INTERVAL ANALYSIS: APPLICATION TO PHASE EQUILIBRIUM PROBLEMS

The reliable calculation of phase equilibrium for multicomponent mixtures is a critical aspect in the simulation, optimization and design of a wide variety of industrial processes, especially those involving separation operations such as distillation and extraction. It is also important in the simulation of enhanced oil recovery processes such as miscible or immiscible gas flooding. Unfortunately, however, even when accurate models of the necessary thermodynamic properties are available, it is often very difficult to actually solve the phase equilibrium problem reliably.

Background. The computation of phase equilibrium is often considered in two stages, as outlined by `M. L. Michelsen` [12, 13]. The first involves the *phase stability* problem, that is, to determine whether or not a given mixture will split into multiple phases. The second involves the *phase split* problem, that is to determine the amounts and compositions of the phases assumed to be present. After a phase split problem is solved it may be necessary to do phase stability analysis on the results to determine whether the postulated number of phases was correct, and if not repeat the phase split problem. Both the phase stability and phase split problems can be formulated as minimization problems, or as equivalent nonlinear equation solving problems.

For determining phase equilibrium at constant temperature and pressure, the most commonly considered case, a model of the Gibbs free energy of the system is required. This is usually based on an excess Gibbs energy model (activity coefficient model) or an equation of state model. At equilibrium the total Gibbs energy of the system is minimized. Phase stability analysis may be interpreted as a global optimality test that determines whether the phase being tested corresponds to a global optimum in the total Gibbs energy of the system. If it is determined that a phase will split, then a phase split problem is solved, which can be interpreted as finding a *local* minimum in the total Gibbs energy of the system. This local minimum can then be tested for global optimality using phase stability analysis. If necessary the phase split calculation must then be repeated, perhaps changing the number of phases assumed to be present, until a solution is found that meets the global optimality test. Clearly the correct solution of the phase stability problem, itself a global optimization problem, is the key in this two-stage global optimization procedure for phase equilibrium. As emphasized in [10], while it is possible to apply rigorous global optimization techniques directly to the phase equilbrium problem, it is computationally more efficient to use a two-stage approach such as outlined above, since the dimensionality of the global optimization problem that must be solved (phase stability problem) is less than that of the full phase equilibrium problem.

In solving the phase stability problem, 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 a 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., [12, 13]), there has been significant interest in the development of more reliable methods. For example, the methods of `A. C. Sun` and `W. D. Seider` [16], who use a homotopy-continuation approach, and of `S. K. Wasylkiewicz`, `L. N. Sridhar`, `M. F. Malone` and `M. F. Doherty` [18], who use an approach based on topological considerations, can offer significant improvements in reliability. `C. M. McDonald` and `C. A. Floudas` [7, 8, 9, 10] show that, for certain activity coefficient models, the phase stability and equilibrium problems can be made amenable to solution by powerful global optimization techniques, which provide a mathematical guarantee of reliability.

An alternative approach for solving the phase stability problem, based on interval analysis,

phase stability
phase split

that provides both mathematical and computational guarantees of global optimality, was originally suggested by `M. A. Stadtherr`, `C. A. Schnepper` and `J. F. Brennecke` [15], who applied it in connection with activity coefficient models, as later done also in [11]. This technique, in particular the use of an *interval Newton/generalized bisection* algorithm, is initialization independent and can solve the phase stability problem with mathematical certainty, and, since it deals automatically with rounding error, with computational certainty as well. `J. Z. Hua`, `J. F. Brennecke` and `M. A. Stadtherr` [3, 4, 5, 6] extended this method to problems modeled with cubic *equation of state* models, in particular the Van der Waals, Peng-Robinson, and Soave-Redlich-Kwong models. Though interval analysis provides a *general purpose* and *model independent* approach for guaranteed solution of the phase stability problem, the discussion below will focus on the use of cubic equation of state models.

Phase stability analysis. The determination of phase stability is often done using tangent plane analysis [1, 12]. A phase at specified temperature T, pressure P, and feed mole fraction vector $\mathbf{z}$ is unstable and can split (in this context, 'unstable' refers to both the thermodynamically metastable and classically unstable cases), if the molar Gibbs energy of mixing surface $m(\mathbf{x}, v)$ ever falls below a plane tangent to the surface at $\mathbf{z}$. That is, if the tangent plane distance

$$D(\mathbf{x}, v) = m(\mathbf{x}, v) - m_0 - \sum_{i=1}^{n} \left(\frac{\partial m}{\partial x_i}\right)_0 (x_i - z_i)$$

is negative for any composition (mole fraction) vector $\mathbf{x}$, the phase is unstable. The subscript zero indicates evaluation at $\mathbf{x} = \mathbf{z}$, n is the number of components, and v is the molar volume of the mixture. A common approach for determining if D is ever negative is to minimize D subject to the mole fractions summing to one

$$1 - \sum_{i=1}^{n} x_i = 0 \qquad (1)$$

and subject to the equation of state relating $\mathbf{x}$ and v:

$$P - \frac{RT}{v-b} + \frac{a}{v^2 + ubv + wb^2} = 0 \; . \qquad (2)$$

Here a and b are functions of $\mathbf{x}$ determined by specified mixing rules. The 'standard' mixing rules are $b = \sum_{i=1}^n x_i b_i$ and $a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij}$, with $a_{ij} = (1-k_{ij})\sqrt{a_i a_j}$. The $a_i(T)$ and b_i are pure component properties determined from the system temperature T, the critical temperatures T_{ci}, the critical pressures P_{ci} and acentric factors ω_i. The binary interaction parameter k_{ij} is generally determined experimentally by fitting binary vapor-liquid equilibrium data. Equation (2) is a generalized cubic equation of state model. With the appropriate choice of u and w, common models such as Peng-Robinson ($u = 2$, $w = -1$), Soave-Redlich-Kwong ($u = 1$, $w = 0$), and Van der Waals ($u = 0$, $w = 0$) may be obtained. It is readily shown that the stationary points in this optimization problem must satisfy

$$s_i(\mathbf{x}, v) - s_i(\mathbf{z}, v_0) = 0 \quad i = 1, \ldots, n-1 \quad (3)$$

where

$$s_i = \left(\frac{\partial m}{\partial x_i}\right) - \left(\frac{\partial m}{\partial x_n}\right) .$$

The $(n+1) \times (n+1)$ system given by equations (1), (2) and (3) above can be used to solve for the stationary points in the optimization problem.

The equation system for the stationary points has a trivial root at $(\mathbf{x}, v) = (\mathbf{z}, v_0)$ and frequently has multiple nontrivial roots as well. Thus conventional equation solving techniques may fail by converging to the trivial root or give an incorrect answer to the phase stability problem by converging to a stationary point that is not the global minimum of D. This is aptly demonstrated by the experiments of `K. A. Green`, `S. Zhou` and `K. D. Luks` [2], who show that the pattern of convergence from different initial guesses demonstrates a complex fractal-like behavior for even very simple models like

interval Newton
generalized bisection
equation of state

Van der Waals. The problem is further complicated by the fact that the cubic equation of state (2) may have multiple real volume roots v.

As an example of a system that causes numerical difficulties, consider the binary mixture of hydrogen sulfide (component 1) and methane (component 2) at a temperature of 190 K and pressure of 40.53 bar (40 atm) modeled using the Soave-Redlich-Kwong equation of state, and with an overall feed composition of $z_1 = 0.0187$. Figure 1 shows a plot of the reduced Gibbs energy of mixing m vs. x_1 for this system (in the reduced composition space where $x_2 = 1 - x_1$), and also shows the tangent at the feed composition.

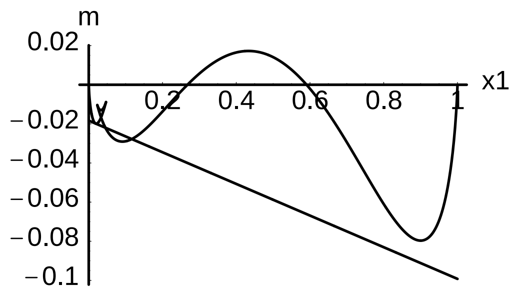

Figure 1. Reduced Gibbs energy of mixing m vs. x_1 for the system hydrogen sulfide and methane, showing tangent at a feed composition of 0.0187.

The corresponding tangent plane distance function is shown in Figures 2 and 3.

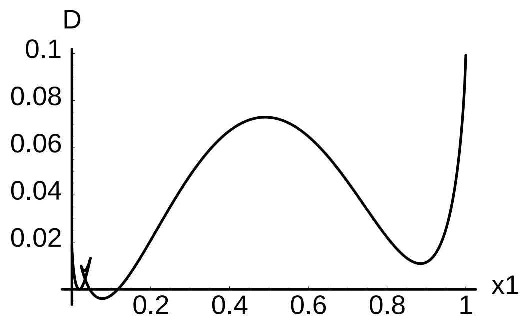

Figure 2. Tangent plane distance D vs. x_1 for example system of Figure 1. See Figure 3 for enlargement of area near the origin.

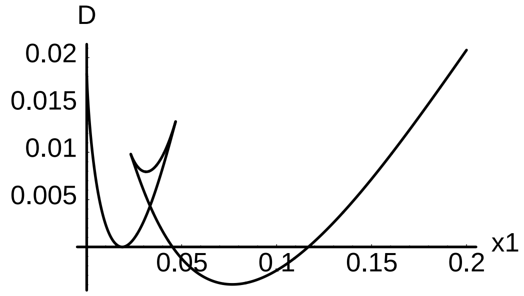

Figure 3. Enlargement of part of Figure 2, showing area near the origin.

Note that this system has a region, around x_1 of 0.03 to 0.05, where multiple real volume roots occur and thus multiple values of m and D exist; only the lowest values are physically significant. This system has five stationary points, four minima and one maximum. Conventional locally convergent methods are typically used with multiple initial guesses, generally at or near the pure components ($x_1 = 0$ and $x_1 = 1$). When this is done convergence will likely be to the local minimum at the feed composition (0.0187) and to the local minimum around 0.88. The global minimum with $D < 0$ is missed, leading to the incorrect conclusion that the mixture is stable.

Interval analysis. Interval analysis makes possible the mathematically and computationally guaranteed solution of the phase stability problem. Since the mole fraction variables x_i are known to lie between zero and one, and it is easy to put physical upper and lower bounds on the molar volume v as well, a feasible interval for all variables is readily identified. By applying an interval Newton/generalized bisection approach to the entire feasible interval, enclosures of *all* the stationary points of the tangent plane distance D can be found by solving the nonlinear equation system (1)–(3), and the *global* minimum of D thus identified. This approach requires no initial guess, and is applicable to any model for the Gibbs energy, not just those derived from equations of state. For the binary system used as an example above, all five stationary points are easily found, and the global minimum at $x_1 = 0.0767$, $v = 64.06$ cm^3/mol, and $D = -0.004$ thus identified [3, 6].

The efficiency of the interval approach can depend significantly on how tightly one can compute *interval extensions* for the functions involved. The interval extension of a function over a given interval is an enclosure for the range of the function over that interval. When the *natural* interval extension, that is the function range computed using interval arithmetic, is used, it may tightly bound the actual function range. However, it is not uncommon for the natural interval extension to provide a significant overestimation of the true function range, especially for functions of the complexity encountered in the phase stability and equilibrium problems.

Some tightening of bounds can be achieved by taking advantage of information about function monotonicity. Another simple and effective way to alleviate this difficulty in this context is to focus on tightening the enclosure when computing interval extensions of mole fraction weighted averages, such as $\bar{r} = \sum_{i=1}^{n} x_i r_i$, where the r_i are constants. Due to the mixing rules for determining a and b, such expressions occur frequently, both in the equation of state (2) itself, as well in the derived model $m(\mathbf{x}, v)$ for the Gibbs energy of mixing and thus in equation (3). The natural interval extension of $\bar{r}$ will yield the true range (within roundout) of the expression in the space in which all the mole fraction variables x_i are independent. However, the range can be tightened by considering the constraint that the mole fractions must sum to one. One approach for doing this is simply to eliminate one of the mole fraction variables, say x_n. Then an enclosure for the range of $\bar{r}$ in the constrained space can be determined by computing the natural interval extension of $r_n + \sum_{i=1}^{n-1}(r_i - r_n)x_i$. However, this may not yield the sharpest possible bounds on $\bar{r}$ in the constrained space.

For constructing the *exact* (within roundout) bounds on $\bar{r}$ in the constrained space, `S. R. Tessier` [17] and `J. Z. Hua`, `J. F. Brennecke` and `M. A. Stadtherr` [5] have presented a very simple method, based on the observation that at the extrema of $\bar{r}$ in the constrained space, at least $n-1$ of the mole fraction variables must be at their upper or lower bound. This observation can be derived by viewing the problem of bounding the range of $\bar{r}$ in the constrained space as a linear programming problem. As shown in [5], when the constrained space interval extensions for mole fraction weighted averages are used, together with information about function monotonicity, significant improvements in computational efficiency, nearly an order of magnitude even for small (binary and ternary) problems, can be achieved in using the interval approach for solving the phase stability problem.

For small problems, it is usually efficient to globally minimize D by finding all of its stationary points, since this does not require repeated evaluation of the range of D. However, in general, for making a determination of phase stability or instability, finding *all* the stationary points is not really necessary, nor for larger problems, desirable. For example, if an interval is encountered over which the interval extension of D has a negative upper bound, this guarantees that there is a point at which $D < 0$, and so one can immediately conclude that the mixture is unstable without determining all the stationary points. It is also possible to easily make use of the underlying global minimization problem. Since the objective function D has a known value of zero at the mixture feed composition (tangent point), any interval over which the interval extension of D has a lower bound greater than zero cannot contain the global minimum and can be discarded, even though it may contain a stationary point (at which D will be positive and thus not of interest). Thus, one can essentially combine the interval-Newton technique with an interval branch and bound procedure in which lower bounds are generated using interval techniques.

Also, it should be noted that the global interval approach described here can easily be combined with existing local methods for determining phase stability and equilibrium. First, some (fast) local method is used. If it indicates instability then this is the correct answer as it means a point at which $D < 0$ has been found. If the local method indicates stability, however, this may not be the correct answer since the local

interval extensions

method may have missed the global minimum in D. Applying interval analysis as 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.

Conclusion. As demonstrated in [3, 4, 5, 6, 11, 15], interval analysis can be used to solve phase stability and equilibrium problems efficiently and with complete reliability, providing a method that can guarantee with mathematical and computational certainty that the correct result is found, and thus eliminating computational problems that are encountered with conventional techniques. The method is initialization independent; it is also model independent, straightforward to use, and can be applied in connection with any equation of state or activity coefficient model for the Gibbs free energy of a mixture. There are many other problems in the analysis of phase behavior, and in chemical process analysis in general [14], that likewise are amenable to solution using this powerful approach.

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Mark A. Stadtherr
Department of Chemical Engineering
University of Notre Dame
Notre Dame, Indiana 46556
USA
E-mail address: markst@nd.edu

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