

## Thermodynamic calculations for chemical engineering using a simulated annealing optimization method

Adrián Bonilla-Petriciolet <sup>a</sup>, Juan Gabriel Segovia-Hernández <sup>b</sup>, Florianne Castillo-Borja <sup>a</sup> and Ulises Ivan Bravo-Sánchez <sup>a</sup>

<sup>a</sup> *Instituto Tecnológico de Aguascalientes, Depto. Ing. Química, Aguascalientes, 20256, México. petriciolet@hotmail.com*

<sup>b</sup> *Universidad de Guanajuato, Facultad de Química, Guanajuato, 36050, México.*

### Abstract

In this paper, a memory-based Simulated Annealing is proposed to solve several thermodynamic calculations that are related to the modeling of phase equilibrium and thermodynamic properties. Specifically, we have tested the numerical performance of this optimization method in Gibbs energy minimization for flash calculations, calculation of homogeneous azeotropes and data fitting in thermodynamic models. Our results indicate that, in general, proposed method is reliable to solve these problems and shows a reasonable computational effort.

**Keywords:** thermodynamic calculations, global optimization, simulated annealing

### 1. Introduction

In Chemical Engineering, several thermodynamic calculations can be formulated as constrained or unconstrained optimization problems. Some examples are phase equilibrium and stability problems and parameter estimation for thermodynamic models [1-3]. These problems are non-linear, multivariable and the objective function used as optimization criterion is generally non-convex with several local optimums. These difficulties have promoted the

development and application of global optimization strategies for this kind of calculations. In this context, metaheuristic methods are playing an important role because they are generally robust numerical tools that present a reasonable computational effort in the optimization of multivariable functions, are applicable to unknown structure problems, they require only calculations of the objective function and can be used with all models without problem reformulation [2]. Simulated Annealing (SA) is one of the most applicable metaheuristic and have been used in several thermodynamic problems [1-3]. Recently, numerical performance of a new memory-based SA has been reported for phase stability analysis of non-reacting and reacting mixtures [4]. Experimental results show that this method appears to be robust in the global minimization of multivariable and non-convex functions. Considering these results, we have decided to extend its application for other thermodynamic calculations. Specifically, this paper reports the performance of this stochastic method in different calculations related to the modeling of phase equilibrium and thermodynamic properties in non-reactive and electrolyte mixtures.

## 2. Problem Statement and Description of Stochastic Optimization Method

### 2.1. Formulation of the Optimization Problem

We consider thermodynamic calculations that can be formulated as the problem of finding a global minimum of the unconstrained optimization problem: minimize  $f(x)$  subject to  $x \in \Omega$  where  $f: R^n \rightarrow R$  and  $\Omega$  is a compact set which contains in its interior a global minimum point  $x^*$  of  $f(x)$ .

### 2.2. Description of the Stochastic Optimization Method

The optimization method employed in this work is a modified version of SA proposed by Ali *et al.* [5]. It is a memory-based SA that associates a set of points with a Markov chain and uses a probabilistic point generation mechanism. This algorithm starts with  $N$  random points and their functions stored in an array  $A$  and a single starting point of the initial Markov chain. Trial points are generated in a Markov chain using the configuration of  $np + 1$  points stored in  $A$  with a user-defined probability  $P_w$  or using a random point generation mechanism with probability  $1 - P_w$ . The generation mechanism of probability  $P_w$  starts with the random selection of  $np$  points  $x_2, \dots, x_{np+1}$  from  $A$  (where  $np < N$ ), excluding the best point  $x_1$  of  $A$  with function  $f_1$ . The centroid  $G$  is calculated from  $x_2, \dots, x_{np}$  and the trial point is given by  $x_{new} = 2G - x_{np+1}$  where  $np = 4$ . For the random point generation mechanism, we use  $x_{new} = x_{old} + V(2u - 1)$  being  $u$  a random number and  $V$  a step length. The new point is accepted or rejected using a modified Metropolis criterion  $M(T_{SA}) = \exp(-(f_{new} - f_h)/T_{SA})$  where  $T_{SA}$  is the annealing temperature,  $f_{new}$  is the trial function value and  $f_h$  is

the worst function value stored in  $A$ , respectively. The accepted point replaces the worst point in  $A$  and the new best and worst points are found in array  $A$  before the process continues. This process continues until the Markov chain ends. The length of the Markov chain is  $L_t = NT + \lfloor NT * F \rfloor$  where  $NT$  is the iteration number before  $T_{SA}$  reduction. The function  $F$  is given by  $F = 1 - \exp[-(f_h - f_i)]$  which allows increasing the number of function evaluations at a given annealing temperature if the difference between  $f_h$  and  $f_i$  increases. To avoid convergence to local optimums, we have used a full Markov chain and a linear cooling schedule with a reduction factor for annealing temperature equal to 0.85 units. We called this algorithm DSAM method and it has been implemented in a FORTRAN® subroutine. In this work, algorithm stops when the difference between  $f_h$  and  $f_i$  is less than 1.0E-06. From results of Bonilla-Petriciolet *et al.* [4], we have considered the following values for principal parameters of DSAM method:  $T_{SA} = 10$ ,  $P_w = 0.2$ , size of array  $A$  equal to  $5(n_{var} + 1)$  and  $NT = n_{var}$  where  $n_{var}$  is the overall number of optimization variables.

### **3. Paper approach**

#### *3.1. Test examples*

Performance of the optimization method is tested using several thermodynamic problems related to the modeling of phase equilibrium and thermodynamic properties in non-reactive and electrolyte systems. These problems are multivariable, highly non-linear and its objective function is non-convex with several local optimums. All examples are solved 25 times (each time using different random initial value for optimization variables and random number seed). Reliability and efficiency of DSAM method is tested considering the following standard criterions for stochastic methods: a) success rate (SR) of finding the global minimum given as percent and b) mean total number of function evaluations (NFEV) during the optimization procedure. CPU time is also reported for all examples where all calculations are performed on a Processor Intel Pentium M 1.73 GHz with 504 MB of RAM. Problem formulation and details of all examples are described below.

##### *3.1.1. Flash calculations in multicomponent non-reacting mixture*

Phase equilibrium calculations are a recurrent and important element in the simulation of separation processes. Basically, this problem can be stated as the global minimization of the total Gibbs energy of mixing  $g$  (considering a  $c$  component mixture with  $\pi$  phases at equilibrium)

$$g = \sum_{k=\alpha}^{\pi} n^k g^k \quad (1)$$

subject to the mole number restrictions where  $n^k$  is the total mole number at phase  $k$  and  $g^k$  is the Gibbs energy of mixing of phase  $k$ , respectively. Gibbs minimization is a challenging optimization problem due to the presence of trivial solutions and unstable equilibrium states. However, Gibbs energy function can be minimized with respect to a set of  $c$  independent variables  $\chi_i \in [0, 1]$  to eliminate the restrictions imposed by the material balances and to reduce problem dimensionality [3]. For a two-phase equilibrium problem, optimization variables are related to mole numbers using

$$\left. \begin{aligned} n_i^\alpha &= n_i^z \chi_i \\ n_i^\beta &= n_i^z - n_i^\alpha \end{aligned} \right\} i = 1, \dots, c \quad (2)$$

where  $\alpha$  and  $\beta$  corresponds to the equilibrium mole numbers and  $z$  denotes feed composition. For illustrative purposes, we have considered the multicomponent mixture  $C_1 - C_2 - C_3 - iC_4 - C_4 - iC_5 - C_5 - C_6 - iC_{15}$  at 19.84 atm and 314 K with a feed composition  $z(0.614, 0.10259, 0.04985, 0.00898, 0.02116, 0.00722, 0.01187, 0.01435, 0.16998)$ . This mixture is modeled with SRK EoS.

### 3.1.2. Calculations of homogeneous azeotropes in non-reactive mixtures

Homogeneous azeotropy is a condition of vapor-liquid equilibrium in which the composition is identical on both phases. Description of this phase equilibrium condition is essential for the selection of strategies in separation process. Considering the necessary condition for phase equilibrium (equality of chemical potentials), a homogeneous azeotrope can be located by minimizing

$$f = \sum_{i=1}^c (\mu_i^\alpha - \mu_i^\beta)^2 \quad (3)$$

where  $\mu_i$  is the chemical potential of component  $i$  in the mixture. Global optimum is  $f = 0$  if an azeotrope exists. Minimization of this function is performed considering mole numbers (for  $c \geq 3$ ),  $T$  or  $P$  as optimization variables. In this example, we have calculated the homogeneous azeotrope for the binary mixture  $CO_2 - Ethane$  at 1730.445 Kpa using SRK EoS and objective function is minimized using  $x_{CO_2} \in (0, 1)$  and  $T \in (200, 270)$  Kelvin.

### 3.1.3. Correlation of activity coefficients in electrolyte systems

Thermodynamic properties of aqueous electrolyte systems have been widely studied due to its environmental and industrial applications. Generally,

developed models can fit and predict the activity coefficients of electrolytes using few adjustable parameters. However, the non-linearity of thermodynamic models may cause computational difficulties in the parameter estimation due to the possibility of several local optimums in the objective function [6]. Failing to identify the global optimum in parameter estimation may cause errors and uncertainties in process design and erroneous conclusions about model performance. So, this problem is a good choice to test numerical performance of DSAM method. In this example, we use the NRTL-electrolyte model [6] to fit the activity coefficients of aqueous electrolyte solutions. The following objective function is used to correlate the data of mean activity coefficient  $\gamma_{\pm}$

$$f = \sum_{i=1}^{ndat} \left[ \ln(\gamma_{\pm}^{\text{exp}} - \gamma_{\pm}^{\text{calc}})_i \right]^2 \quad (4)$$

where *exp* and *calc* denote experimental and calculated quantities. This function is minimized using the same parameters ( $\tau_{cas}$ ,  $\tau_{sca}$ ) and initials intervals reported by Belveze *et al.* [6]. Experimental data of the quaternary ammonium salt  $[(\text{CH}_3)_4\text{N}^+][\text{Br}^-]$  at 25 °C is considered as study case.

### 3.2. Results & discussions

Table 1 shows the numerical performance of DSAM method for the examples considered in this paper. Reported results and, our numerical experience with others test conditions and several case studies, indicate that it is generally robust to perform Gibbs energy minimization and homogeneous azeotrope calculation in non-reactive mixtures. Specifically, the calculation of homogeneous azeotropes using an optimization approach and this method is very reliable and can be applied with any thermodynamic model. In fact, this paper reports the first application of a stochastic optimization for the calculation of homogeneous azeotropes. On the other hand, our experience with data fitting of activity coefficients in electrolyte systems indicates that DSAM is not suitable for this purpose. Generally, it showed several failures to find the global optimum in the parameter estimation of NRTL-electrolyte model for several electrolyte systems reported by Belveze *et al.* [6]. These results suggest that parameter estimation in electrolyte systems is a very challenging optimization problem and can be used for testing global optimization strategies. With respect to efficiency, this optimization strategy shows a reasonable CPU time in the resolution of these thermodynamic problems even for multivariable examples. Finally, based on our numerical practice using metaheuristic methods, DSAM is more reliable than other SA-type optimization methods as Very Fast Simulated Annealing and Stochastic Differential Equations.

#### 4. Conclusions and future work

Reliability and efficiency of a memory-based Simulated Annealing method have been tested in several thermodynamic calculations related to Chemical Engineering. In general, experimental results show that this optimization method is robust to perform flash calculations through the Gibbs energy minimization and the prediction of homogeneous azeotropes. However, it is not suitable for data correlation in thermodynamic models, particularly in electrolyte systems. In forthcoming studies, we will test and compare other stochastic optimization methods with the aim of identifying a more reliable and efficient strategy for thermodynamic calculations in Chemical Engineering.

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Table 1. Numerical Performance of DSAM method in several thermodynamic calculations

Thermodynamic problem	Global optimum	Numerical performance		
		SR, %	NFEV	CPU time, s
Gibbs energy minimization for two-phase equilibrium	$x^\alpha$ (0.083652, 0.054879, 0.061769, 0.017338, 0.04676, 0.020578, 0.035595, 0.049032, 0.630398) $x^\beta$ (0.809794, 0.120204, 0.04545, 0.005895, 0.011709, 0.002288, 0.003111, 0.001546, 0.000003) $g = -0.76977$	100	91769 0	32.7
Homogeneous azeotrope calculation	$x^{azeo}$ (0.652211, 0.347789) and 243.15 K	100	15049	0.3
Parameter estimation of activity coefficients in aqueous electrolyte	$\tau_{cas} = -4.3242$ $\tau_{sca} = 9.3821$ $f = 1.75E-03$	64	37130	2.0

#### References

1. N. Henderson, L. Freitas and G.M. Platt, *AIChE J.*, 50 (2004) 1300.
2. Y.S. Teh and G.P. Rangaiah, *Comput. Chem. Eng.*, 27 (2003) 1665.
3. G.P. Rangaiah, *Fluid Phase Equilib.*, 187-188 (2001) 83.
4. A. Bonilla-Petriciolet, R. Vazquez-Roman, G.A. Iglesias-Silva and K.R. Hall, *Ind. Eng. Chem. Res.*, 45 (2006) 4764.
5. M.M. Ali, A. Torn, S. Viitanen, *Comput. Oper. Res.*, 29 (2002) 87.
6. L.S. Belveze, J.F. Brennecke and M.A. Stadtherr, *Ind. Eng. Chem. Res.*, 43 (2004) 815.