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Phase stability analysis using a modified affine arithmetic

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ABSTRACT

Phase stability analysis is a crucial step in the determination of multiphase equilibrium. This analysis by the tangent plane distance (TPD) minimization is a well-known technique, as well as the difficulties in providing guarantees that the global minimum has been found. On this regard, interval methods are powerful tools since they provide such guarantees. In this work, an interval Newton method plus generalized bisection, based on a modified affine arithmetic, is used to reliably find all possible stationary points of the TPD function. Additionally, an improved convergence test is suggested as well as a special treatment for mole fraction weighted averages. Several mixtures with up to 5 components, including LLE island type ternary systems, were studied. Both activity coefficient models and cubic equations of state were considered. For all the cases tested, the proposed modified affine arithmetic method was superior to other interval-based methods.

1. Introduction

One of the most difficult problems in chemical engineering is the evaluation of phase equilibrium of multicomponent mixtures. In solving this problem, a crucial step is the prediction of phase splitting due to thermodynamic instability. The tangent plane criterion for phase stability, proven by Baker, Pierse, and Luks (1982), was first implemented by Michelsen (1982a, 1982b) in a stepwise solution algorithm for phase equilibrium and is the most used method to analyze multicomponent mixtures behavior being available in many commercial simulation tools.

At present, different approaches are available in the literature to solve the challenging problem of phase stability, *e.g.* Castier, Rasmussen, and Fredenslund (1989), Gupta, Raj Bishnoi, and Kalogerakis (1991), Lucia, Padmanabhan, and Venkataraman (2000), Tan and Radosz (2002), Schmitz, Zemp, and Mendes (2006), Alsaifi and Englezos (2011), Henderson, Barufatti, and Sacco (2011), and Mikyka and Firoozabadi (2012). Most of these methods can be separated into two main categories. The first one, is the use of optimization algorithms to minimize the tangent plane distance (TPD) while the second class of methods is based on the direct solution of the TPD problem as a nonlinear system of equations.

The use of global optimization techniques for the TPD function minimization has been studied by several researchers. For instance, McDonald and Floudas (1995a, 1995b) used a branch and bound based method with Wilson, UNIFAC, UNIQUAC and ASOG activity models and a global optimization algorithm (GOP) for phase stability analysis with NRTL model. Six different systems were tested with success. Zhu and Xu (1999) used a simulated annealing algorithm with NRTL and UNIQUAC equations and discussed the influence of the optimization method parameters in the stability problem solution. In Lucia et al. (2000) an elaborate optimization based algorithm is suggested to solve multiphase equilibrium problems. Novel initialization strategies and binary tangent plane analysis (instead of the usual full composition space analysis) make the method very efficient. In Zhu, Wen, and Xu (2000) an enhanced simulated annealing procedure was applied to the TPD function minimization with Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) equations of state. Rangaiah (2001) compared genetic algorithm and simulated annealing performances showing that the former was generally more efficient and reliable for phase equilibrium calculations. In Nichita, Gomez, and Luna (2002) the global tunneling optimization method was tested for phase stability analysis with cubic equations of state and in Nichita, García-Sánchez, and Gómez (2008) the same method was used with the PC-SAFT model. In Saber and Shaw (2008), the DIRECT method was efficiently used for phase stability test with PR and SRK equations, requiring, according to the authors, one to three orders of magnitude fewer function evaluations compared with some competing methods. Zhang, Fernández-Vargas, Rangaiah, Bonilla-Petriciolet, and Segovia-Hernández (2011) compared the performance of some stochastic global methods: unified bare-bones particle swarm optimization (UBBPSO), integrated differential evolution (IDE) and IDE without tabu list and radius (IDEN). The IDE methodology presented higher reliability and efficiency for phase equilibrium,

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chemical equilibrium and phase stability problems. Recently, Fateen, Bonilla-Petriciolet, and Rangaiah (2012) compared three different methods: Covariant Matrix Adaptation-Evolution Strategy (CMA-ES), Shuffled Complex Evolution (SCE) and Firefly Algorithm (FA) and concluded that the CMA-ES was the most effective algorithm in finding the global minimum of TPD function. Finally, Bhargava, Fateen, and Bonilla-Petriciolet (2012) published the application of the Cuckoo Search method for phase equilibrium and stability calculations in both reactive and non-reactive systems showing that this technique offered a reliable performance for solving these thermodynamic calculations and was better than other stochastic methods previously applied.

Still regarding the TPD function minimization by global optimization techniques, another strategy that has been tested in the literature is the use of hybrid algorithms, combining global and local search methods. In McDonald and Floudas (1997) the GLOPEQ, a procedure for phase equilibria and stability analysis, was developed combining local search, with MINOS5.4 as a nonlinear solver, and global search, using a branch and bound algorithm. In Rangaiah (2001) a genetic algorithm was coupled with a modified simplex method for solution refinement and different thermodynamic models were tested. Srinivas and Rangaiah (2007) compared two global optimization methods, differential evolution (DE) and tabu search (TS), coupled with local optimization techniques (quasi-Newton method) for phase equilibrium and stability prediction and concluded that DE is more reliable but computationally less efficient than TS. In Bonilla-Petriciolet and Segovia-Hernández (2010) the particle swarm optimization algorithm (PSO) and some of its variants were applied to phase stability and equilibrium of reactive and non-reactive systems together with a quasi-Newton gradient-based method and a Nelder–Mead (NM) simplex method. The authors claimed that the classical version of PSO combined with NM offered the best performance for global minimization of the TPD function. Even though all the works previously cited have reported success, none of the optimization methods studied provide mathematical guarantee of finding the TPD global minimum. While in deterministic methods there is a strong initial guess dependency (Hua, Brennecke, & Stadtherr, 1998a), in stochastic methods there is a compromise between number of function evaluations and reliability (Staudt & Soares, 2009).

When considering the direct solution of the TPD problem as a nonlinear system of equations, various methods have been used in the literature, *e.g.*: homotopy-continuation (Bausa & Marquardt, 2000; Sun & Seider, 1995), bounded homotopies Kangas, Malinen, and Tanskanen (2011), Newton homotopy Malinen, Kangas, and Tanskanen (2012) and interval arithmetic (Gau & Stadtherr, 2002; Hua, Brennecke, & Stadtherr, 1996; Tessier, Brennecke, & Stadtherr, 2000; Xu, Brennecke, & Stadtherr, 2002). The use of interval arithmetic in solving phase stability problems has gathered attention because a reliable solution is found with mathematical guarantee of global optimality. Hua et al. (1996) implemented a general-purpose computation method based on techniques from interval mathematics. Two binary and one ternary mixtures were modeled using the van der Waals equation to attest the reliability of interval methods in solving phase stability problem. In Hua, Brennecke, and Stadtherr (1998b) the methodology was applied to four examples using the PR and SRK cubic equations of state. In Hua et al. (1998a) and Gau and Stadtherr (2002), enhancements were proposed to the interval technique reducing the computational time of phase stability analysis in orders of magnitude for some cases. Following the works of the same researchers, Tessier et al. (2000) applied the methodology with activity coefficient models (NRTL and UNIQUAC) and Xu, Haynes, and Stadtherr (2005) to asymmetric models (different models for vapor and liquid phases). Although interval arithmetic techniques are reliable alternatives for phase stability calculations, they are not (at present) available for use in commercial solvers and simulators. This occurs mainly because these methods are more recent and the guarantee of solution is potentially accompanied by the drawback of high computational cost.

In this work, the modified affine arithmetic presented in Soares (2013) is used to treat phase stability analysis. In the original paper, different examples were tested, including nonlinear CSTR, flash, flow distribution in a pipeline network and a hydrocarbon combustion process. It was shown that the modified affine arithmetic required less computation effort than the similar methods available in the literature for the studied examples and the same result is expected in the present work, applying this methodology to phase stability problems. Here the nonlinear system of equations given by the gradient of the TPD function is solved by an affine Newton/generalized bisection (AN/GB) algorithm. The method guarantees that the global minimum is found within a prescribed tolerance (Soares, 2013). In addition, the method is extended, giving special attention to the convergence test and to mole fraction weighted averages. These averages are very common in thermodynamic models and can strongly interfere in the efficiency of interval-based methods Hua et al. (1998b). The results and computational performance obtained in this work are compared with other methods from literature, attesting the reliability and efficiency of the suggested AN/GB algorithm.

In Section 2, the phase stability problem is presented along with the thermodynamic models used in this work. In Section 3 the main aspects of the affine algorithm of Soares (2013) are presented, with a new convergence test and a special treatment for mole fraction weighted averages to improve the computation efficiency. In Section 4 the results of phase stability for 17 literature systems, modeled by cubic equations of state and activity coefficient models, are presented and discussed. The special case of liquid–liquid equilibria (LLE) for island type ternary systems, which is not consistently handled by commercial softwares Olaya, Reyes-Labarta, Velasco, Ibarra, and Marcilla (2008), is explored in this work in order to emphasize the reliability of the proposed AA interval Newton method.

2. Phase stability problem

2.1. The tangent plane analysis

The tangent plane analysis has been extensively reported in the literature as a necessary and sufficient criteria for phase stability determination (Baker et al., 1982; Michelsen, 1982a). According to this criteria, if the tangent plane distance, denoted as TPD($\mathbf{x}$), provide only nonnegative values for all possible phases in the system at specified temperature T and pressure P (McDonald & Floudas, 1995b), an equilibrium state is then characterized.

The TPD($\mathbf{x}$) function is expressed by:

$$\mathrm{TPD}(\mathbf{x}) = \sum_i x_i(\mu_i(\mathbf{x}) - \mu_i(\mathbf{z})) \tag{1}$$

where $\mathbf{x}$ is any composition vector; $\mathbf{z}$ is the feed composition; x_i and z_i are elements of $\mathbf{x}$ and $\mathbf{z}$, respectively; and μ_i is the chemical potential of component i in mixture.

It is usually convenient to define a reduced tangent plane distance and rewrite it in terms of fugacity coefficients $\hat{\phi}_i$ (Michelsen, 1982a):

$$\mathrm{tpd}(\mathbf{x}) = \frac{\mathrm{TPD}(\mathbf{x})}{RT} = \sum_i x_i(\ln x_i + \ln \hat{\phi}_i(\mathbf{x}) - \ln z_i - \ln \hat{\phi}_i(\mathbf{z})) \tag{2}$$

which can also be written in terms of activity coefficients by simply exchanging $\hat{\phi}_i$ for γ_i in Eq. (2).