Chemical Engineering Science 66 (2011) 5684–5702

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

The Least Dot Products method: A new numerical paradigm for phase stability analysis of thermodynamic mixtures

Nélio Henderson [a,c,*], Nelza E. Barufatti [a,c], Wagner F. Sacco [b,c]

[a] Instituto Politécnico, Universidade do Estado do Rio de Janeiro, 28601-970 Nova Friburgo, RJ, Brazil
[b] Universidade Federal do Oeste do Pará, 68040-070 Santarém, PA, Brazil
[c] Thermodynamics and Optimization Group (TOG), Brazil

ARTICLE INFO

Article history:
Received 8 February 2011
Received in revised form
20 July 2011
Accepted 2 August 2011
Available online 10 August 2011

Keywords:
Phase equilibria
Stability
Thermodynamics process
Mathematical modeling
Gibbs plane tangent criterion
Tangent plane distance function

ABSTRACT

This work introduces the Least Dot Products (LDP) method, a new algorithm for phase stability analysis of thermodynamic mixtures. Starting with the fact that tangent plane distance function (the objective function used in global stability tests) is, essentially, the dot product between the vector of compositions of a trial phase and the vector that describes the differences among the chemical potential of the components in the phases, our approach tries to obtain the least values of an auxiliary function that represents an appropriate dot product on a unitary sphere of the n-dimensional space, which is a good approximation for the stability test function. In agreement with the foundations of the Gibbs plane tangent criterion, the new algorithm simply tries to find points where the objective function is negative, which are not (necessarily) stationary points or global minima. Thus, our main contribution is not a new method for general nonlinear problems, or a rule-based termination criteria for a classical optimization method. Consequently, if such points do not exist, then LDP method is not capable to recognize the stability condition. To overcome this problem, we develop also a powerful safeguard algorithm, denominated Projected Simulated Annealing (PJSA) algorithm, which is obtained by projecting the Simulated Annealing algorithm onto the unitary sphere.

In the present article, firstly we consider liquid–liquid equilibria at low or moderate pressures, where the excess Gibbs energy is described by NRTL or UNIQUAC models. Secondly, we address vapor–liquid equilibria at high pressures with cubic equations of state.

To illustrate the performance of the new methodology, we use here 20 systems studied by other authors. Such problems possess 2–12 variables and constitute severe tests for many optimization methods. For some mixtures, we show that LDP method is capable of determining the instability condition using just two iterations.

1. Introduction

The stability analysis is an important step in the phase equilibrium study. In fact, such analysis is present in various chemical engineering processes where the prediction of number of phases and composition calculations take place.

As demonstrated by Baker et al. (1982), at constant temperature T and pressure P, the phase stability analysis of an n-component thermodynamic mixture uses the called tangent plane distance (TPD) function, given by

$$TPD(\boldsymbol{x}) = \sum_{i=1}^{n} x_i[\mu_i^{(\beta)}(\boldsymbol{x}) - \mu_i^{(\alpha)}(\boldsymbol{z})], \tag{1}$$

where $\boldsymbol{z}=(z_1, \ldots, z_n)$ is the vector of compositions (mole fractions) of the phase under consideration (denoted by α) and $\boldsymbol{x}=(x_1, \ldots, x_n)$ is the vector of compositions of a trial phase (denoted by β). In Eq. (1), $\mu_i^{(j)}$ is the chemical potential of component $i(=1,\ldots,n)$ in the phase $j=\alpha, \beta$.

This thermodynamic analysis constitutes a criterion for global stability, called Gibbs plane tangent (GPT) criterion, which can be stated as follows.

GPT Criterion. Let $\mathcal{S}$ be the subset of $\mathbb{R}^n$ given by

$$\mathcal{S} = \left\{ \boldsymbol{x} = (x_1,\ldots,x_n) \in \mathbb{R}^n; \quad 0 < x_i < 1 \text{ and } \sum_{i=1}^{n} x_i = 1 \right\}. \tag{2}$$

If $TPD(\boldsymbol{x}) \geq 0$, for all $\boldsymbol{x} \in \mathcal{S}$, then the mixture is stable, and exhibits a single phase; otherwise, i.e., if there exists some $\boldsymbol{x}^* \in \mathcal{S}$ such that $TPD(\boldsymbol{x}^*) < 0$, then the mixture is unstable, and a new phase will appear.

Michelsen (1982a) was the first to formulate numerical methodologies for the global stability analysis based on GPT criterion.

* Corresponding author at: Instituto Politécnico, Universidade do Estado do Rio de Janeiro, 28601-970 Nova Friburgo, RJ, Brazil.
E-mail addresses: nelio@iprj.uerj.br, neliohenderson@gmail.com (N. Henderson).

0009-2509/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2011.08.004

This author used two different methods. In one of the implementations, Michelsen proposes a direct substitution scheme based on the following paradigm: the numerical method seeks to determine stationary points of $TPD(\boldsymbol{x})$. The other approach taken by Michelsen uses a different paradigm: the numerical method seeks to determine minimum points of $TPD(\boldsymbol{x})$. In both cases, the signs of $TPD(\boldsymbol{x})$ on the found points determine the outcome of the stability test.

Today, nearly 30 years after the seminal article by Baker et al. (1982), we can observe a tremendous growth of publications in the area of phase equilibrium with emphasis on the global stability analysis, using the GPT criterion. Among several works, we can mention Michelsen (1982a, b, 1984a), Nghiem and Li (1984), Nghiem et al. (1985), Trangenstein (1987), Nagarajan et al. (1991a, b), Sun and Seider (1995), Hua et al. (1996, 1998a, b), McDonald and Floudas (1995a, b, 1997), Wasylkiewicz et al. (1996), Wasylkiewicz and Ung (2000), Pan and Firoozabadi (1998), Zhu and Xu (1999a, b), Zhu et al. (2000), Zhu and Inoue (2001), Harding and Floudas (2004), Jalali and Seader (2000), Lucia et al. (2000, 2005), Tessier et al. (2000), Henderson et al. (2001, 2004, 2010), Gomes et al. (2001), Rangaiah (2001), Nichita et al. (2002, 2006), Nichita and Gomez (2010), Xu et al. (2002, 2005), Balogh et al. (2003), Gecegormez and Demirel (2005), Bonilla-Petriciolet et al. (2006), Bonilla-Petriciolet and Segovia-Hernández (2010), Hoteit and Firoozabadi (2006), Schmitz et al. (2006), Srinivas and Rangaiah (2007), Nagatani et al. (2008), Saber and Shaw (2008) and Rahman et al. (2009), for example.

The works mentioned above show also that the development of the numerical analysis related with the phase stability is intimately linked to the exponential growth that has been occurring in global optimization, both deterministic and stochastic. Such fact is an obvious consequence of the mathematical structure of the test stability problem and of the paradigms initially proposed by Michelsen: the (here) called *Paradigm 1* that approaches the stationary points of $TPD(\boldsymbol{x})$, and the (here) called *Paradigm 2* that approaches the minimum points of $TPD(\boldsymbol{x})$. Such paradigms are, in general, the keys in almost all algorithms used for phase stability analysis.

Thus, following Paradigm 1, methods are used to solve the nonlinear system:

$$\begin{cases} Grad\ TPD(\boldsymbol{x}) = 0, \\ \boldsymbol{x} \in \mathcal{S}, \end{cases} \tag{3}$$

where $Grad\ TPD(\boldsymbol{x})=0$ represents an appropriate stationary condition for $TPD(\boldsymbol{x})$ on $\mathcal{S}$.

On the other hand, following Paradigm 2, methods are used to solve the optimization problem:

$$\begin{cases} \text{Min}\ TPD(\boldsymbol{x}), \\ \boldsymbol{x} \in \mathcal{S}. \end{cases} \tag{4}$$

In the present work, we develop a method for the stability test which simply tries to find a point $\boldsymbol{x}$ such that $TPD(\boldsymbol{x}) < 0$, since such a point exists in $\mathcal{S}$. In this case, $\boldsymbol{x}$ is not, necessarily, a minimum or a stationary point of $TPD(\boldsymbol{x})$. Here, this more general approach will be called *Paradigm 3*. Thus, using Paradigm 3, we seek to solve the following problem:

$$\begin{cases} \text{Find}\ \boldsymbol{x} \in \mathcal{S}\ \text{such that} \\ TPD(\boldsymbol{x}) < 0. \end{cases} \tag{5}$$

It is worth emphasizing that our approach is not a rule-based termination criteria for a classical optimization method, which simply tries to stop an iterative process, when $TPD(\boldsymbol{x}) < 0$. In fact, the main result of this work is a method especially developed to solve the problem shown in Eq. (5).

Our methodology is developed using an auxiliary function $h(\boldsymbol{x}) = (1/n)\sqrt{\boldsymbol{x}} \cdot \boldsymbol{\psi}$, which essentially defines the dot product between two vectors of $\mathbb{R}^n$, the vector $\sqrt{\boldsymbol{x}} = (\sqrt{x_1}, \ldots, \sqrt{x_n})$ and a specific (non-zero) vector denoted here by $\boldsymbol{\psi}$ that is associated to the thermodynamic model. As shown later in this work, since there exists a mapping $f : \mathcal{S} \to S$, which maps $\mathcal{S}$ onto the unitary sphere $S \subset \mathbb{R}^n$, then a Lagrangian condition can be used to generate a sequence of points related to least dot products among $\boldsymbol{\psi}$ and points on the unitary sphere of $\mathbb{R}^n$. This procedure gives name to the numerical scheme called the Least Dot Products (LDP) method. The form of $h(\boldsymbol{x})$ was adopted for being easy to handle. Besides, as we show, this auxiliary function has aspects that make it a good approximation for the tangent plane distance function.

In spite of the use of a Lagrangian condition, the LDP method is not an optimization method for the problem described in Eq. (4). Consequently, if there are no points in $\mathcal{S}$ such that $TPD(\boldsymbol{x}) < 0$, then the LDP method is not capable to determine the stability condition. To overcome this problem, following Paradigm 2, we use a safeguard algorithm, which is called to detect stability states or when the LDP method fails to determine $\boldsymbol{x} \in \mathcal{S}$, such that $TPD(\boldsymbol{x}) < 0$, at a given iteration number, for example, 100 iterations.

In the present work, we develop a powerful safeguard algorithm denominated Projected Simulated Annealing (PJSA) algorithm. This stochastic algorithm is obtained by projecting the Simulated Annealing algorithm (as described by Corana et al., 1987) onto the unitary sphere S.

Here, we consider liquid–liquid equilibria, where the excess Gibbs energy is described by the Non-Random Two Liquid (NRTL) or UNIversal QUAsi-Chemical (UNIQUAC) models, see Prausnitz et al. (1986), and vapor–liquid equilibria modeled with cubic equations of state. More precisely, we use the cubic equations developed by Soave (1972) and Peng and Robinson (1976).

To illustrate the performance of the LDP method, we attack benchmark problems studied by other authors, among them we can cite Michelsen (1982b), Nagarajan et al. (1991a), McDonald and Floudas (1995b), Tessier et al. (2000), Gecegormez and Demirel (2005), Bonilla-Petriciolet et al. (2006), and Saber and Shaw (2008). Such test problems have 2–12 variables, presenting several stationary points. In many cases, we show that our new methodology is capable of obtaining $\boldsymbol{x} \in \mathcal{S}$, such that $TPD(\boldsymbol{x}) < 0$, in just two iterations.

2. The thermodynamic models

We consider the tangent plane distance function in dimensionless form:

$$D(\boldsymbol{x}) = \frac{TPD(\boldsymbol{x})}{RT}, \tag{6}$$

where R is the universal gas constant.

2.1. NRTL and UNIQUAC

At low or moderate pressures, the function $D(\boldsymbol{x})$ can be written in terms of activity coefficients as

$$D(\boldsymbol{x}) = \sum_{i=1}^{n} x_i[\ln(x_i\gamma_i^{(\beta)}(\boldsymbol{x})) - \ln(z_i\gamma_i^{(\alpha)}(\boldsymbol{z}))], \tag{7}$$

where $\gamma_i^{(j)}$ is the activity coefficient of component $i(=1,\ldots,n)$ in the phase $j=\alpha, \beta$.