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Reliable Computation of High Pressure Phase Behavior

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1 Introduction

Computational problems such as convergence to a trivial or incorrect root, or to a local rather than global optimum, or failure to converge to a physically feasible solution at all, are not uncommon difficulties in the modeling of high pressure phase behavior. Many techniques have been developed in attempts to provide increased reliability. However, until now, there has been no general-purpose technique that could provide complete reliability for a wide variety of phase behavior computations. In this paper we report on the development and use of a robust new computational technique, based on interval analysis, for solving the difficult nonlinear problems arising in the modeling of high pressure phase behavior. This technique can be used, with mathematical and computational guarantees of certainty, to find the global optimum of a nonlinear function or to find (enclose) any and all roots to a system of nonlinear equations. This technique has the potential to be applied to a wide variety of phase behavior calculations. Since the technique is model independent and completely general, its use can be readily extended to phase behavior computations for any thermodynamic model.

2 Methodology

The technique used here is based on interval analysis, in particular the use of an interval-Newton/generalized bisection algorithm. The method can enclose *with mathematical and computational certainty* all roots to a system of nonlinear equations, and can be used to find *with mathematical and computational certainty* the global optimum of a nonlinear function. The technique is general-purpose and can be applied in connection with any thermodynamic models. No model-specific problem reformulations or convex underestimating functions need be derived.

The solution method used is the interval Newton/generalized bisection technique described by Kearfott (1987a,b), and implemented in INTBIS (Kearfott and Novoa, 1990). The algorithm is also summarized, in the context of chemical process modeling, by Schnepper and Stadtherr (1996). For a system of nonlinear equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ with $\mathbf{x} \in \mathbf{X}^{(0)}$, the basic iteration step in interval Newton methods is, given an interval $\mathbf{X}^{(k)}$, to solve the linear interval equation system

$$F'(\mathbf{X}^{(k)})(\mathbf{N}^{(k)} - \mathbf{x}^{(k)}) = -\mathbf{f}(\mathbf{x}^{(k)}) \tag{1}$$

for a new interval $\mathbf{N}^{(k)}$, where k is an iteration counter, $F'(\mathbf{X}^{(k)})$ is an interval extension of the real Jacobian $f'(\mathbf{x})$ of $f(\mathbf{x})$ over the current interval $\mathbf{X}^{(k)}$, and $\mathbf{x}^{(k)}$ is a point in the interior of $\mathbf{X}^{(k)}$, usually taken to be the midpoint. It can be shown (Moore, 1966) that any root $\mathbf{x}^* \in \mathbf{X}^{(k)}$ is also contained in the image $\mathbf{N}^{(k)}$, suggesting the iteration scheme $\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} \cap \mathbf{N}^{(k)}$. While this iteration scheme can be used to tightly enclose a solution, what is also of significance here is the power of equation (1) as an existence and uniqueness test. For several techniques for finding $\mathbf{N}^{(k)}$ from equation (1), it can be proven (e.g., Neumaier, 1990; Kearfott, 1996) that if $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then there is a *unique* zero of $\mathbf{f}(\mathbf{x})$ in $\mathbf{X}^{(k)}$, and that Newton's method with real arithmetic can be used to find it, starting from any point in $\mathbf{X}^{(k)}$. This suggests a root inclusion test for $\mathbf{X}^{(k)}$:

1. (Range Test) Compute an interval extension $\mathbf{F}(\mathbf{X}^{(k)})$ containing the range of $\mathbf{f}(\mathbf{x})$ over $\mathbf{X}^{(k)}$ and test to see whether it contains zero. Clearly, if $0 \notin \mathbf{F}(\mathbf{X}^{(k)}) \supseteq \{\mathbf{f}(\mathbf{x}) \mid \mathbf{x} \in \mathbf{X}^{(k)}\}$ then there can be no solution of $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ in $\mathbf{X}^{(k)}$and this interval need not be further tested.

2. (Interval Newton Test) Compute the image $\mathbf{N}^{(k)}$ by solving equation (1).

   (a) If $\mathbf{X}^{(k)} \ \cap \ \mathbf{N}^{(k)} = \emptyset$, then there is no root in $\mathbf{X}^{(k)}$.

   (b) If $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then there is exactly one root in $\mathbf{X}^{(k)}$.

   (c) If neither of the above is true, then no further conclusion can be drawn.

In the last case, one could then repeat the root inclusion test on the next interval Newton iterate $\mathbf{X}^{(k+1)}$, assuming it is sufficiently smaller than $\mathbf{X}^{(k)}$, or one could bisect $\mathbf{X}^{(k+1)}$ and repeat the root inclusion test on the resulting intervals. This is the basic idea of interval Newton/generalized bisection methods. If $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ has a finite number of real solutions in the specified initial box, a properly implemented interval Newton/generalized bisection method can enclose *with mathematical and computational certainty* any and all solutions to a specified tolerance, or can determine *with mathematical certainty* that there are no solutions in the given box (Kearfott and Novoa, 1990; Kearfott, 1990). The technique can also be readily applied in the context of global optimization (Hansen, 1992).

3 Discussion

The effectiveness of this methodology in solving high pressure phase behavior problems using equations of state with standard mixing rules has been demonstrated by Hua et al. (1998), using a problem formulation based on the Gibbs energy. In this presentation, we show how the technique can be used in problem formulations based on the Helmholtz energy, and how its applicability can be extended to other mixing rules, in particular the Wong-Sandler mixing rule. We also consider how the technique can be used with cubic equation of state models for the calculation of critical points. The technique can also be applied to other problems, including the computation of azeotropes. Results demonstrate the applicability and relability of the technique on a wide variety of high-pressure phase behavior problems.

4 References

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