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Finding multiple stationary points of the Gibbs tangent plane distance function via the topographical global initialization

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ABSTRACT

In order to find multiple stationary points of the Gibbs tangent plane distance function, often required in the stability analysis used in phase equilibrium calculations, in this article we apply a recently revisited version of the topographical global initialization. This initialization technique is a simple and ingenious approach based on elementary concepts of graph theory. Here, the topographical initialization is employed to generate good starting points to solve a constrained global minimization problem, whose solutions are the roots of a nonlinear system, which describes the first-order stationary conditions associated with the Gibbs plane tangent criterion for phase stability analysis. To accomplish the task of local search, in the minimization step we use a well-established interior-point method. Our methodology was compared against another robust method using benchmarks from the literature. Results indicated that the present approach is a powerful strategy for finding multiple stationary points of the Gibbs tangent plane distance function, having demonstrated high efficiency and robustness.

1. Introduction

The phase stability analysis is a fundamental step in the multiphase equilibrium calculation of multicomponent mixtures. This thermodynamic analysis has been widely used to simulate chemical engineering and petroleum industry methods, where the prediction of number of phases and composition calculations take place, such as distillation and extraction processes, and enhanced oil recovery techniques, which are commonly used to increase the amount of oil and gas recovered from hydrocarbon reservoirs, as carbon dioxide injections, for example.

After the seminal article by Michelsen (1982a), the phase stability analysis has been implemented in the light of the so-called Gibbs plane tangent criterion. This criterion is a global thermodynamic stability condition (at specified temperature and pressure) that has been investigated by Gibbs in the past (Gibbs, 1928), but whose formal demonstration is part of a modern work due to Baker et al. (1982).

In this context, the stability test is performed using a key function called Gibbs tangent plane distance function. Geometrically, this function describes the distance from the tangent plane to the Gibbs energy, at a given feed composition, to the surface itself at composition of a trial phase. Thus, a multicomponent mixture is stable if and only if the tangent plane (at given feed composition) lies always below the Gibbs energy surface, i.e., if and only if the Gibbs tangent plane distance function never takes a negative value (Baker et al., 1982).

The most commonly used approach to determining if this distance function is never negative is to minimize it on its feasible set (Michelsen, 1982a).

Another approach is to solve a set of nonlinear equations, which describes the first-order stationary conditions associated with such minimization problem. In this case, the signs of the Gibbs tangent plane distance function on all its stationary points (all solutions of this set of nonlinear equations) determine the outcome of the phase stability analysis.

Often this second approach is preferred in practice applications. In fact, to provide good composition estimates for subsequent multiphase calculations, it is necessary to find not just the global minimizer, but all the stationary points of the Gibbs tangent plane distance function (Lucia et al., 2005). Furthermore, the existence of multiple

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Nomenclature

Symbols

$B(x, \lambda)$	Positive definite matrix
$d(x)$	Gibbs tangent plane distance function
d_α	Descent direction
d_β	Deflection vector
$f(x)$	Objective function
$F(x)$	Nonlinear mapping
$g(x)$	Vector of constraints
$g_i(x)$	i-th inequality constraint
$G(x)$	Diagonal matrix $G_{ii}(x) = g_i(x)$
G_{ij}	Binary interaction parameter for NRTL and UNIQUAC models
$H(x, \lambda)$	Hessian matrix of the Lagrangian function
I	Identity matrix
k	TGO method parameter
K_{ij}	Binary interaction parameter for state equations
k-t-matrix	Submatrix of the t-matrix
k^+-topograph	Graph associated with the k-t-matrix
m	Number of constraints
n	Problem dimension
N	Number of sampling points
P	Pressure
P_i	i-th point of the Sobol sequence
P_{r_i}	Reduced pressure of component i
q_i	Pure component parameter
r_i	Pure component parameter
S	Domain of $d(x)$
t-matrix	Topography matrix
T	Temperature
T_{r_i}	Reduced temperature of component i
X	Vector of compositions of a trial phase
x^*	Stationary point of the distance function
Z	Vector of compositions of a phase under consideration
Z	Compressibility factor

Greek symbols

θ_i	Activity coefficient
θ_i	Weighted average of q_i
Λ	Vector of Lagrange multipliers
Λ	Diagonal matrix $\Lambda_{ii} = \lambda_i$
μ_i	Chemical potential of component i
ρ	Positive scalar
τ_{ij}	Binary interaction parameter for NRTL and UNIQUAC models
ϕ_i	Weighted averages of r_i
φ_i	Fugacity coefficient of component i
ω_i	Acentric factor of component i
Ω	Feasible set
∇f	Gradient vector of $f(x)$
∇g	Jacobian matrix of $g(x)$
$\nabla^2 f(x)$	Hessian matrix of $f(x)$
$\nabla^2 g_i(x)$	Hessian matrix of $g_i(x)$

stationary points indicates the tendency of the multicomponent mixture to exhibiting different types of phase equilibria – "vapor–liquid", "liquid–liquid", "vapor–liquid–liquid" (Stateva and Tsvetkov, 1994).

However, the calculation of all stationary points of this distance function is a challenging problem. Depending on the thermodynamic model used, such function can display distinct difficulties of numerical and/or geometric nature that usually represent barriers to many classical methods. By referring to the difficulty of finding all the stationary points of this function, Lucia et al. (2005) expressed the following: "Unfortunately, finding all stationary points of the tangent distance function is often easier said, than done!"

Considering only solutions of nonlinear systems, we can find in the literature a significant number of different approaches for locating all the stationary points of the tangent plane distance function, which have been performed from distinct numerical methods of solving nonlinear equations. In fact, Sun and Seider (1995), Bausa and Marquardt (2000), Kangas et al. (2011), and Malinen et al. (2012) used homotopy based methods. Wasylkiewicz et al. (1996) developed a self-starting algorithm, which uses ideas from differential geometry and ordinary differential equations. Hua et al. (1996, 1998a, 1998b) employed the interval Newton/generalized bisection method. For more applications of this technique, see also Tessier et al. (2000), Gecegormez and Demirel (2005), Xu et al. (2005), and Staudt et al. (2013). On the other hand, Lucia et al. (2005) used an integral path methodology based on the terrain methods of Lucia and Yang (2003). Corazza et al. (2007) and Nagatani et al. (2008) applied a subdivision algorithm developed by Smiley and Chun (2001). More recently, Ivanov et al. (2013) used a new strategy to ensure the non-repetition of the previously determined stationary points, and Henderson et al. (2014) employed the particle swarm optimization method equipped with a polarization technique.

The topographical global initialization is a simple and ingenious approach based on elementary concepts of graph theory, which was proposed by Törn and Viitanen (1992) to generate good starting points for local search methods, from points distributed uniformly in the search space.

Originally this initialization strategy uses three steps: (i) A uniform sampling of N points in the search space. (ii) The construction of the topograph, which is a graph with directed arcs connecting the sampled points on a k-nearest neighbors basis. In this graph the direction of an arc is towards a point with a larger function value, and k is a positive integer less than N. (iii) The selection of the topograph minima (points better than their neighbors, i.e., the nodes with no incoming arcs), which will be initial guesses.

The choice of the parameter k can affect the performance of this initialization strategy. Törn and Viitanen (1992) calculated this parameter from computational experiments.

Recently, the topographical global initialization was revisited by Henderson et al. (2015b). As a result, now this initialization method can be understood in the context of a more elaborate theoretical framework, where their basic mathematical properties were established.

In addition, Henderson et al. (2015b) developed a formula for estimating k, the key parameter of this method, which uses only information regarding the possible topographs associated with the sampling points. These authors used this new approach to solving constrained optimization problems, where the global minimizers are the desired solutions, illustrating the application of such methodology to the problem of calculating the global minimizer of this distance function.

In the present work, for the first time, we apply the topographical global initialization revisited for finding multiple stationary points of the Gibbs tangent plane distance function. This requires the use of a suitable iterative method for local searches. To accomplish the task, we employ a very robust and efficient interior point method (Herskovits, 1998).

The performance of the present methodology is illustrated using test problems considered in the literature. For this, initially we consider liquid-liquid equilibria at low pressure, where the excess energy is described by the Non-Random Two Liquid (NRTL) or UNIversal QUAsi-Chemical (UNIQUAC) models (Renon and Prausnitz, 1968; Abrams and Prausnitz, 1975; Maurer and Prausnitz, 1978). Then, we address vapor-liquid equilibria at high pressures modeled by the Soave–Redlich–Kowng (SRK) or Peng–Robinson (PR) cubic equations of state (Soave, 1972; Peng and Robinson, 1976).

The rest of the paper is organized as follows. In Section 2, we summarize the formulations and the thermodynamic models used here. The topographical global initialization revisited is presented in Section 3. The Section 4 is devoted to the description of the interior point