Reliable Computation of High Pressure Phase Behavior

Gang Xu, Benito Stradi,
Robert W. Maier, Joan F. Brennecke and
Mark A. Stadtherr*

Department of Chemical Engineering
University of Notre Dame, Notre Dame, IN 46556

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*Author to whom all correspondence should be addressed; Phone: (219) 631-9318; Fax: (219) 631-8366; E-mail: markst@nd.edu

Summary

- In modeling high pressure phase behavior, computational problems due to multiple roots or multiple local optima are well known (e.g., convergence to trivial or incorrect roots; convergence to a local but not global optimum).

- Many clever techniques have been devised to alleviate such difficulties, but there has been no **general-purpose**, **model-independent**, and **completely reliable** method for solving all phase behavior problems.

- Interval analysis provides a **mathematically and computationally guaranteed** method for reliably solving phase behavior problems.

- This is demonstrated using example problems in phase stability and equilibrium and in computing critical points, and can be applied to a variety of other problems, such as computation of azeotropes.

Background—Interval Analysis

- A real interval $X = [a, b] = \{x \in \Re \mid a \leq x \leq b\}$ is a segment on the real number line and an interval vector $\mathbf{X} = (X_1, X_2, ..., X_n)^T$ is an n-dimensional rectangle or "box".

- Basic interval arithmetic for $X = [a, b]$ and $Y = [c, d]$ is X op $Y = \{x \text{ op } y \mid x \in X,\ y \in Y\}$ where op $\in \{+, -, \times, \div\}$. For example, $X + Y = [a + c, b + d]$.

- Computed endpoints are **rounded out** to guarantee the enclosure.

- Interval elementary functions (e.g. $\exp(X)$, $\log(X)$, etc.) are also available.

- The interval extension $F(\mathbf{X})$ encloses the range (all values) of $f(\mathbf{x})$ for $\mathbf{x} \in \mathbf{X}$.

- Interval extensions can be computed using interval arithmetic (the "natural" interval extension), or with other techniques.

Interval Approach

- Interval Newton/Generalized Bisection (IN/GB)
  - Given a system of equations to solve, an initial interval (bounds on all variables), and a solution tolerance
  - IN/GB can find (enclose)

    with mathematical and computational certainty

    either all solutions or determine that no solutions exist. (e.g., Kearfott 1987,1996; Neumaier 1990)

- A general purpose approach : requires no simplifying assumptions or problem reformulations

- Details of algorithm given by Schnepper and Stadtherr (1996)

- Implementation based on modifications of routines from INTBIS and INTLIB packages (Kearfott and coworkers)

Interval Approach (Cont'd)

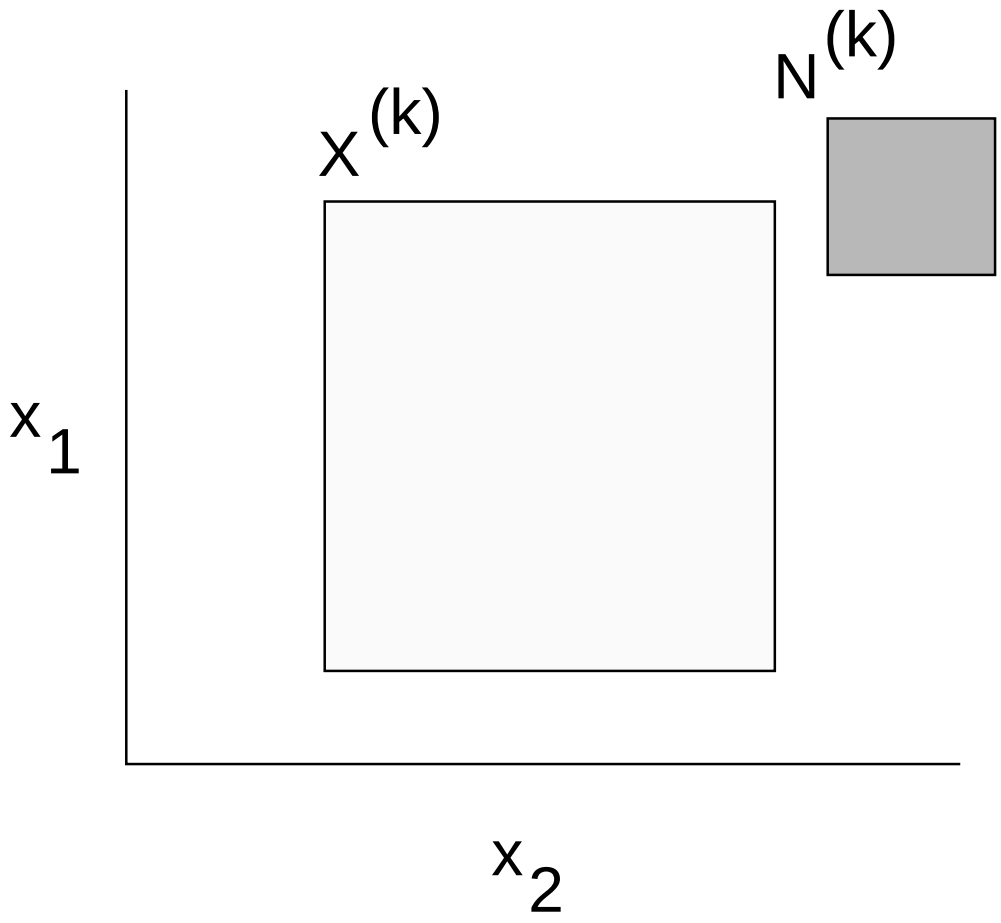
Problem: Solve $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ for all roots in interval $\mathbf{X}^{(0)}$.

Basic iteration scheme: For a particular subinterval (box), $\mathbf{X}^{(k)}$, perform root inclusion test:

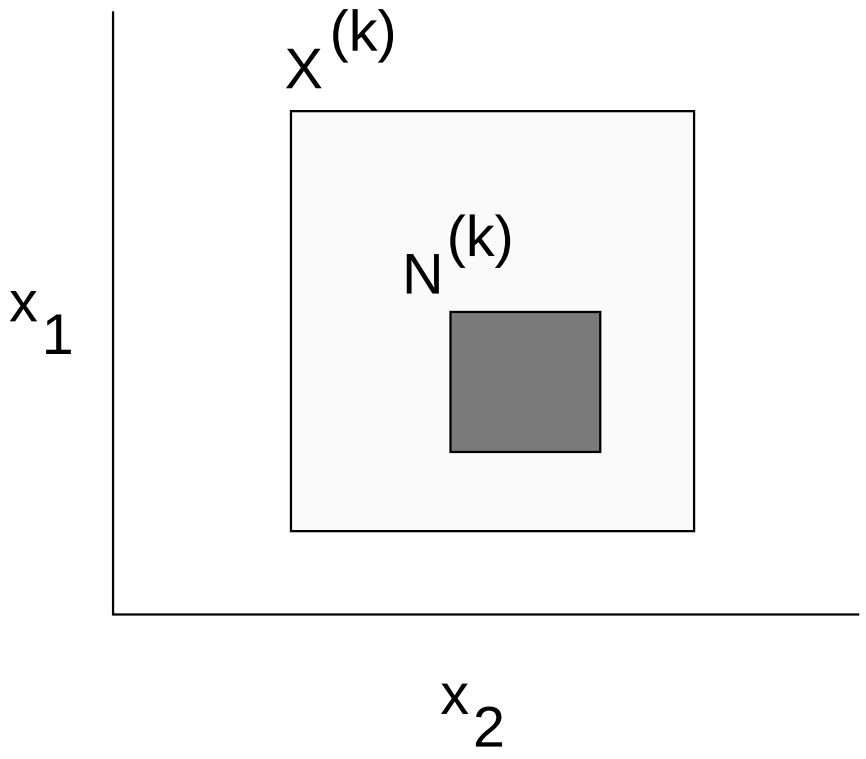
- Compute the interval extension (range) of each function in the system.
- If 0 is not an element of each range, delete the box.
- If 0 is an element of each range, then compute the $image$, $\mathbf{N}^{(k)}$, of the box by solving

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

- $\mathbf{x}^{(k)}$ is some point in the interior of $\mathbf{X}^{(k)}$.
- $F'\left(\mathbf{X}^{(k)}\right)$ is an interval extension of the Jacobian of $\mathbf{f}(\mathbf{x})$ over the box $\mathbf{X}^{(k)}$.



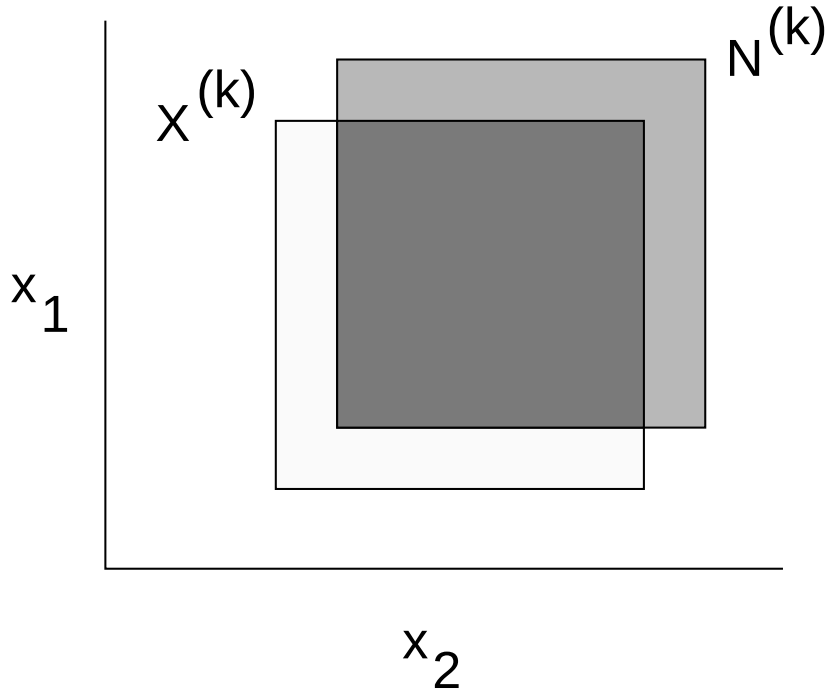
There was no solution in $X^{(k)}$



Unique solution in $X^{(k)}$

This solution is in $N^{(k)}$

Point Newton method will converge to it



Any solutions in $X^{(k)}$ are in intersection of $X^{(k)}$ and $N^{(k)}$

If intersection is sufficiently small, repeat root inclusion test; otherwise bisect the result of the intersection and apply root inclusion test to each resulting subinterval.

Example–Phase Stability Analysis

Gibbs energy formulation T and P constant:

$$\min_{\mathbf{x},v} \quad D(\mathbf{x},v) = \hat{G} - \hat{G}_{\mathbf{z}} - \sum_{i=1}^{n} \left(\frac{\partial \hat{G}}{\partial x_i} \right)_{\mathbf{z}} (x_i - z_i)$$

subject to

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

$$EOS(\mathbf{x}, v) = 0$$

- Trivial local optimum (minimum or maximum) at the feed composition $\mathbf{x} = \mathbf{z}$; may be multiple nontrivial optima. Need technique guaranteed to find the global minimum.

- If global minimum of D is negative, mixture may split (unstable or metastable feed).

Example–Phase Stability Analysis (cont.)

- Stationary points of the optimization problem can be found by solving the nonlinear equation system

$$\left[\left(\frac{\partial \hat{G}}{\partial x_i}\right) - \left(\frac{\partial \hat{G}}{\partial x_n}\right)\right] - \left[\left(\frac{\partial \hat{G}}{\partial x_i}\right) - \left(\frac{\partial \hat{G}}{\partial x_n}\right)\right]_{\mathbf{z}} = 0,$$

$$i = 1, \ldots, n-1$$

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

$$EOS(\mathbf{x}, v) = 0$$

- Trivial root at the feed composition $\mathbf{x} = \mathbf{z}$; may be multiple nontrivial roots. Need technique guaranteed to find all the roots.

Example–Phase Stability Analysis (cont.)

Alternative formulation (Nagarajan $et\ al.$, 1991) for constant T and P based on Helmholtz energy density $E(\mathbf{d})$, where $\mathbf{d}$ is the mole density vector:

$$\min_{\mathbf{d}} D(\mathbf{d}) = E - E_{\mathbf{z}} - \sum_{i=1}^{n} \left(\frac{\partial E}{\partial d_i} \right)_{\mathbf{z}} (d_i - d_{z,i})$$

- Unconstrained optimization with one less variable.
- Attractive for dealing with new equations of state (e.g. SAFT) which are presented naturally in the form $E(\mathbf{d})$.
- Again may have multiple local minima.

Example–Phase Stability Analysis (cont.)

- Equation system for stationary points in Helmholtz energy density formulation:

$$\left(\frac{\partial E}{\partial d_i}\right) - \left(\frac{\partial E}{\partial d_i}\right)_{\mathbf{z}} = 0$$

$$i = 1, \ldots, n$$

- Again trivial root at feed, and may have multiple solutions.

- Interval approach has been applied previously to the Gibbs energy formulation (Hua $et\ al.$, 1996,1998), but not to the Helmholtz energy formulation.

Problem 1

N_2 (1), C_2H_6 (2), $T = 270$ K, $P = 76$ bar, PR EOS model

Feed (z_1, z_2)	Number of Stationary Points	Stable ?	CPU time (sec.)	
			Gibbs	Helmholtz
(0.18,0.82)	3	No	0.20	0.09
(0.44,0.56)	3	No	0.20	0.09
(0.60,0.40)	1	Yes	0.13	0.06

- CPU time on Sun Ultra 30.
- Both formulations give same result for stability analysis

Problem 2

N_2 (1), CH_4 (2), C_2H_6 (3) $T = 270$ K, $P = 76$ bar, PR EOS model

Feed (z_1, z_2, z_3)	Number of Stationary Points	Stable ?	CPU time (sec.)	
			Gibbs	Helmholtz
(0.30,0.10,0.60)	3	No	1.34	1.19
(0.15,0.30,0.55)	3	No	3.37	2.12
(0.08,0.38,0.54)	1	Yes	2.54	1.43
(0.05,0.05,0.90)	1	Yes	0.54	0.60

- CPU time on Sun Ultra 30.
- Both formulations give same result for stability analysis

Example–Alternative Mixing Rules

- Previous applications of the interval method to phase stability and equilibrium problems used standard mixing rules — quadratic for a, linear for b.

- Can the interval approach be used in connection with more complex mixing rules?

- In the example, the interval method is used to compute phase equilibrium when the Wong-Sandler mixing rules are used.

Wong-Sandler Mixing Rules

$$a = \frac{RTQ_{ws}D_{ws}}{1 - D_{ws}} = RTD_{ws}b$$

$$b = \frac{Q_{ws}}{1 - D_{ws}}$$

where

$$D_{ws} = \frac{A^E_\infty}{cRT} + \sum_{i=1}^{n} \frac{x_i a_{ii}}{RTb_i}$$

$$Q_{ws} = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \left(\frac{b_i + b_j}{2} - \frac{\sqrt{a_{ii}a_{jj}}}{RT}(1 - k_{ij}) \right)$$

and

$$\frac{A^E_\infty}{RT} = \sum_i x_i \left(\frac{\sum_j x_j \tau_{ji} g_{ji}}{\sum_k x_k g_{ki}} \right)$$

(NRTL equation)

Problem 3

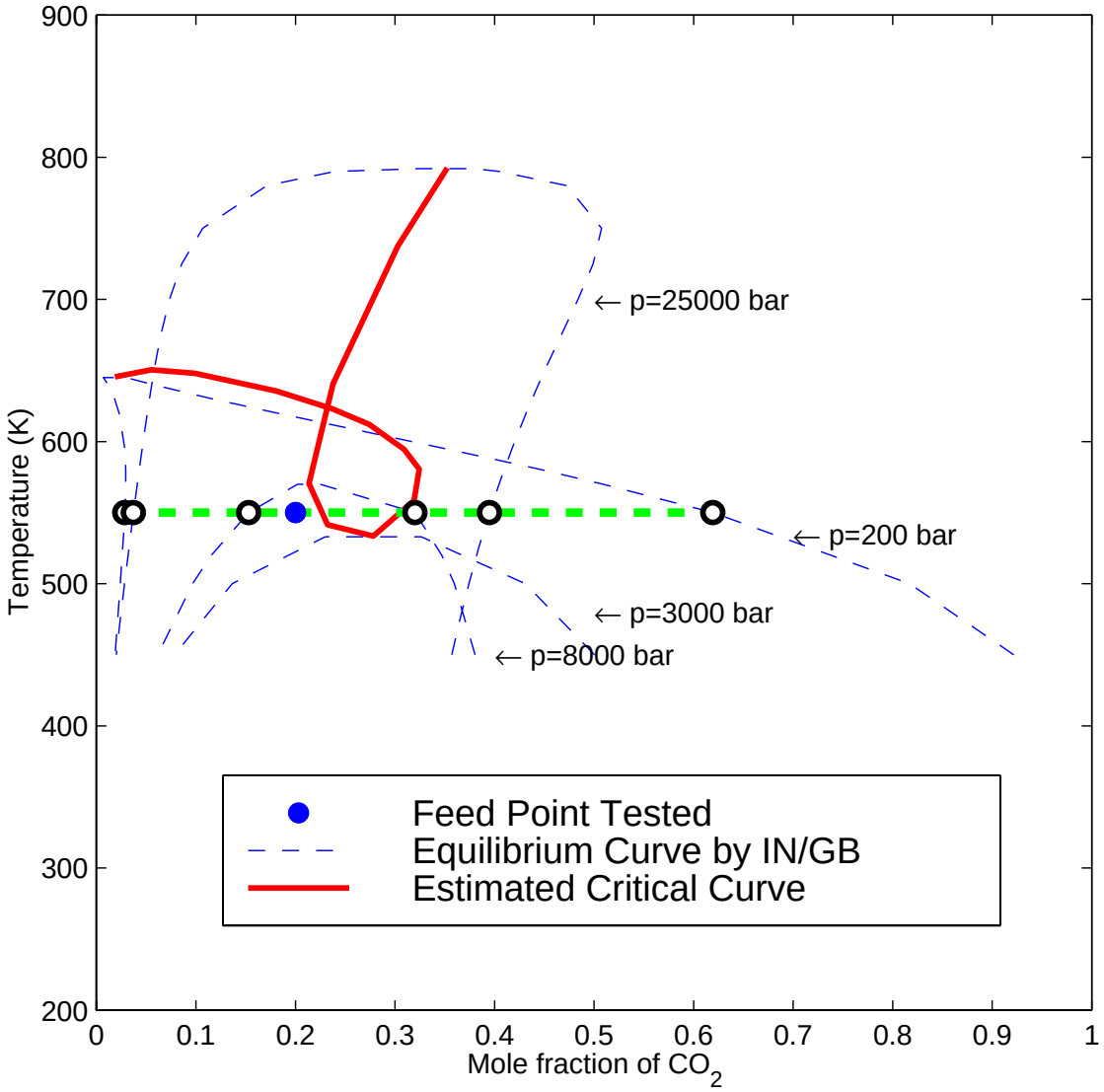
CO_2 (1), H_2O (2), $T = 550$ K, Feed: $z_1 = 0.2$, $z_2 = 0.8$, PRSV EOS with Wong-Sandler mixing rules

Pressure (bar)	Phase Equilibrium		CPU time (seconds)
	Split Fraction	$(x_1, x_2, v$ [cm^3/mol])	
200	0.29	(0.619,0.381,182)	1.11
	0.71	(0.029,0.971,28.9)	
3000	No Phase Split		0.5
8000	0.28	(0.320,0.680,22.3)	1.86
	0.72	(0.153,0.847,22.2)	
25000	0.55	(0.037,0.963,20.3)	1.54
	0.45	(0.395, 0.605,20.2)	

CPU time on Sun Ultra 30.

Problem 3

CO_2 (1), H_2O (2), $T = 550$ K, Feed: $z_1 = 0.2$, $z_2 = 0.8$, PRSV EOS with Wong-Sandler mixing rules



Example–Computing Critical Points

- Formulation as system of nonlinear equations
  - Determinants
  - Method of Heidemann and Khalil (1979)

- Nonlinear equation system to be solved for critical points has unknown number of roots

- Interval method provides an approach guaranteed to find all roots, or to determine with certainty that there are none.

- Example problem computes critical point(s) for mixture of CH_4 and H_2S at various compositions

- Temperature range searched is 110–800 K; Volume range searched is $1.1b - 4.0b$.

Problem 4

CH_4 (1), H_2S (2), SRK EOS

Feed (z_1, z_2)	Critical Point(s)			CPU time (seconds)
	V_c [cm^3/mol]	T_c [K]	P_c [bar]	
(0.97,0.03)	107.70	196.74	50.37	1.26
(0.93,0.07)	97.75	204.78	56.72	4.97
	44.72	114.77	-283.57	
(0.85,0.15)	74.03	212.99	64.51	21.03
	59.41	190.98	22.53	

CPU time on Sun Ultra 30.

Problem 4 (Cont.)

CH_4 (1), H_2S (2), SRK EOS

Feed (z_1, z_2)	Critical Point(s)			CPU time (seconds)
	V_c [cm^3/mol]	T_c [K]	P_c [bar]	
(0.53,0.47)	no critical point			17.35
(0.52,0.48)	59.26	270.02	146.07	30.02
	54.93	260.27	149.00	
(0.51,0.49)	63.37	279.25	145.02	25.60
	50.31	249.01	160.10	

CPU time on Sun Ultra 30.

Concluding Remarks

Interval analysis is a **general-purpose** and **model-independent** approach for solving phase behavior problems, providing a **mathematical and computational guarantee** of reliability

- Phase stability and equilibrium
  - Gibbs energy formulation (e.g., Hua $et\ al.$, 1998)
  - Helmholtz energy density formulation
  - Any EOS and mixing rule
  - Or any activity coefficient model (e.g., Stadtherr $et\ al.$, 1995)

- Critical Points
  - Any EOS and mixing rule

- Azeotropes
  - Homogeneous (Maier $et\ al.$, 1998a)
  - Heterogeneous
  - Reactive (Maier $et\ al.$, 1998b)
  - From any EOS or activity coefficient model

Concluding Remarks (Cont.)

- Interval analysis provides powerful problem solving techniques with many other applications in the modeling of thermodynamics and phase behavior and in other process modeling problems.

- Continuing advances in computing hardware and software (e.g., compiler support for interval arithmetic) will make this approach even more attractive.

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- For more information:

  - Contact Prof. Stadtherr at markst@nd.edu
  - See also
    http://www.nd.edu/~markst