Interval Analysis for Thermodynamic Calculations in Process Design: A Novel and Completely Reliable Approach

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Summary

- In modeling phase behavior for process design, 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 analysis and in finding homogeneous azeotropes, and can be applied to a variety of other problems.

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 all values of $f(\mathbf{x})$ for $\mathbf{x} \in \mathbf{X}$. That is, $F(\mathbf{X}) \supseteq \{f(\mathbf{x}) \mid \mathbf{x} \in \mathbf{X}\}$.

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

Interval Newton Method

- For a system of nonlinear equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$, find (enclose) all roots in a given initial interval $\mathbf{X}^{(0)}$ or determine that there are none.

- At iteration k, given the interval $\mathbf{X}^{(k)}$, if $0 \in \mathbf{F}(\mathbf{X}^{(k)})$ solve the linear interval equation system

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

  for the "image" $\mathbf{N}^{(k)}$, where $F'(\mathbf{X}^{(k)})$ is an interval extension of the Jacobian of $f(\mathbf{x})$ over the current interval $\mathbf{X}^{(k)}$, and $\mathbf{x}^{(k)}$ is a point inside $\mathbf{X}^{(k)}$.

- Any root $\mathbf{x}^* \in \mathbf{X}^{(k)}$ is also contained in the image $\mathbf{N}^{(k)}$, suggesting the iteration scheme $\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} \cap \mathbf{N}^{(k)}$ (Moore, 1966).

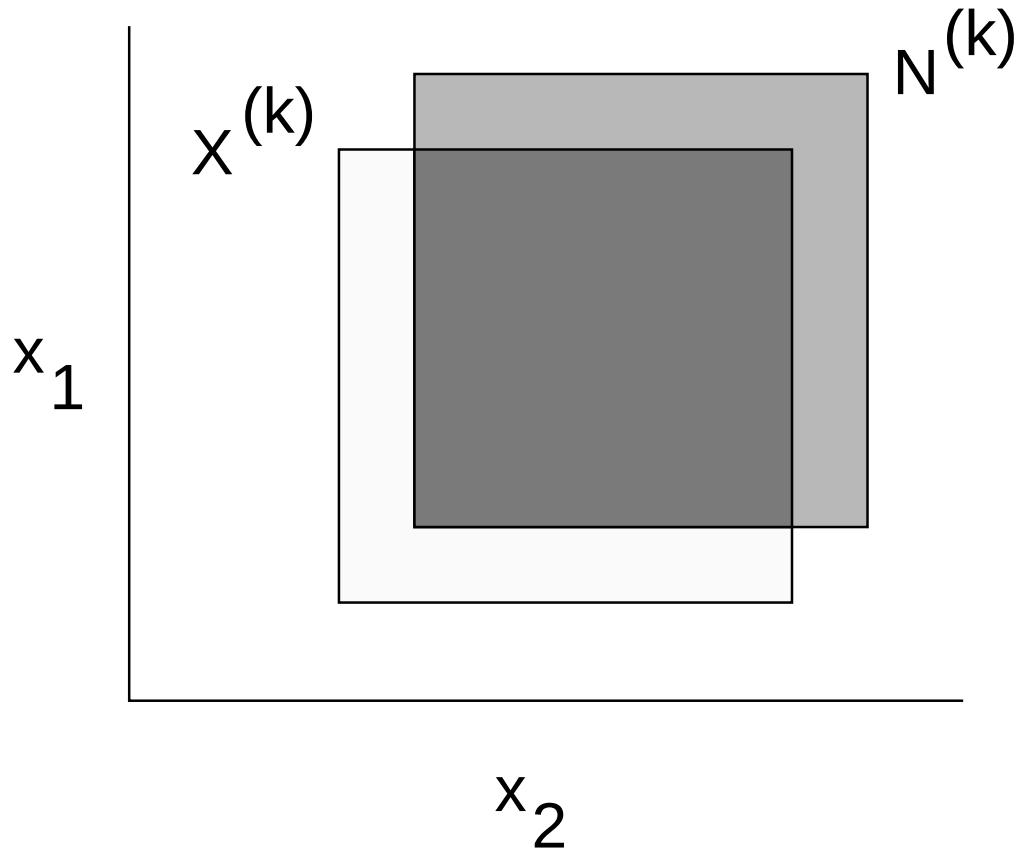
- It follows that if $\mathbf{X}^{(k)} \cap \mathbf{N}^{(k)} = \emptyset$, then there is no root in $\mathbf{X}^{(k)}$. This is also the conclusion if $0 \notin \mathbf{F}(\mathbf{X}^{(k)})$.

Interval Newton Method (continued)

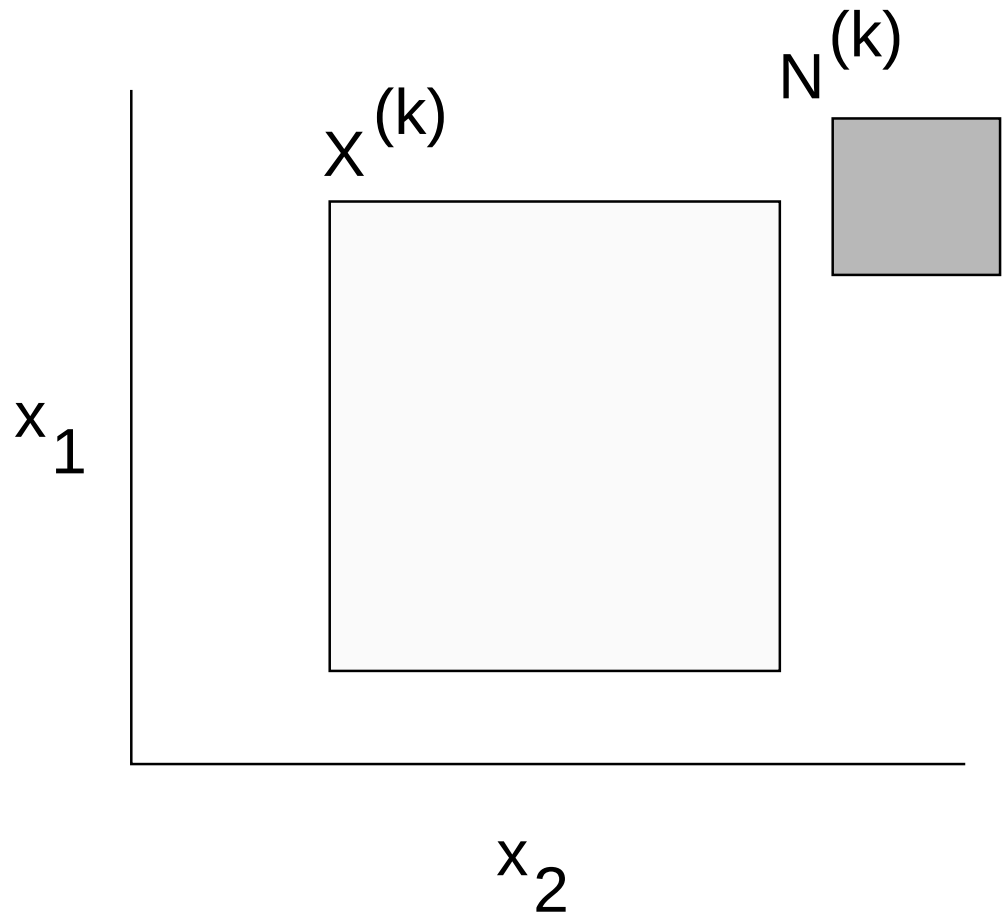
- Interval Newton provides an existence and uniqueness test: If $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then:
  - There is a **unique** zero of $\mathbf{f}(\mathbf{x})$ in $\mathbf{X}^{(k)}$.
  - The interval Newton iteration $\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} \cap \mathbf{N}^{(k)}$ will converge quadratically to a tight enclosure of the root.
  - The point Newton method will converge quadratically to the root starting from any point in $\mathbf{X}^{(k)}$.

- If a unique root cannot be confirmed ($\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$) or ruled out ($\mathbf{X}^{(k)} \cap \mathbf{N}^{(k)} = \emptyset$), then either:
  - Continue with the next iterate $\mathbf{X}^{(k+1)}$ if it is sufficiently smaller than $\mathbf{N}^{(k)}$, or
  - **Bisect** $\mathbf{X}^{(k+1)}$ and perform interval Newton on the resulting intervals.

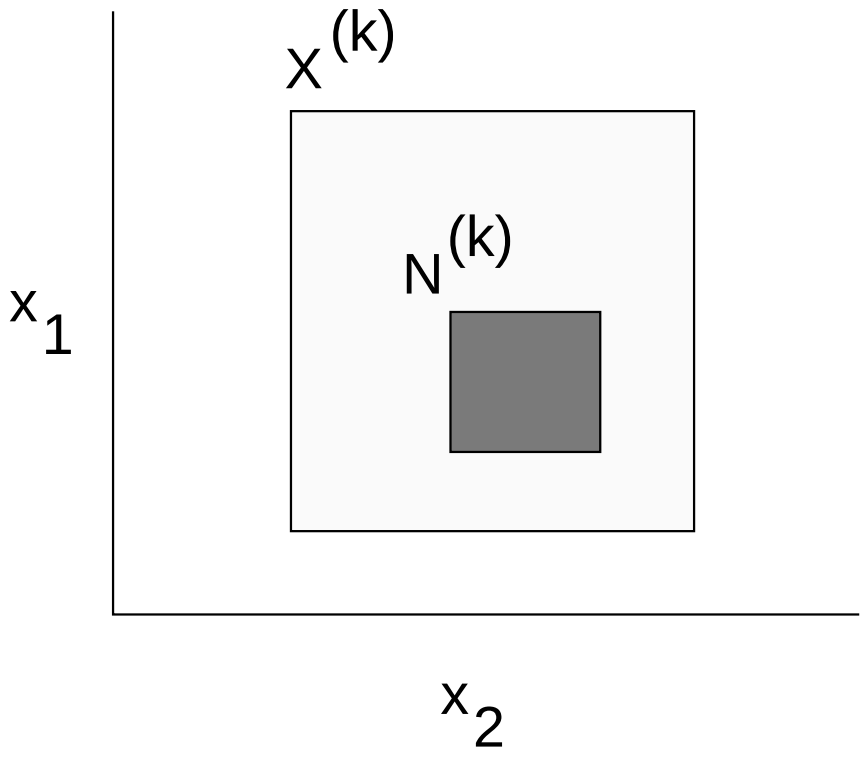
  This is the interval Newton/generalized bisection (IN/GB) approach.



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



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

Interval Newton Method (continued)

- For $\mathbf{f}(\mathbf{x}) = \mathbf{0}$, this method can enclose **with mathematical and computational certainty** any and all solutions in a given initial interval, or can determine that there are none.

- A preconditioned interval Gauss-Seidel-like technique is often used to solve for the image $\mathbf{N}^{(k)}$ (Hansen and coworkers).

- Our implementation is based on modifications of routines taken from the packages INTBIS and INTLIB (Kearfott and coworkers).

- The interval Newton procedure can be performed on multiple intervals independently and in parallel.

- IN/GB was first implemented for process modeling problems by Schnepper and Stadtherr (1990).

Phase Stability Problem

- Will a mixture (feed) at a given T, P, and composition $\mathbf{z}$ split into multiple phases?

- A key subproblem in determination of phase equilibrium, and thus in the design and analysis of separation operations.

- Using tangent plane analysis, can be formulated as a minimization problem, or as an equivalent nonlinear equation solving problem.

- Equation system to be solved may have trivial and/or multiple roots (optimization problem has multiple local optima).

- Conventional techniques may fail to converge, or converge to false or trivial solutions.

Tangent Plane Analysis

- A phase at T, P, and feed composition $\mathbf{z}$ is unstable if the Gibbs energy of mixing vs. composition surface

$$m(\mathbf{x}, v) = \Delta g_{mix} = \Delta \hat{G}_{mix}/RT$$

  ever falls below a plane tangent to the surface at $\mathbf{z}$

$$m_{tan}(\mathbf{x}) = m(\mathbf{z}, v_{\mathbf{z}}) + \sum_{i=1}^{n} \left(\frac{\partial m}{\partial x_i} \right) \Bigg|_{\mathbf{z}} (x_i - z_i)$$

- That is, if the *tangent plane distance*

$$D(\mathbf{x}, v) = m(\mathbf{x}, v) - m_{tan}(\mathbf{x})$$

  is negative for any composition $\mathbf{x}$, the phase is unstable.

- In this context, "unstable" refers to both the metastable and classically unstable cases.

Optimization Formulation

- To determine if D ever becomes negative, determine the minimum of D and examine its sign

$$\min_{\mathbf{x},v} \quad D(\mathbf{x},v)$$

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.

Equation Solving Formulation

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

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

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

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

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

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

Some Current Solution Methods

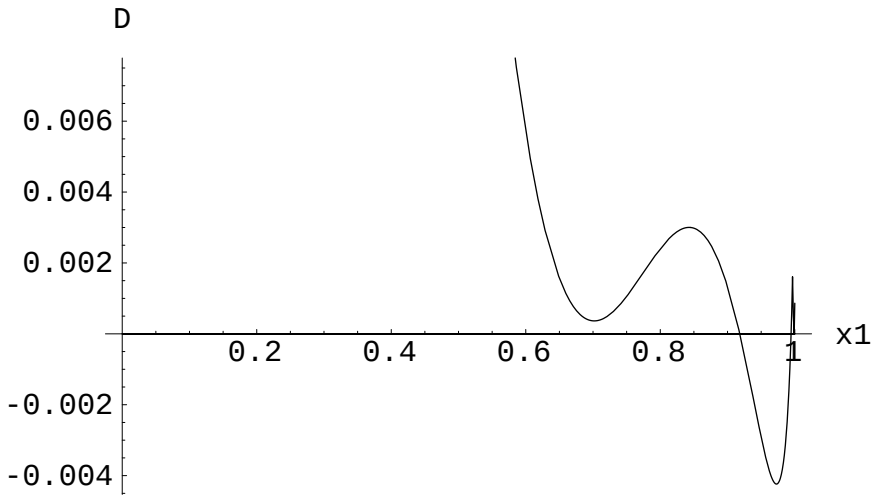
- Various local methods — Fast, but initialization dependent (may use multiple initial guesses), and not always reliable.

- Some more reliable approaches
  - Exhaustive search on grid (Eubank *et al.*, 1992)
  - Homotopy-continuation (Sun and Seider, 1995)
  - Topological degree (Wasylkiewicz *et al.*, 1996)
  - Branch and bound (McDonald and Floudas, 1995, 1997): Guarantee of global optimum when certain activity coefficient models are used.

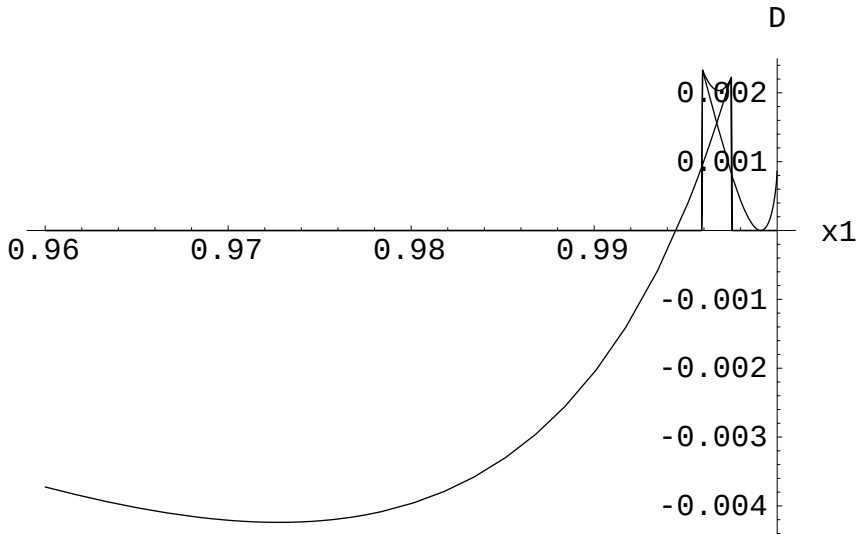
- Interval analysis
  - Provides a general-purpose, model-independent method for solving phase stability problem with complete certainty.
  - Stadtherr *et al.* (1994,1995), McKinnon *et al.* (1995,1996): Activity coefficient models
  - Hua *et al.* (1995,1996,1997): Equation of state models

Example 1

CO_2 (1), *trans*-2-hexen-1-ol (2), $T = 303.15$ K, $P = 69.7016$ bar, $z_1 = 0.9991$, PR EOS model (standard mixing rules). Tangent plane distance D vs. x_1:



region near $x_1 = 1$ (has multiple real v roots):



Example 1 (continued)

- Five stationary points (four minima, one maximum).
- Standard local methods (e.g. Michelsen, 1982) known to fail (predict stability when system is actually unstable) because global minimum is not found.
- Easily solved (see Table 1) using interval method. Initial interval includes all physically feasible values of mole fraction and molar volume (no point initialization needed).
- Many other problems (two to five components) also easily solved using either EOS or excess Gibbs energy models (NRTL, UNIQUAC).
- Easily combined with fast, local flash algorithms to perform reliable phase equilibrium (split) calculations. Several two or three phase problems easily solved.

Example 1 — Phase Stability

CO_2 (1), *trans*-2-hexen-1-ol (2), $T = 303.15$ K, $P = 69.7016$ bar, $z_1 = 0.9991$, PR EOS model

Table 1

Feed (z_1, z_2) and CPU time	Stationary Points (roots) $(x_1, x_2, v$ [cm^3/mol])	D
(0.9991,0.0009)	(0.9991,0.0009,160.8)	0.0
0.71 sec	(0.9968,0.0032,106.1)	0.0020
	(0.9728,0.0272,61.59)	-0.004
	(0.8428,0.1572,57.97)	0.0030
	(0.7018,0.2982,65.53)	3.6×10^{-4}

- CPU time on Sun Ultra 2/1300.
- All stationary points easily found, showing the feed to be unstable.
- Presence of multiple real volume roots causes no difficulties.

Computing Homogeneous Azeotropes

- Why
  - Identify limitations in separation operations.
  - Construction of residue curve maps for design and synthesis of separation operations.
  - Evaluation of thermodynamic models.

- How
  - Solve system(s) of nonlinear equations derived from equifugacity condition; can use sequential or simultaneous approach to formulate problem.
  - These equation system(s) often have multiple and/or trivial roots, or may have no solutions.
  - Account for temperature dependence using Antoine equation (ideal vapor phase) and temperature dependent activity coefficient model parameters (or evaluate parameters at a guessed "reference temperature" T_{REF} assumed close to the azeotropic T).

Formulation : Sequential Approach

- $\ln P - \ln P_i^{sat}(T) - \ln \gamma_i^L(T) = 0,\ i \in \mathcal{C}_{nz}$

$$1 - \sum_{i \in \mathcal{C}_{nz}} x_i = 0$$

- $\mathcal{C}_{nz}$ is a set of k nonzero components out of N total components.

- All k-ary azeotropes $(k \leq N)$ for the chosen $\mathcal{C}_{nz}$ are solutions; there may be no solutions.

- Solve (unordered) sequence of problems :

  For $k = 2 \rightarrow N$:

  For all combinations of k nonzero components, solve for all k-ary azeotropes.

- Need solution method guaranteed to find all solutions of all problems, and to determine with certainty when there are no solutions.

Some Current Solution Methods

- Various local methods — Fast, but initialization dependent and hard to find all roots.

- Fidkowski $et\ al.$ (1993) use a homotopy-continuation method.
  - Simultaneous approach with explicit T-dependence of γ_i.
  - Improved reliability but no guarantee that all roots are found.

- Harding $et\ al.$ (1997) use a branch and bound method.
  - Simultaneous and sequential approaches; T_{REF} approach for T-dependence of γ_i.
  - Reformulation as a global optimization problem using convex underestimating functions.
  - Mathematical guarantee that all roots are found in T_{REF} approach.

Example 2 — Homogeneous Azeotropes

UNIQUAC, Benzene(B), Ethanol(E) and Water(W), $P = 1.0$ atm. CPU time is on a Sun Ultra 1/140.

Comps.	Mole Fr. (B E W)	T (°C)	CPU (s)
BE	0.552 0.448 0.000	67.66	0.036
BW	(0.572 0.000 0.428)*	(61.98)*	0.037
EW	0.000 0.886 0.115	78.11	0.041
BEW	no azeotrope		1.21
total			1.32

* This is a solution to the equifugacity condition, but is not a homogeneous azeotrope since the liquid phase will split.

- Explicit T-dependence of activity coefficient model parameters accounted for (no T_{REF} needs to be guessed).
- Many other problems (two to five components) easily solved, using Wilson, NRTL or UNIQUAC models, finding all azeotropes.

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
  - Phase equilibrium (split)
  - Homogeneous azeotropes

- 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
    http://www.nd.edu/~markst/preprints.html
    http://www.nd.edu/~markst/presentations.html