Application of the Stretched Simulated Annealing Method in the Stability Analysis of Multicomponent Systems using Excess Gibbs Energy Models

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Summary

In this work, the Stretched Simulated Annealing Method was applied to identify the stationary points of the tangent plane distance function defined for the Gibbs energy. The classic excess Gibbs energy Non Random Two Liquid model was used for these studies in several multicomponent mixtures, for which specific numerical difficulties were shown. The results obtained by applying the methodology developed in this work were very satisfactory.

Keywords: *Multilocal optimization; Global optimization; Phase stability.*

1 Introduction

The multilocal optimization problem consists of finding all the local solutions of the following minimization problem reduce

$$\begin{aligned} &\min_{x\in\Re^n} \quad f(x) \\ &\text{subject to} \\ &g_i(x)<0, \quad i\in I \\ &a_i<x_i<b_i, \quad i\in \Xi \end{aligned} \tag{1}$$

where $f:\Re^n\to\Re$ is a given multimodal objective function, $g_i:\Re^n\to\Re$ for all $i\in I$, I and Ξ are two sets of indices. Consider the feasible set Ω, the set of all points that satisfy the constraints, that is

$$\Omega=\left\{x\in\Re^n : a_i<x_i<b_i, i\in\Xi; g_i(x)<0, i\in I\right\} \tag{2}$$

So, our purpose is to find all points $x^*\in\Omega$ such that $\forall x\in V_\varepsilon(x^*), f\left(x^*\right)\le f\left(x\right)$.

This type of problem appears in many practical situations, for example, in ride comfort optimization [1] and in some areas of the chemical engineering (such as process synthesis, design and control) [2]. Reduction methods for solving semi-infinite programming problems also require multilocal optimizers [3].

To solve this problem we propose the penalty method combined with the l_1 exact penalty function, defined as

$$P(x,\mu)=f(x)+\frac{1}{\mu}\sum_{i\in I}\left[g_i(x)\right]^+ \tag{3}$$

where $\left[g_i(x)\right]^+=\max\left\{0,g_i(x)\right\}$ for all $i\in I$ [4].

So, in iteration l, we have to solve the minimization problem

$$\min P^l(x) \equiv P(x,\mu^l) \tag{4}$$

where $\{\mu^l\}_{l\geq 1}$ is a decreasing sequence of positive values, updated using $\mu^l = \max\{c\mu^0, \mu^{max}\}$, where $0 < c < 1$ and μ^0 is a positive value. For each μ^l the minima are obtained by the Stretched Simulated Annealing Method (SSA).

The most used methods for solving a multilocal and unconstrained optimization problem rely on, for example, evolutionary algorithms [5], the particle swarm optimization algorithm [6] and variants of the multi-start algorithm (clustering, domain elimination, zooming, repulsion) [7]. Other contributions can be found in [8-10].

In this work, a new variant of the SSA method is proposed to solve constrained optimization problems obtained from the tangent plane distance function defined for the Gibbs energy.

This paper is organized as follows. In section 2, the stretched simulated annealing method is described and in section 3, the application of this method to several phase equilibria stability problems is shown. Finally, the last section presents the main conclusions and future work.

2 Stretched simulated annealing method

The Stretched Simulated Annealing method combines simulated annealing algorithm with local applications of the function stretching technique.

In this section, the simulated annealing method is described as well as its most known variant. Then, the stretched technique is presented and, finally, the details of the SSA algorithm are shown.

2.1 Simulated annealing method

The simulated annealing, proposed in 1983 by Kirkpatrick, Gelatt and Vecchi [11], and in 1985 by Cërny [12], appeared as a method to solve combinatorial optimization problems. Since then, the simulated annealing method has been applied in many areas such as the graph partitioning, graph coloring, number partitioning, circuit design, composite structural design, data analysis, image reconstruction, neural networks, biology, geophysics and finance [13-14].

The main characteristic of this method is the fact that it does not require any derivative information or specific conditions on the objective function. Furthermore, the asymptotical convergence to a global solution is guaranteed.

The main phases of the simulated annealing method are the following: the generation of a new candidate point, the acceptance criterion, the reduction of the control parameters and the stopping criterion.

One of the most known variants of this method is Adaptive Simulated Annealing (ASA) method. In this variant, the generation of a new candidate point is crucial as it should provide a good exploration of the search region as well as a feasible point. A generating probability density function, $f_{x^k y}\left(c_G^k\right)$, is used to find a new point y based on the current approximation, x^k, see [13, 15-18].

The acceptance criterion allows the ASA algorithm to avoid getting stuck in local solutions when searching for a global one. For that matter, the process accepts points whenever an increase of the objective function is verified.

The acceptance criterion is described as

$$x^{k+1} = \begin{cases} y & if \quad \tau \leq \min\left\{1, e^{\frac{P^l\left(x^k\right) - P^l(y)}{c_A^k}}\right\} \\ x^k & \text{otherwise} \end{cases} \tag{5}$$

where x^k is the current approximation to the global minimum, y is the new candidate point, τ is a random number drawn from $U(0,1)$ and c_A^k is a positive control parameter.

This criterion accepts all points where the objective function value decreases, *i.e.*, $P^l\left(x^k\right) \geq P^l(y)$. However, if $P^l\left(x^k\right) < P^l(y)$, the point y might be accepted with some probability. During the iterative process, the probability of ascendant movements decreases slowly to zero. Different acceptance criteria can be proposed [13, 18]. The control parameter c_A^k, also known as temperature or cooling schedule, must be updated in order to define a positive decreasing sequence slowly reduced to zero.

When c_A^k is high, the minimization searches in the whole feasible region, looking up for promising regions to find the global minimum. As the algorithm develops, c_A^k is slowly reduced and the algorithm computes better precision approximations to the optimum. For a good performance of the algorithm, the initial control parameter must be sufficiently high (to search for promising regions) but not extremely high because the algorithm becomes too slow. To solve this dilemma, some authors suggested that a preliminary analysis of the problem should be done in order to find an appropriate value. For more details see [13, 16, 19].

In ASA, the control parameter c_A^k is updated by

$$\begin{cases} k_A = k_A + 1 \\ c_A^k = c_A^0 e^{-\kappa \left(k_A\right)^{\frac{1}{n}}} \end{cases} \tag{6}$$

for an initial value c_A^0.

Similarly, c_G^k parameters are updated by

$$\begin{cases} k_{G_i} = k_{G_i} + 1 \\ c_{G_i}^k = c_{G_i}^0 e^{-\kappa \left(k_{G_i}\right)^{\frac{1}{n}}} \end{cases} \quad \text{for} \quad i \in I \tag{7}$$

where $c_{G_i}^0$ is the initial value of the control parameter c_{G_i}, κ is defined by $\kappa = -\ln\left(\varepsilon\right) e^{-\frac{\ln\left(N_\varepsilon\right)}{n}}$, for positive values of ε and N_ε, for more details see [19].

To speed up the search process, the variant of the ASA algorithm also considers the reannealing of the process. This means that the control parameters are redefined during the iterative process. More details are available in [19].

The stopping criteria of ASA is based on the idea that the algorithm should terminate when no further changes occur. The usual stopping criterion limits the number of function evaluations, or defines a lower limit for the value of the control parameter. See [13, 16] for different alternatives.

For details on the algorithm convergence analysis, see [13, 20].

2.2 Stretching technique

For multimodal functions, some global optimization algorithms converge prematurely to local solutions. This is the case with the simplest versions of the particle swarm optimization algorithm. To overcome this problem, Parsopoulos *et al.* [21] proposed a function stretching technique that provides a way to escape from local optima when the particle swarm optimization convergence stagnates, driving the search to a global solution. This technique works in the following way. When a local minimizer $\bar{x}$ is detected, a two-stage transformation of the original objective function is carried out as follows:

$$\overline{P}^l\left(x\right) = P^l\left(x\right) - \frac{\delta_1}{2}\left\|x - \bar{x}\right\|\left(\operatorname{sgn}\left(P^l\left(\bar{x}\right) - P^l\left(x\right)\right) + 1\right) \tag{8}$$

$$\widetilde{P}^l\left(x\right) = \overline{P}^l\left(x\right) - \frac{\delta_2}{2}\frac{\operatorname{sgn}\left(P^l\left(\bar{x}\right) - P^l\left(x\right)\right) + 1}{\tanh\left(\mu\left(\overline{P}^l\left(\bar{x}\right) - \overline{P}^l\left(x\right)\right)\right)} \tag{9}$$

where δ_1, δ_2 and μ are positive constants and sgn defines the well-known sign function.

At points x that verify $P^l\left(x\right) > P^l\left(\bar{x}\right)$, the transformation defined in (8) increases the original objective function values by $\delta_1\left\|x - \bar{x}\right\|$. The second transformation (9) emphasizes the increase of the penalty function by making a substantial growth on the function values.

For all points x such that $P^l\left(x\right) \le P^l\left(\bar{x}\right)$, the penalty function values remain unchanged, so allowing the location of the global minimizer. When applying the global algorithm to the function $\widetilde{P}^l$, the method is capable

of finding other local solutions, $\tilde{x}$, that satisfy $P^l(\tilde{x}) \leq P^l(\bar{x})$. If another local (non-global) solution is found, the process is repeated until the global minimum is encountered.

2.3 SSA algorithm

This method is capable of locating some local solutions of problem (3) that satisfy the following condition

$$\left| P^l(x^l) - P^l(x^*) \right| \leq \delta^{ML} \tag{10}$$

where $P^l(x^*)$ is the global minimum of problem (3).

Assume now that the following assumption is verified.

Assumption 1: *All local solutions of problem (3) that satisfy condition (5) are isolated points.*

At each iteration k, the SSA algorithm solves, using the ASA algorithm, the following global optimization problem:

$$\min_{x \in \Re^n} \Phi_k(x) = \begin{cases} P^l(x) & \text{if} \quad k = 1 \\ w^l(x) & \text{if} \quad k > 1 \end{cases} \tag{11}$$

where the function $w^l(x)$ is defined as

$$w^l(x) = \begin{cases} \tilde{P}^l(x) & \text{if} \quad x \in V_\varepsilon(\bar{x}_i) \\ P^l(x) & \text{otherwise} \end{cases} \tag{12}$$

and $\bar{x}_i (i = 1,2,...,\bar{m})$ denotes a previously found global minimizer. $V_\varepsilon(\bar{x}_i)$ represents a neighbourhood of $\bar{x}_i$, with ray ε, $\bar{m}$ is the number of previously found global solutions of (3) and $\tilde{P}^l$ is the function defined in (9).

The SSA algorithm solves a sequence of global optimization problems whose objective functions are the original P^l, in the first iteration, and the transformed w^l in the subsequent iterations [19].

3 Computational results

One constrained optimization problem is the determination of phase stability using tangent plane analysis [22-25]. For a given temperature, pressure and feed composition, the phase is stable if the tangent plane distance function $D(x)$ is non negative for any composition x. This function can be written as [25]:

$$D(x) = m(x) - m(z) - \sum_{i=1}^{nc} \left(\frac{\partial m}{\partial x_i} \right)_{x=z} (x_i - z_i) \tag{13}$$

Where $m(x)$ is the molar Gibbs energy of mixing, nc is the number of components and z is the feed composition. To verify if function $D(x)$ is ever negative, it can be minimized subject to the restriction

$$\sum_{i=1}^{nc} x_i = 1 \tag{14}$$

The classic NRTL model was chosen to describe phase equilibria of several multicomponent mixtures. For this particular thermodynamic model, $m(x)$ is given by

$$m(x) = \sum_{i=1}^{nc} x_i \ln(x_i) + \sum_{k=1}^{nc} x_k \frac{\sum_{i=1}^{nc} \tau_{ik} G_{ik} x_i}{\sum_{i=1}^{nc} G_{ik} x_i} \tag{15}$$

So the constrained optimization problem can be defined as

$$\begin{aligned} &\min_{x \in \Re^{nc}} \quad m(x) \\ &\text{subject to} \\ &\sum_{i=1}^{nc} x_i = 1 \\ &0 < x_i < 1, \quad i \in \{1,...,nc\} \end{aligned} \tag{16}$$

Several phase stability problems were solved by applying the stretched simulated annealing method. These examples were selected in order to test the robustness of the optimization method for especially difficult phase equilibria systems [25]. Two systems were selected: system I comprises a mixture of three components (n-propanol, n-butanol and water) and system II includes a mixture of four components (n-propanol, n-butanol, benzene and water). The correspondent NRTL parameters G_{ik} and τ_{ik} used in this work are presented on Tables 1 and 2.

Table 1. NRTL parameters for system I [26]

G_{ij}	1	2	3
1	1.0	1.2017478×10^{0}	1.0216786×10^{0}
2	8.066060×10^{-1}	1.0	6.490629×10^{-1}
3	4.392221×10^{-1}	1.852084×10^{-1}	1.0
τ_{ij}	1	2	3
1	0.0	-6.1259×10^{-1}	-7.149×10^{-2}
2	7.1640×10^{-1}	0.0	9.0047×10^{-1}
3	2.7425×10^{0}	3.51307×10^{0}	0.0

Table 2. NRTL parameters for system II [27]

G_{ij}	1	2	3	4
1	1.0	3.4320×10^{-1}	9.3449×10^{-1}	9.6384×10^{-1}
2	1.80967×10^{0}	1.0	1.02932×10^{0}	9.3623×10^{-1}
3	5.6132×10^{-1}	5.9659×10^{-1}	1.0	3.2322×10^{-1}
4	5.1986×10^{-1}	2.2649×10^{-1}	3.1656×10^{-1}	1.0
τ_{ij}	1	2	3	4
1	0.0	2.16486×10^{0}	2.3689×10^{-1}	1.3060×10^{-1}
2	-1.2007×10^{0}	0.0	-9.730×10^{-2}	1.9154×10^{-1}
3	2.01911×10^{0}	1.73912×10^{0}	0.0	4.01932×10^{0}
4	2.31985×10^{0}	4.31706×10^{0}	4.09334×10^{0}	0.0

The SSA method was implemented in C programming language on a Pentium II, Celeron 466 MHz with 64 Mb of RAM.

The following constants are fixed: $\delta_1 = 100$, $\delta_2 = 1$, $\kappa = 10^{-3}$, $\varepsilon_0 = 0.05$, $\varepsilon_{max} = 5\varepsilon_0$, $\delta^{ML} = 0.5$, $c = 10^{-1}$, $\mu^0 = 1$ and $\mu^{max} = 10^{-4}$.

As a complement, the "fminunc" routine from the optimization toolbox of the commercial software MATLAB was used to improve the precision of the solutions found by the SSA method. This routine is based on the BFGS Quasi-Newton method with a cubic line search procedure [28]. It should be mentioned that this method, used without the SSA method, only finds one local solution.

The stationary points for the tangent plane distance function were calculated for two different systems and several feed compositions. The results are presented on Tables 3 and 4.

Table 3. Stationary points for system I using the NRTL model and several feed compositions

System I. n-propanol (1) + n-butanol (2) + water (3)		
Feed composition (z_1, z_2)	Stationary points (x_1, x_2)	Tangent plane distance function
$(1.48\times10^{-1}, 5.20\times10^{-2})$	$(1.48\times10^{-1}, 5.20\times10^{-2})$ $(1.14\times10^{-1}, 3.60\times10^{-2})$	1.3726×10^{-13} -9.9851×10^{-6}
$(1.20\times10^{-1}, 8.00\times10^{-2})$	$(1.20\times10^{-1}, 8.00\times10^{-2})$ $(1.30\times10^{-1}, 8.91\times10^{-2})$ $(5.97\times10^{-2}, 2.82\times10^{-2})$	1.3323×10^{-17} -3.0693×10^{-6} -7.4818×10^{-4}
$(1.30\times10^{-1}, 7.00\times10^{-2})$	$(1.30\times10^{-1}, 7.00\times10^{-2})$ $(1.38\times10^{-1}, 7.56\times10^{-2})$ $(7.38\times10^{-2}, 3.03\times10^{-2},)$	1.44329×10^{-17} -8.6268×10^{-7} -3.2762×10^{-4}
$(1.20\times10^{-1}, 5.00\times10^{-2})$	$(1.58\times10^{-1}, 7.29\times10^{-2})$ $(9.40\times10^{-2}, 3.49\times10^{-2})$	-5.7360×10^{-5} -3.0888×10^{-5}

Table 4. Stationary points for system II using the NRTL model and several feed compositions

System II. n-propanol (1) + n-butanol (2) + benzene (3) + water (4)		
Feed composition (z_1, z_2, z_3)	Stationary points (x_1, x_2, x_3)	Tangent plane distance function
$(1.48\times10^{-1}, 5.20\times10^{-2}, 6.00\times10^{-1})$	$(1.81\times10^{-2}, 6.20\times10^{-4}, 4.48\times10^{-3})$	-3.3982×10^{-1}
$(2.50\times10^{-1}, 2.50\times10^{-1}, 2.50\times10^{-1})$	$(2.50\times10^{-1}, 2.50\times10^{-1}, 2.50\times10^{-1})$	0.0000
$(1.48\times10^{-1}, 5.20\times10^{-2}, 7.00\times10^{-1})$	$(2.41\times10^{-2}, 7.86\times10^{-4}, 4.74\times10^{-3})$	-3.1097×10^{-1}
$(2.50\times10^{-1}, 1.50\times10^{-1}, 4.00\times10^{-1})$	$(2.50\times10^{-1}, 1.50\times10^{-1}, 4.00\times10^{-1})$ $(3.67\times10^{-2}, 2.98\times10^{-3}, 7.37\times10^{-3})$	2.3831×10^{-13} -3.867×10^{-2}
$(2.50\times10^{-1}, 1.50\times10^{-1}, 3.50\times10^{-1})$	$(2.50\times10^{-1}, 1.50\times10^{-1}, 3.50\times10^{-1})$ $(3.32\times10^{-2}, 2.69\times10^{-3}, 6.71\times10^{-3})$	0.0000 -7.363×10^{-2}

The most important result is that the SSA method combined with the "fminunc" routine is always able to find the global minimum known in the literature [25] which allows concluding about phase stability.

From the numerical results, it is possible to verify that all the tested feed compositions are unstable with the exception of the second feed of system II (Table 4). This is in agreement with the results presented by Tessier *et al.* [25].

Furthermore, in some cases, other stationary points are found. To find all the stationary points, the values of the constants must be adjusted to each problem using a preliminary analysis.

4 Conclusions

In this work, a new variant of the stretched simulated annealing method was developed to solve constrained optimization problems, based on penalty method, simulated annealing method and stretching technique. The resulting method was satisfactorily applied to solve phase stability problems, by finding all the correspondent global solutions.

It should be mentioned that the mathematical methodology herein described for the NRTL model can be straightforwardly extended to other thermodynamic models.

As future work, we intend to combine SSA with derivative information in order to locate a better candidate point to the solution of the optimization problem.

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