Reliable Computation of Phase Behavior Using Interval Methods

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Summary

- In modeling 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, including the determination of phase stability and the computation of azeotropes and critical points.

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 $Y = \{x$ 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 Method Used

- 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; applied to phase behavior problems requires no simplifying assumptions or problem reformulations.

- First implemented for process modeling problems by Schnepper and Stadtherr (1990) and for phase behavior problems by Stadtherr, Schnepper and Brennecke (1994).

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

Interval Method (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:

- (Range Test) Compute an interval extension of each function in the system.

  - If 0 is not an element of any interval extension, delete the box.
  - Otherwise,

- (Interval Newton Test) Compute the *image*, $\mathbf{N}^{(k)}$, of the box by solving the linear interval equation system

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

  - $\mathbf{x}^{(k)}$ 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 $\mathbf{X}^{(k)}$.
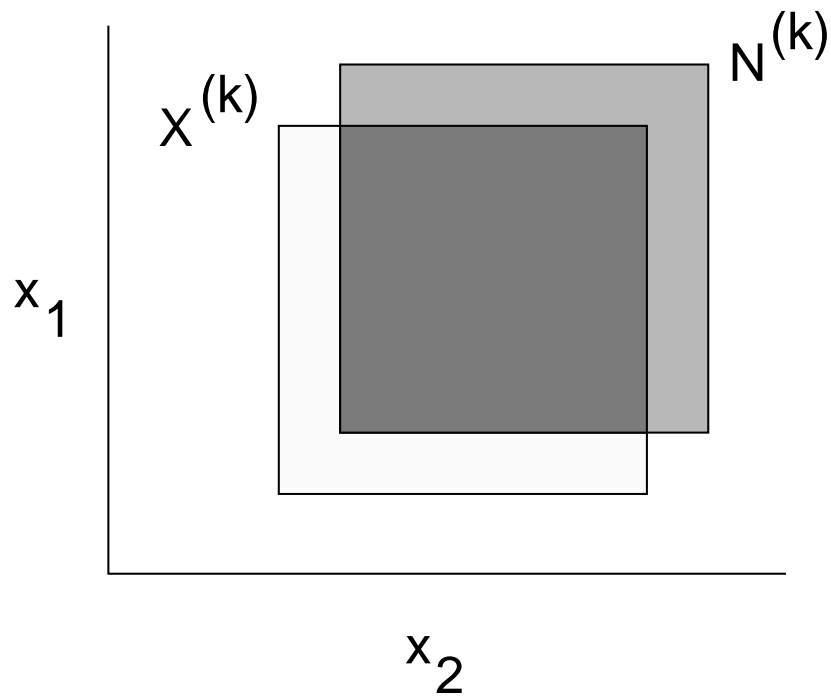
$N^{(k)}$

$X^{(k)}$

x_1

x_2
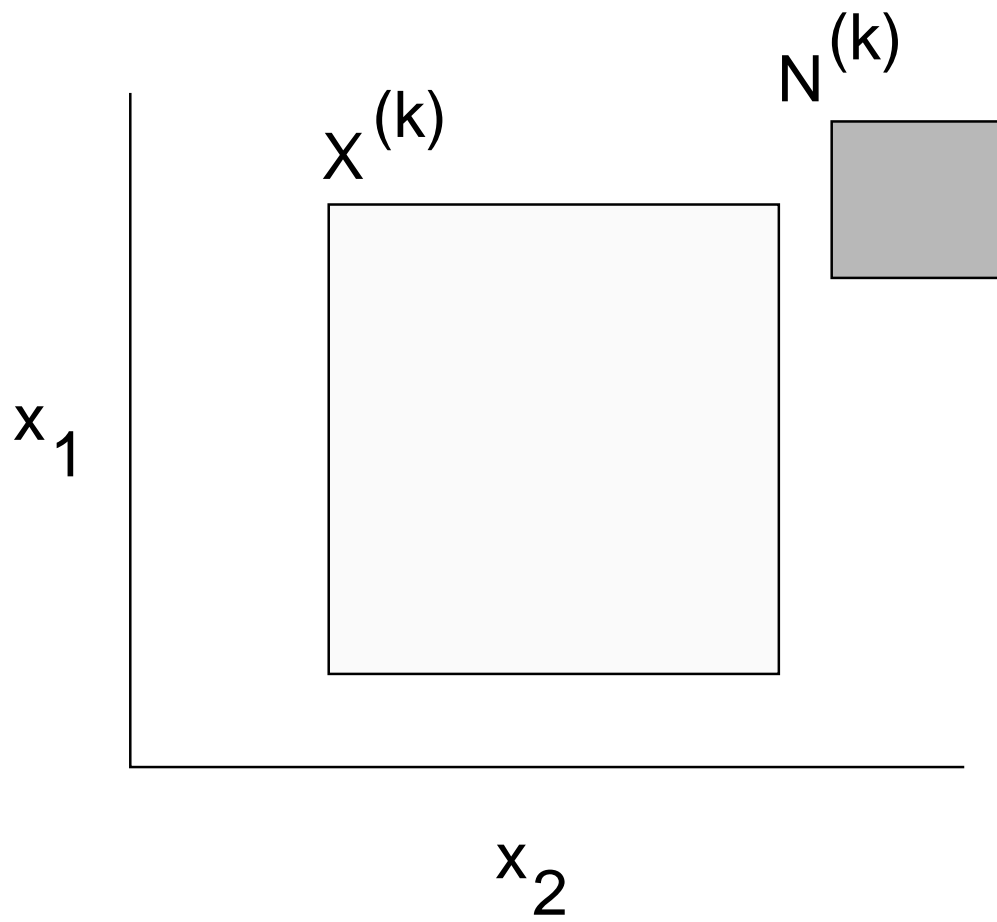
There was no solution in $X^{(k)}$
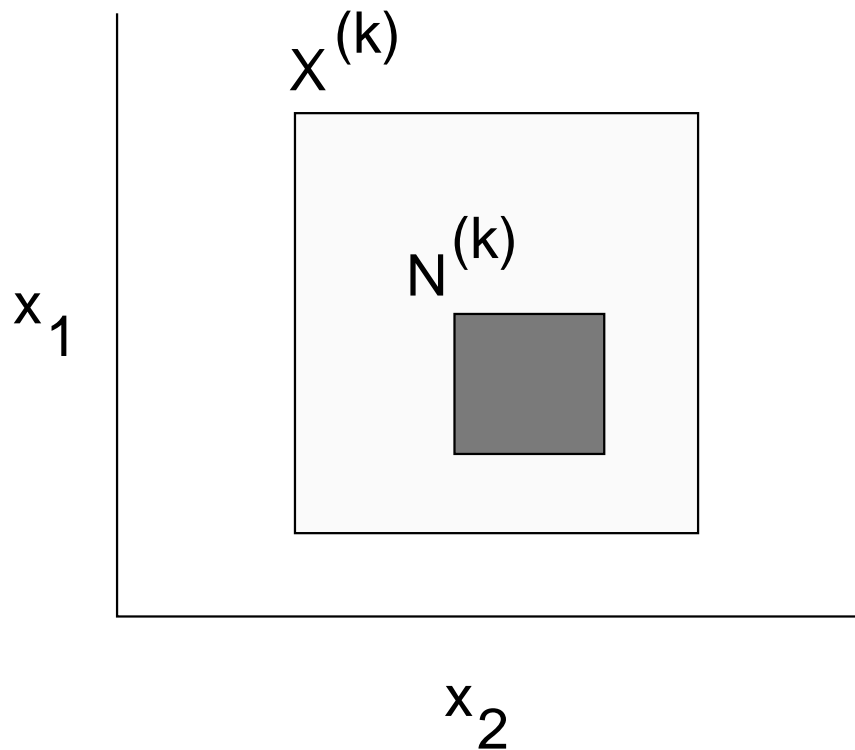
Unique solution in $X^{(k)}$

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.

Phase Stability Problem

- Will a mixture (feed) at a given T, P, and composition $\mathbf{x}$ 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*

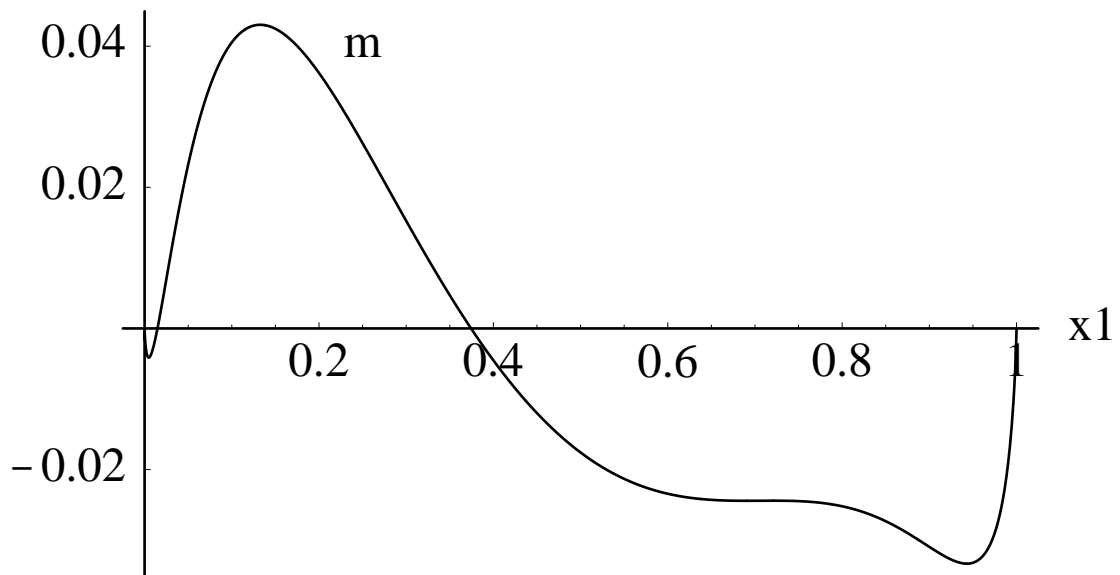$$D(\mathbf{x}, v) = m(\mathbf{x}, v) - m_{tan}(\mathbf{x})$$

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

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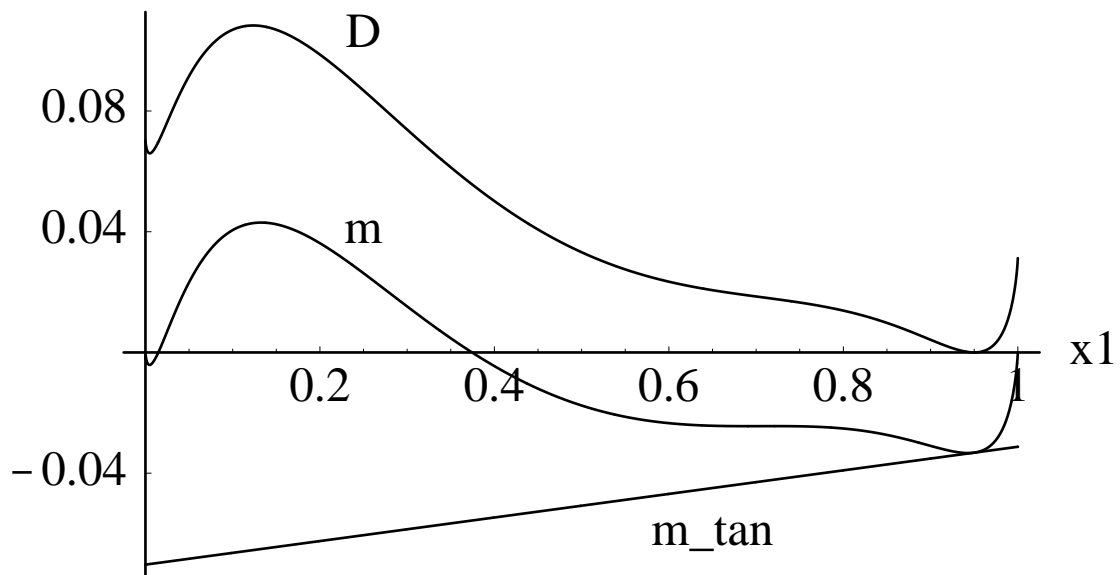
Example

n-Butyl Acetate—Water, NRTL Model

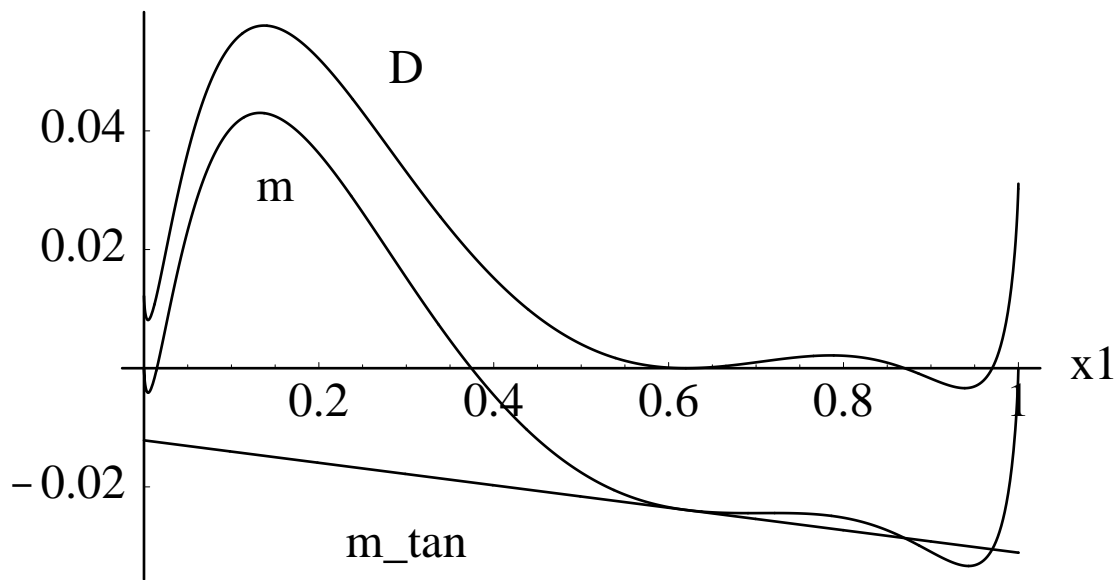Gibbs energy of mixing m vs. x_1

Example (continued)

Feed composition $z_1 = 0.95$

Phase of this composition is stable (D is never negative).

Example (continued)

Feed composition $z_1 = 0.62$

Phase of this composition is unstable and can split (D becomes negative).

Optimization Formulation

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

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

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 <u>guaranteed</u> to find the <u>global</u> 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 <u>guaranteed</u> to find <u>all</u> the roots.

Equation Solving Formulation–Generalized Cubic Equation of State

Solve for $v, x_i, i = 1, \ldots, n$

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

$$P - \frac{RT}{v - b} + \frac{a}{v^2 + ubv + wb^2} = 0$$

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

where

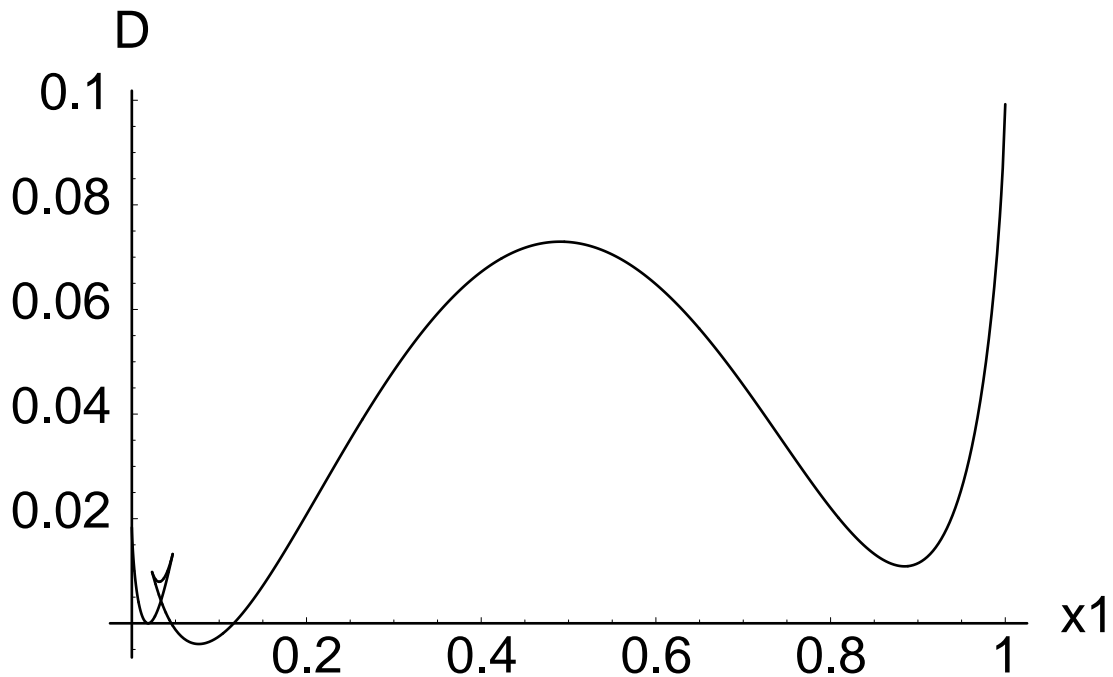$$s_i = \frac{b_i - b_n}{b}\left(\frac{Pv}{RT} - 1\right) + \frac{a}{bRT\Delta}\left(\frac{2(\bar{a}_i - \bar{a}_n)}{a} - \frac{b_i - b_n}{b}\right)\ln\left(\frac{2v + ub - b\Delta}{2v + ub + b\Delta}\right) + \ln\frac{x_i}{x_n} - (g_i^o - g_n^o)$$

$$b = \sum_{i=1}^{n} x_i b_i, \qquad a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij}, \qquad \bar{a}_i = \sum_{k=1}^{n} x_k a_{ik}, \qquad \Delta = \sqrt{u^2 - 4w}$$

Example 1

CH_4, H_2S, $T = 190$ K, $P = 40$ atm, $z_1 = 0.0187$, SRK model. Tangent plane distance D vs. x_1

- Five stationary points (four minima, one maximum).

- Standard local methods (e.g. Michelsen, 1982) known to fail (predict stability when system is actually unstable).

Example 1 (continued)

CH$_4$, H$_2$S, $T = 190$ K, $P = 40$ atm, $z_1 = 0.0187$, SRK model. Tangent plane distance D vs. x_1 (region near origin)
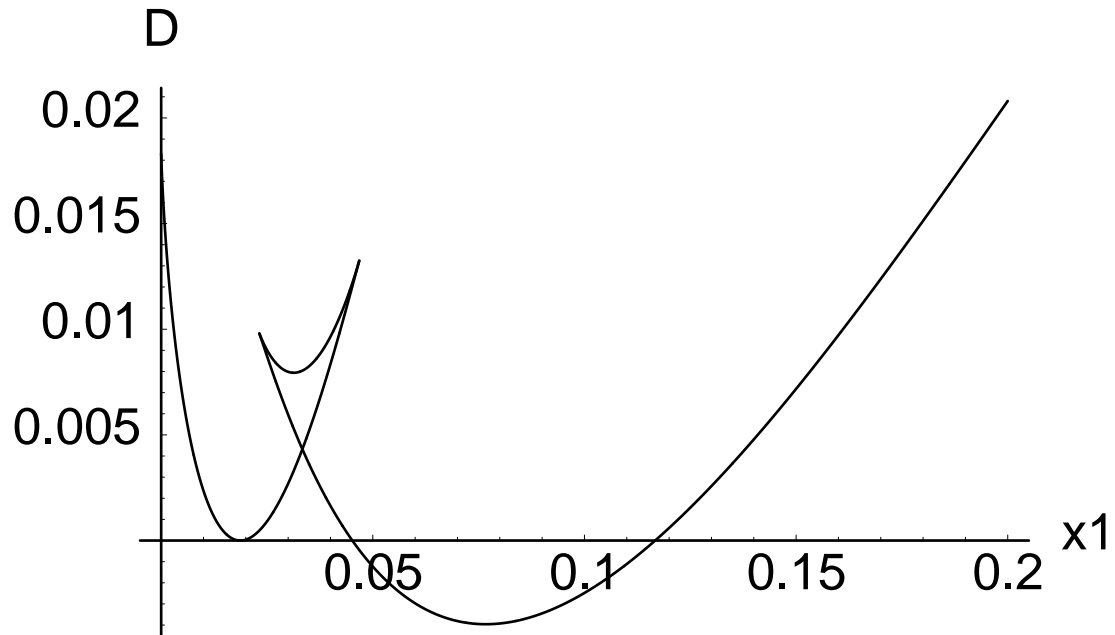
Some Current Solution Methods

- 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; Harding and Floudas, 1998): Guarantee of global optimum when for certain types of models

- 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.* (1995-1999), Xu *et al.* (1998,1999): Equation of state models, including cubic

Interval Analysis for Phase Stability

- Initial interval includes all physically feasible values of mole fraction and molar volume.

- To reduce overestimation in interval extensions due to dependency problem:

  - Can identify and use function monotonicity.
  - Can let monotonicity information be inherited when an interval is bisected.
  - Can use special properties of mole fraction weighted averages.

- "Standard" mixing rules used with cubic equation of state

  - Quadratic for a
  - Linear for b

Example 1 — Phase Stability

CH$_4$, H$_2$S, $T = 190$ K, $P = 40$ atm, $z_1 = 0.0187$, SRK model

Feed (z_1, z_2) and CPU time	Stationary Points (roots) $(x_1, x_2, v$ [cm^3/mol])	D
(0.0187, 0.9813)	(0.885, 0.115, 36.6)	0.011
0.20 sec	(0.0187, 0.9813, 207.3)	0.0
	(0.031, 0.969, 115.4)	0.008
	(0.077, 0.923, 64.1)	-0.004
	(0.491, 0.509, 41.5)	0.073

- 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.

Example 2 — Phase Stability

N_2, CH_4, C_2H_6, $T = 270$ K, $P = 76$ bar, PR model

Feed (z_1, z_2, z_3)	Number of Stationary Points	D_{min}	CPU time (sec)
(0.30,0.10,0.60)	3	-0.015	1.3
(0.15,0.30,0.55)	3	-0.001	3.4
(0.08,0.38,0.54)	1	0.0	2.5
(0.05,0.05,0.90)	1	0.0	0.54

- CPU times on Sun Ultra 2/1300.

- It is not really necessary to find **all** the stationary points; only need to find the global minimum.

- Many other problems have been solved.

- Phase equilibrium problems have also been solved.

Computing Phase Equilibrium Using 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.

$$b = \sum_{i=1}^{n} x_i b_i$$

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij}$$

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

- In this 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

$$D_{ws} = \frac{A_\infty^E}{cRT} + \sum_{i=1}^{n} \frac{x_i a_{ii}}{RT b_i}$$

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

and

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

(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 |
	Split Fraction	$(x_1, x_2, v \text{ [cm}^3\text{/mol]})$	(seconds)
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.

Computing Homogeneous Azeotropes

- What?

  - A mixture has a homogeneous azeotrope when there are vapor and liquid phases are in equilibrium, and these two phases have the same composition.
  - Problem: For a given pressure, determine if any azeotropes exist and find their temperature and composition.

- Why?

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

Computing Homogeneous Azeotropes (Cont'd)

- How?

  - Solve system(s) of nonlinear equations derived from equifugacity condition; can use either a sequential or simultaneous approach to formulate problem (sequential is used here).
  - 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 <u>guaranteed</u> to find <u>all</u> solutions of <u>all</u> problems, and to determine <u>with certainty</u> 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 4 — 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 Frac. (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.

Computing Mixture Critical Points

- A mixture critical point is a point (temperature, pressure, molar volume, composition) that is stable, but on the limit of stability.

- Problem can be formulated 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 5

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

| Feed (z_1, z_2) | Critical Point(s) | | | CPU time |
	V_c [cm^3/mol]	T_c [K]	P_c [bar]	(seconds)
(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 5 (Cont.)

CH$_4$ (1), H$_2$S (2), SRK EOS

| Feed (z_1, z_2) | Critical Point(s) | | | CPU time |
	V_c [cm^3/mol]	T_c [K]	P_c [bar]	(seconds)
(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
    - Helmholtz energy density formulation (Xu *et al.*, 1998)
    - Any EOS and mixing rule
    - Or any activity coefficient model (e.g., Stadtherr *et al.*, 1994)

- Azeotropes
    - Homogeneous
    - Heterogeneous (Maier *et al.*, 1999)
    - Reactive (Maier *et al.*, 1998b)
    - From any EOS or activity coefficient model

- Critical Points
    - Any EOS and mixing rule

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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