, the VFSA and SDE methods being the best. The compositions of the phase stability analysis agree with those previously reported.\(^{8,31}\)

**Problem 2** \( C_2-C_3-C_4-C_5-C_6 \) at 390 K and 5583 KPa. This example comes from Ammar and Renon,\(^{36}\) and all interaction parameters are zero. Again, we have considered five different global compositions as shown in Table 3. In this case, the VFSA method converges several times to local minima of the TPDF where the global minimum is not the trivial solution \( (x_i = zi) \). In this case, the order of reliability of the algorithms in finding the global minimum is \( \text{SDE} = \text{SA} = \text{MDSA} > \text{VFSA} \) while the mean total number of function evaluations for each method is \( \text{SDE} > \text{MDSA} \approx \text{SA} > \text{VFSA} \). In this case, the AAD is less than 0.11% and the MDSA method has the highest.
value. The SDE method always converges to the global minimum, but it requires a great number of function evaluations.

**Problem 3** $C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8-C_9-C_{10}$ at 353 K and 38 500 KPa. This is an eight component mixture analyzed by Harding and Floudas using a deterministic global optimization approach. We set the interaction parameters equal to zero and use the global compositions as reported. The SA and MDSA methods are 100% reliable, but they exhibit the highest number of function evaluations, while the SDE and VFSA methods fail several times to find the minimum for the second global composition as shown in Table 3. The order of reliability and the mean total number of function evaluations are SA > MDSA > VFS > SDE and MDSA ≈ SA > SDE > VFS. In all optimization methods, the AAD is less than 0.2%.

**Problem 4** $C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8-C_9-C_{10}$ at 162.2°C. This ten-component system comes from Ammar and Renon and Henderson et al. All interaction parameters are zero, and we use the global composition $z = (0.6436, 0.0752, 0.0474, 0.0412, 0.0297, 0.0138, 0.0303, 0.0371, 0.0415, 0.0402)$ at four different pressures between 18 650 and 19 150 kPa, as suggested by Henderson et al. In this example, the SA and MDSA methods always find the global minimum in the 100 calculations as shown in Table 4. At 19 150 KPa, the SDE and VFSA methods fail 2% in the global minimization of TPDF. The order of the method in the number of function evaluations is MDSA ≈ SA > SDE > VFS. The AAD for this example is less than 0.35%.

**Test Problems for Reactive Mixtures.** **Problem 5** $A + B \rightarrow C$. We analyze the hypothetical ternary system reported by Ung and Doherty. Choosing component C as the reference component, the two transformed compositions are

$$X_A = \frac{x_A + x_C}{1 + x_C}$$

$$X_B = \frac{x_B + x_C}{1 + x_C} = 1 - X_A$$

A one-parameter Margules solution model with the thermodynamic data reported by Ung and Doherty represents the liquid-phase nonidealities. The RTPDF is minimized with respect to $X_A$ inside the interval $[0,1]$, and Table 5 contains

| Problem 3 | $C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8-C_9-C_{10}$ at 353 K and 38 500 KPa. | 100% reliable | Highest number of function evaluations | SA, MDSA > VFS > SDE | MDSA ≈ SA > SDE > VFS. | AAD < 0.2% |
| Problem 4 | $C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8-C_9-C_{10}$ at 162.2°C. | 100% reliable | Highest number of function evaluations | SA > MDSA > VFS > SDE and MDSA ≈ SA > SDE > VFS. | In all optimization methods, the AAD is less than 0.2% |
is a quaternary hypothetical mixture with liquid–liquid
250 times more function evaluations than the MDSA algorithm.
methods with very low AAD values. The SDE algorithm needs
atures, and equilibrium constants. In all the calculations, the
results obtained for different global compositions, temper-
Problem 4

<table>
<thead>
<tr>
<th>Problem 1</th>
<th>x_min</th>
<th>TPDF_min</th>
<th>NFEV (AAD, SR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>z</td>
<td></td>
<td></td>
<td>MDSA</td>
</tr>
<tr>
<td>(0.3, 0.1, 0.6)</td>
<td>(0.134 159 4, 0.067 989 0, 0.798 142 6)</td>
<td>-0.015 767</td>
<td>82.611</td>
</tr>
<tr>
<td>(0.15, 0.3, 0.55)</td>
<td>(0.096 356 8, 0.243 832 9, 0.659 810 3)</td>
<td>-0.001 570</td>
<td>81.854</td>
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<tr>
<td>(0.08, 0.38, 0.54)</td>
<td>(0.08, 0.38, 0.54)</td>
<td>0.0</td>
<td>79.736</td>
</tr>
<tr>
<td>(0.05, 0.05, 0.9)</td>
<td>(0.05, 0.05, 0.9)</td>
<td>0.0</td>
<td>86.212</td>
</tr>
<tr>
<td>(0.25, 0.2, 0.55)</td>
<td>(0.119 382 6, 0.141 070, 0.739 547 3)</td>
<td>-0.007 287 4</td>
<td>81.681</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Problem 2</th>
<th>x_min</th>
<th>TPDF_min</th>
<th>NFEV (AAD, SR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.398 42, 0.293 13, 0.200 06, 0.071 43, 0.036 96)</td>
<td>(0.388 709 0, 0.292 700 4, 0.204 465 9, 0.074 648 2, 0.039 476 5)</td>
<td>-1.30 \times 10^{-6}</td>
<td>264.514</td>
</tr>
<tr>
<td>(0.3.0.15.0.05.0.01.0.49)</td>
<td>(0.3.0.15.0.05.0.01.0.49)</td>
<td>0.0</td>
<td>274.948</td>
</tr>
<tr>
<td>(0.401, 0.293, 0.199, 0.070 7, 0.036 3)</td>
<td>(0.38 234 0, 0.292 458 8, 0.204 796 5, 0.074 923 2, 0.039 587 5)</td>
<td>-2.10 \times 10^{-6}</td>
<td>268.960</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Problem 3</th>
<th>x_min</th>
<th>TPDF_min</th>
<th>NFEV (AAD, SR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.721 2, 0.092 05, 0.044 55, 0.031 23, 0.012 73, 0.013 61, 0.072 15, 0.012 48)</td>
<td>(0.594 816 3, 0.087 115 1, 0.048 486 6, 0.037 744 3, 0.016 593 2, 0.019 560 5, 0.134 560 6, 0.061 123 3)</td>
<td>-0.002 687 6</td>
<td>752.571</td>
</tr>
<tr>
<td>(0.659 8, 0.090 84, 0.047 26, 0.035 09, 0.014 92, 0.016 57, 0.104 7, 0.030 82)</td>
<td>(0.770 526 4, 0.090 622 5, 0.040 464 9, 0.026 595 7, 0.010 260 1, 0.010 172, 0.047 103 2, 0.004 255 17)</td>
<td>-0.001 722 0</td>
<td>752.811</td>
</tr>
<tr>
<td>(0.585 4, 0.195 1, 0.048 8, 0.048 8, 0.024 4, 0.024 35, 0.048 8, 0.024 35)</td>
<td>(0.585 4, 0.195 1, 0.048 8, 0.048 8, 0.024 4, 0.024 35, 0.048 8, 0.024 35)</td>
<td>0.0</td>
<td>738.771</td>
</tr>
<tr>
<td>(0.13, 100)</td>
<td>(0.07, 100)</td>
<td>(0.03, 100)</td>
<td>(0.01, 100)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Problem 4</th>
<th>x_min</th>
<th>TPDF_min</th>
<th>NFEV (AAD, SR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (KPa)</td>
<td>x_min</td>
<td>TPDF_min</td>
<td>MDSA</td>
</tr>
<tr>
<td>19 000</td>
<td>(0.595 944 2, 0.073 882 25, 0.048 561 2, 0.044 017 4, 0.032 988 3, 0.015 911 1, 0.036 225 6, 0.045 943 5, 0.053 212 1, 0.053 314 4)</td>
<td>-6.10 \times 10^{-5}</td>
<td>1 174 409</td>
</tr>
<tr>
<td>18 650</td>
<td>(0.574 105 6, 0.073 034 6, 0.048 871 9, 0.045 100 4, 0.034 360 9, 0.016 835 9, 0.038 920 7, 0.050 092 1, 0.058 865 6, 0.059 812 4)</td>
<td>-2.56 \times 10^{-4}</td>
<td>1 172 635</td>
</tr>
<tr>
<td>18 900</td>
<td>(0.589 140 0, 0.073 634 0, 0.048 672 5, 0.044 368 6, 0.033 425 0, 0.016 202 2, 0.037 067 1, 0.047 230 1, 0.054 954 6, 0.055 306 0)</td>
<td>-1.07 \times 10^{-4}</td>
<td>1 173 895</td>
</tr>
<tr>
<td>19 150</td>
<td>(0.607 703 9, 0.074 276 9, 0.048 337 5, 0.043 380 6, 0.032 214 1, 0.015 401 8, 0.034 768 1, 0.043 735 2, 0.050 241 3, 0.049 942 7)</td>
<td>-2.05 \times 10^{-5}</td>
<td>1 167 211</td>
</tr>
</tbody>
</table>

| Problem 6 | A + B ↔ C + D. The second reactive example is a quaternary hypothetical mixture with liquid–liquid equilibrium at 298.15 K. We use a regular solution model to describe the nonidealities in the liquid phase with activity coefficients: |

\[
T \ln \gamma_k = \frac{1}{2} \sum \sum (a_{ij} + a_{ji} - a_j x_j)
\]

(34)

where \(a_j = a_{ij} = a_{ji} = 0\) and \(a_{12} = 900, a_{13} = 700, a_{14} = -300, a_{23} = -500, a_{24} = 700, a_{34} = 350. The equilibrium constant is \(K_{eq} = \exp(450/T + 0.8)\) where \(T\) is in Kelvin. We
choose the component \( D \) as reference component so the transformed mole fractions are

\[
X_A = x_A + x_D \quad (35)
\]

\[
X_B = x_B + x_D \quad (36)
\]

\[
X_C = x_C - x_D = 1 - X_A - X_B \quad (37)
\]

We minimize the RTPF function with respect to \( X_A \) and \( X_B \) in the interval of \([0,1]\) for both variables. Three global compositions analyzed at 298.15 K have the stability results in Table 6. The SA and SDE methods find the global minimum in the 100 calculations, while the MDSA and VFSA methods fail at the second global composition. Again, the reliability of optimization methods is at the expense of more function evaluations and therefore a higher computational effort. The order of efficiency in the optimization methods is MDSA > VFSA > SA > SDE.

**Table 5. Global Minimum of the RTPDF and Numerical Performance of the Stochastic Optimization Methods in Problems 5 and 8**

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( T ) (K)</th>
<th>( K_{eq} )</th>
<th>( X_{min} )</th>
<th>RTPDF(_{min} )</th>
<th>MDSA</th>
<th>SA</th>
<th>VFSA</th>
<th>SDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.6, 0.4)</td>
<td>323.15</td>
<td>3.5</td>
<td>0.494 496, 0.505 504</td>
<td>-0.077 795</td>
<td>(0, 100)</td>
<td>(0, 100)</td>
<td>(0, 100)</td>
<td>(0, 100)</td>
</tr>
<tr>
<td>(0.8, 0.2)</td>
<td>300</td>
<td>3.5</td>
<td>0.492 925, 0.507 075</td>
<td>-0.100 247</td>
<td>(0, 100)</td>
<td>(0, 100)</td>
<td>(0, 100)</td>
<td>(0, 100)</td>
</tr>
<tr>
<td>(0.55, 0.45)</td>
<td>350</td>
<td>4</td>
<td>0.920 459, 0.079 541</td>
<td>-0.233 872</td>
<td>(0, 100)</td>
<td>(0, 100)</td>
<td>(0, 100)</td>
<td>(0, 100)</td>
</tr>
</tbody>
</table>

**Table 6. Global Minimum of the RTPDF and Numerical Performance of Different Stochastic Optimization Methods in the Phase Stability Analysis in Problem 6**

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( X_{min} )</th>
<th>RTPDF(_{min} )</th>
<th>MDSA</th>
<th>SA</th>
<th>VFSA</th>
<th>SDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.6, 0.35, 0.05)</td>
<td>0.158 672, 0.227 891, 0.613 437</td>
<td>-0.039 829</td>
<td>17 626</td>
<td>61 381</td>
<td>27 811</td>
<td>910 400</td>
</tr>
<tr>
<td>(0.5, 0.7, -0.2)</td>
<td>0.817 929, 0.805 042, -0.622 971</td>
<td>-0.020 465</td>
<td>20 138</td>
<td>61 357</td>
<td>27 539</td>
<td>913 714</td>
</tr>
<tr>
<td>(0.7, 0.6, -0.3)</td>
<td>0.156 343, 0.417 391, 0.426 266</td>
<td>-0.048 268</td>
<td>17 420</td>
<td>61 327</td>
<td>27 533</td>
<td>934 510</td>
</tr>
</tbody>
</table>

The search intervals for \( X_A \) and \( X_B \) are \([0.2] \) and \([-1.1]\), respectively, and the RTPDF is minimized with respect to \( X_A \) at different global compositions, pressures, temperatures, and equilibrium constants. The conditions and stability results appear in Table 7. At each global composition, three stationary points exist for the RTPDF as shown in Figure 1. In this example, the optimization methods can find the global minimum but, again, a significant difference exists with respect to number of evaluations between the SDE and the rest of the optimization methods.

**Problem 8** \( A + B \leftrightarrow C + D \). In this example, we have considered a system with liquid–liquid equilibrium and we use the NRTL equation with the parameters reported in Table 8. The component \( D \) is the reference component so the transformed variables are those given by eqs 35–37. The RTPDF is minimized with respect to \( X_A \) and \( X_B \) in the interval of \([0.1]\) for both variables. Three feed compositions are analyzed at different temperatures and equilibrium constants, and the results are in Table 7. All optimization methods are 100% reliable, but the order of the computational effort in terms of function evaluations is MDSA > VFSA > SA > SDE. The AAD value is less than 0.01%.

Finally, we compare the mean computation time employed in all the examples by the SA with those reported by Xu et al. We have selected this method because it is the most reliable in the calculations presented in this work. Xu et al. modeled the vapor phase with either the Peng–Robinson (PR) or the...
SRK equation of state and the liquid phase with the NRTL solution model. They solved the phase stability analysis of nonreactive systems using a deterministic technique based upon interval analysis. In binary systems, their method required a computation time not higher than 0.1 s to find all the stationary points in an Intel Pentium 4 CPU (3.2 GHz). Also, they reported that the computation time increased when they solved multi-component systems. For eight components systems, their method required from 14.8 to 13 505 s at different feed conditions. We have found that the most reliable method in these problems is simulated annealing (SA) while the least reliable is very fast simulated annealing (VFSA). For systems with few components, all optimization methods converge to the global minimum, but a timewise, deterministic method should be a better approach. The VFSA algorithm requires fewer function evaluations, but it can converge more frequently to local minima. Although the simulated annealing method\(^ {20}\) does not have the least mean number of function evaluations, it is the most reliable method for stability calculations for the reactive and nonreactive mixtures treated in this work.

### Table 8. NRTL Model Parameters for Example 8

<table>
<thead>
<tr>
<th>system</th>
<th>(A_12) (cal·mol(^{-1}))</th>
<th>(A_3) (cal·mol(^{-1}))</th>
<th>(\alpha_{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-B</td>
<td>1850.2001</td>
<td>-80.4396</td>
<td>0.3</td>
</tr>
<tr>
<td>A-C</td>
<td>79.4397</td>
<td>369.0624</td>
<td>0.3006</td>
</tr>
<tr>
<td>A-D</td>
<td>-327.5173</td>
<td>256.8999</td>
<td>0.3044</td>
</tr>
<tr>
<td>B-C</td>
<td>667.4489</td>
<td>3280.604</td>
<td>0.2564</td>
</tr>
<tr>
<td>B-D</td>
<td>-219.7238</td>
<td>842.6079</td>
<td>0.2997</td>
</tr>
<tr>
<td>C-D</td>
<td>-484.8901</td>
<td>1126.4792</td>
<td>0.3</td>
</tr>
</tbody>
</table>

### Table 9. Computation Time in Phase Stability Calculations Using the Simulated Annealing Method Proposed by Corana et al.\(^ {20}\)

<table>
<thead>
<tr>
<th>problem</th>
<th>time (s)</th>
<th>problem</th>
<th>time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.8</td>
<td>2</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>12.0</td>
<td>3</td>
<td>23.2</td>
</tr>
<tr>
<td>3</td>
<td>6.9</td>
<td>4</td>
<td>9.9</td>
</tr>
<tr>
<td>4</td>
<td>7.5</td>
<td></td>
<td>0.2</td>
</tr>
</tbody>
</table>

Conclusions

We have applied four different annealing-type optimization methods in the phase stability analysis of reactive and nonreactive mixtures and present their numerical performance for systems reported in the literature. Also, we report the application of stochastic optimization methods in the global minimization of the reactive tangent plane distance function.

We have found that the most reliable method in these problems is simulated annealing (SA) while the least reliable is very fast simulated annealing (VFSA). For systems with few components, all optimization methods converge to the global minimum, but a timewise, deterministic method should be a better approach. The VFSA algorithm requires fewer function evaluations, but it can converge more frequently to local minima. Although the simulated annealing method\(^ {20}\) does not have the least mean number of function evaluations, it is the most reliable method for stability calculations for the reactive and nonreactive mixtures treated in this work.

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CONACYT, Instituto Tecnológico de Celaya, Instituto Tecnológico de Aguascalientes, Texas A&M University, and the Texas Engineering Experiment Station have provided financial support for this work.

### Literature Cited


