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Combined Local and Global Approach to Reliable Computation of Phase Equilibria

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1 Introduction

The computation of phase equilibrium can be thought of as comprising two subproblems: phase stability analysis–whether or not a given feed will split into multiple phases; and phase split analysis–computing the phase fractions and compositions at equilibrium. Both subproblems can be formulated as minimization problems, or as equivalent nonlinear equation solving problems.

In solving these subproblems, the conventional solution methods are initialization dependent, and may fail by converging to trivial or nonphysical solutions or to a point that is a local but not global minimum. Thus there is no guarantee that the phase equilibrium problem has been correctly solved. Because of the difficulties that may arise in solving phase equilibrium problems by standard methods (e.g., Michelsen, 1982a,b), there has been significant recent interest in the development of more reliable methods. For example, the methods of Sun and Seider (1995), who use a homotopy-continuation approach, and of Wasylkiewicz *et al.* (1996), who use an approach based on topological considerations, can offer significant improvements in reliability. McDonald and Floudas (1995a,b,c; 1997) show that for certain activity coefficient models, the phase stability and equilibrium problems can be reformulated to be amenable to solution by powerful global optimization techniques, which guarantee the correct answer.

An alternative approach, based on interval analysis, in particular the use of an interval Newton/generalized bisection (IN/GB) algorithm, has been suggested by Stadtherr *et al.* (1995) and Hua *et al.* (1996a,b; 1997a,b), and applied to both activity coefficient models and cubic equation of state models, including van der Waals, SRK, and Peng-Robinson. This technique is initialization independent, general purpose and can solve the phase stability problem with complete mathematical certainty. We focus here on how to combine the reliability of this global method with the speed of local methods for the phase stability problem. Then, we show how the global stability solver can be applied in connection with a local method for reliable solution of the phase split problem.

2 Phase stability

The interval method for global stability analysis can easily be combined with existing local methods for determining phase stability. First, the (fast) local method is used. If it indicates instability then this is the correct answer as it means, in terms of tangent plane analysis (Baker *et al.*, 1982), that a point has been found at which the tangent plane distance is negative. If the local method indicates stability, however, this may not be the correct answer since the local method may have missed the global minimum in the tangent plane distance function. Applying the global stability analysis method described here can then be used to confirm that the mixture is stable if that is the case, or to correctly determine that it is really unstable if that is the case. Results show that for unstable mixtures the use of the local method in connection with the global method can greatly speed the solution of the phase stability problem.

3 Phase split

In the phase split problem we seek a global minimum in the total Gibbs energy. However, it is possible to successfully employ *local* solution methods, since phase stability analysis can be used as a global optimality test that can be applied to any local solution of the phase split problem (Baker *et al.*, 1982). That is, if the phases determined by local solution of the phase split problem are determined to be stable, by solving a phase stability problem, then this is the desired global solution to the phase split problem. Correct solution of the phase stability problem is thus the key, and the interval method provides a completely reliable method for doing this.

To demonstrate this, we will use a direct Gibbs energy minimization approach to address the phase split problem. In using the interval method to first determine that the mixture will split, multiple minima of the tangent plane distance function are located. These stationary points are extremely good initial estimates for the minimization of Gibbs energy to solve the phase split problem. The successive quadratic programming (SQP) method of Chen *et al.* (1984) is then used to perform a local minimization of the Gibbs energy to locate prospective global minima. The interval stability solver is then used to verify if a global minimum has been found. By combining the speed of the local SQP solver with the reliability of the interval approach an efficient and completely reliable method for computing multiphase equilibria can be obtained. Computational results for problems involving high pressure phase equilibria modeled using cubic equation of state models are presented.

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