Reliable Process Modeling Using Interval Analysis

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Outline

- Motivation
- Background
- Methodology
- Examples
  - Phase Stability Analysis
  - Phase Equilibrium
  - Computation of Azeotropes
  - Other

Computing Technology

- Faster and faster single processor performance

- High performance computing (HPC)
  - Many forms of scalar multiprocessing
  - Vector multiprocessing
  - Metacomputing

- Capability to
  - Solve problems faster
  - Solve larger problems
  - Solve more complex problems
  - **Solve problems more reliably**

Solving Problems More Reliably

- Global vs. local optimization
- Finding multiple solutions
- Existence and uniqueness of solutions
- Feasibility of NLPs
- Floating point arithmetic problems (e.g., rounding errors)

Common Misconceptions

- Dennis and Schnabel (1983)

  “In general, the questions of existence and uniqueness—does a given problem have a solution and is it unique?—are beyond the capabilities one can expect of algorithms that solve nonlinear problems”

- Heath (1997)

  “It is not possible, in general, to guarantee convergence to the correct solution or to bracket the solution to produce an absolutely safe method” [for solving nonlinear equations]

Solving Problems More Reliably

- In fact there do exist methods, based on **interval analysis**, that, within given initial bounds on each variable, can:
    - Find (enclose) any and all solutions to a nonlinear equation system to a desired tolerance
    - Determine that there is no solution of a nonlinear equation system
    - Find the global optimum of a nonlinear objective function

- These methods:
    - Provide a mathematical guarantee of reliability
    - Deal automatically with rounding error, and so also provide a **computational** guarantee of reliability

Rounding Error

- Rump's (1988) problem

$$\begin{aligned} f(x,y) &= 333.75y^6 \\ &\quad +x^2(11x^2y^2 - y^6 - 121y^4 - 2) \\ &\quad +5.5y^8 + x/2y \end{aligned}$$

- Evaluate $f(x,y)$ for $x = 77617$ and $y = 33096$.

- All inputs are machine numbers (representable exactly in floating point arithmetic), so only rounding errors occur during function evaluation.

Rounding Error

- Evaluation on an IBM S/370 using a FORTRAN program

- Single precision

$$f = 1.172603\ldots$$

- Double precision

$$f = 1.1726039400531\ldots$$

- Extended precision

$$f = 1.172603940053178\ldots$$

- The correct answer is

$$f = -0.827396059946\ldots$$

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

- 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 $Y = \{x \text{ op } y \mid x \in X,\ y \in Y\}$

$$\begin{gathered}
X + Y = [a + c, b + d] \\
X - Y = [a - d, b - c] \\
X \times Y = [min(ac, ad, bc, bd), max(ac, ad, bc, bd)] \\
X \div Y = [a, b] \times [1/d, 1/c], \quad 0 \notin Y
\end{gathered}$$

- For $X \div Y$ when $0 \in Y$, an extended interval arithmetic is available.

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

Interval Analysis (continued)

- 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

- If a variable occurs more than once in an expression, the natural interval extension may not tightly bound the true range

Interval Analysis (continued)

- Example: $f(x) = x/(x-1)$ evaluated for the interval $X = [2,3]$

- The natural interval extension is

$$\begin{aligned} F([2,3]) &= [2,3]/([2,3]-1) \\ &= [2,3]/[1,2] = [1,3] \end{aligned}$$

- Rearranged $f(x) = x/(x-1) = 1 + 1/(x-1)$, the natural interval extension is

$$\begin{aligned} F([2,3]) &= 1 + 1/([2,3]-1) \\ &= 1 + 1/[1,2] \\ &= 1 + [0.5,1] = [1.5,2] \end{aligned}$$

  which is the true range.

- This is the “dependency” problem. In the first case, each occurrence of x was treated as a independent interval in performing interval arithmetic.

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).

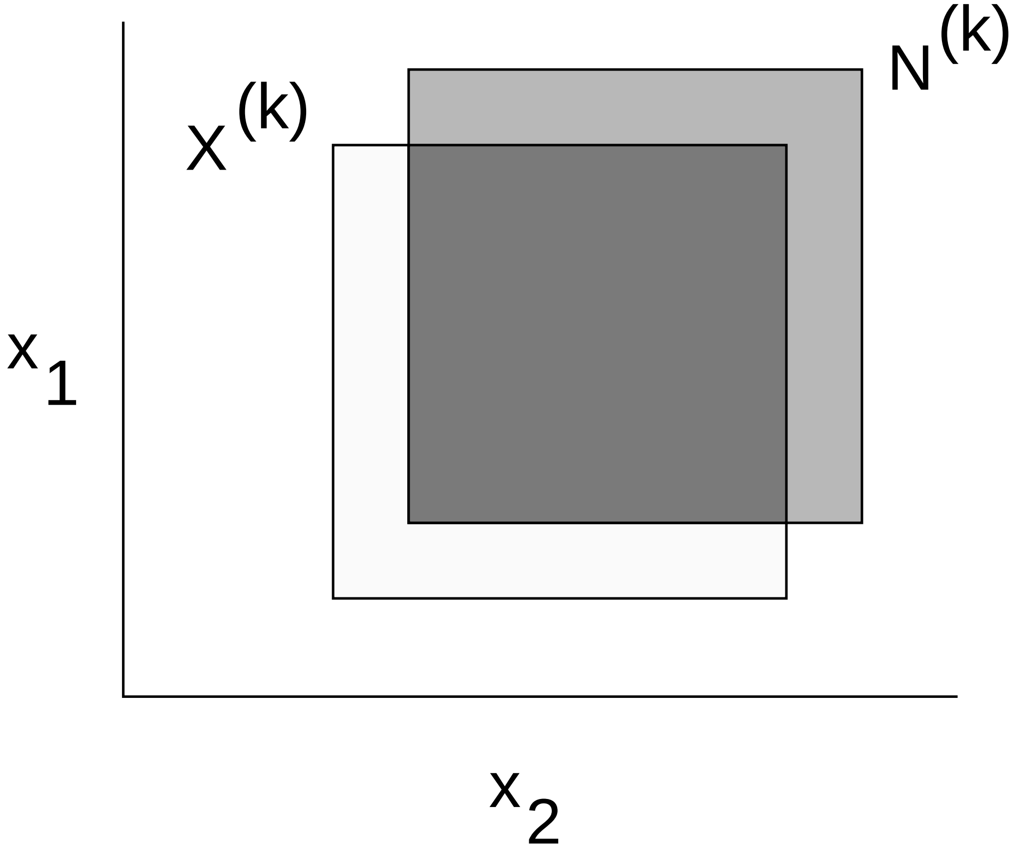
- It follows that if $\mathbf{X}^{(k)} \cap \mathbf{N}^{(k)} = \emptyset$, then there is no root in $\mathbf{X}^{(k)}$. This is also the conclusion if $0 \notin \mathbf{F}(\mathbf{X}^{(k)})$

Interval Newton Method (continued)

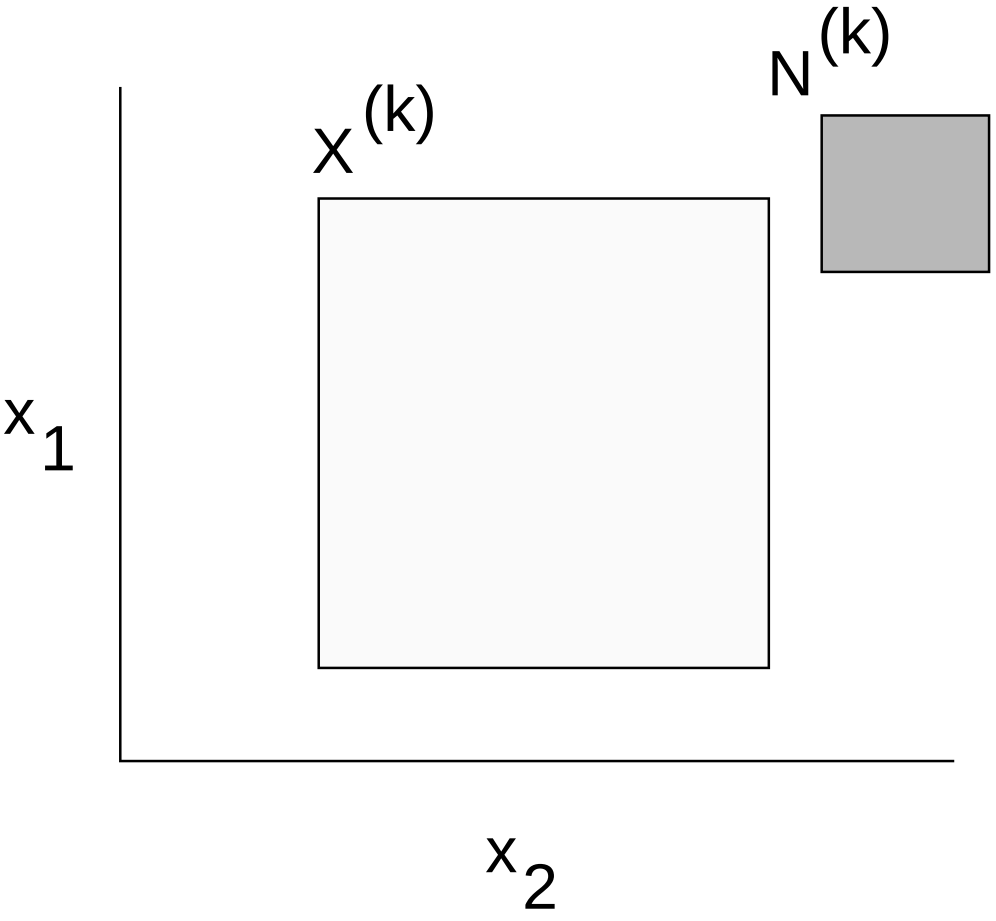
- Interval Newton provides an existence and uniqueness test: If $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then:
  - There is a **unique** zero of $\mathbf{f}(\mathbf{x})$ in $\mathbf{X}^{(k)}$.
  - The interval Newton iteration $\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} \cap \mathbf{N}^{(k)}$ will converge 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 $\mathbf{N}^{(k)}$
  - **Bisect** $\mathbf{X}^{(k+1)}$ and perform interval Newton on the resulting intervals

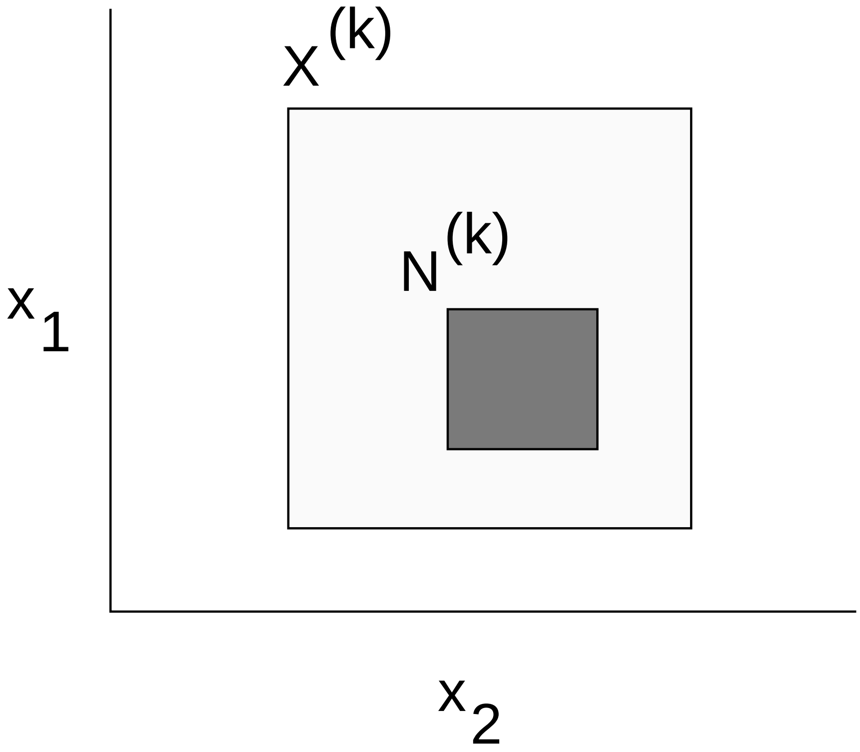
  This is the interval Newton/generalized bisection (IN/GB) approach.



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 $\mathbf{x}$ 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*

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

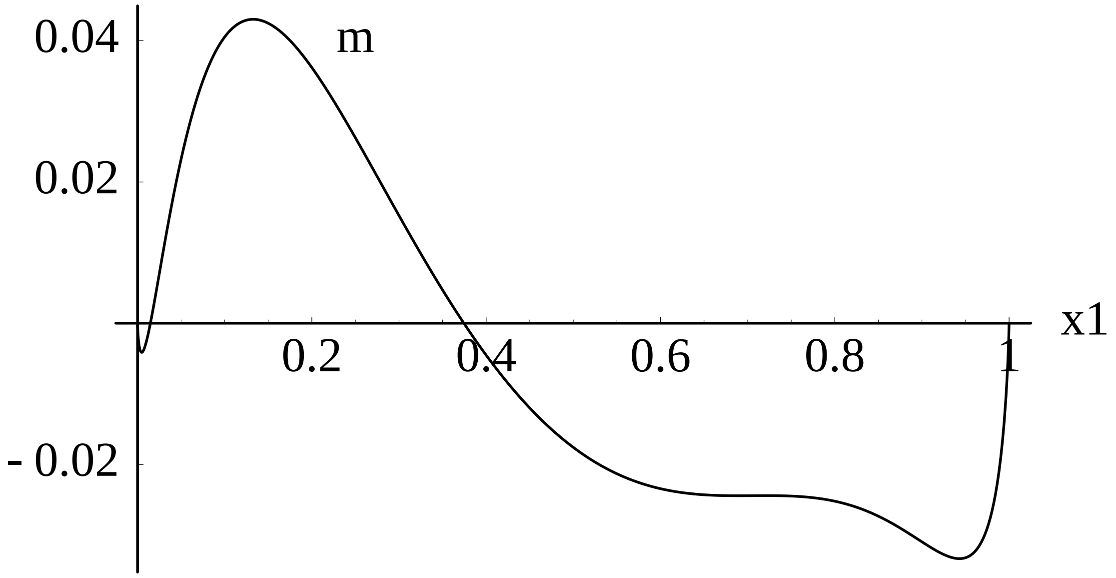
  is negative for any composition $\mathbf{x}$, the phase is unstable.

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

Example 0

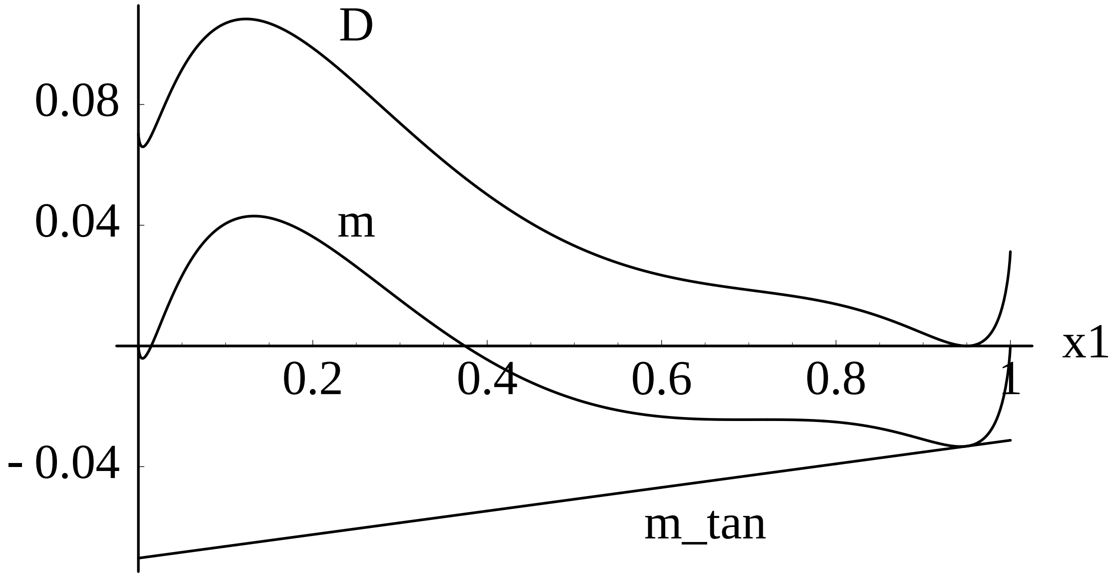
n-Butyl Acetate—Water, NRTL Model

Gibbs energy of mixing m vs. x_1



Example 0 (continued)

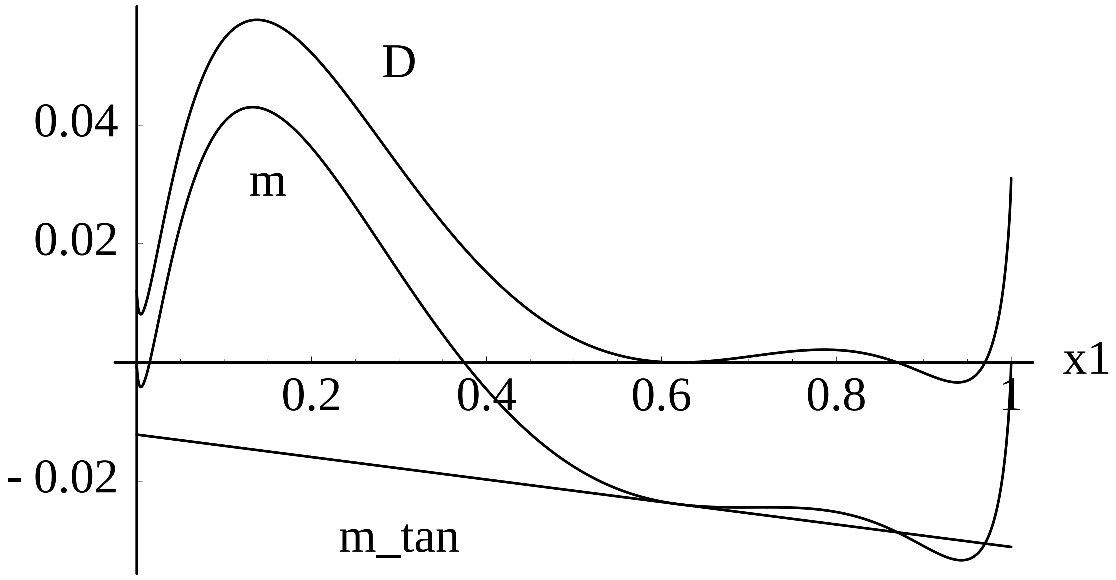
Feed composition $z_1 = 0.95$



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

Example 0 (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

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

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 <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

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

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

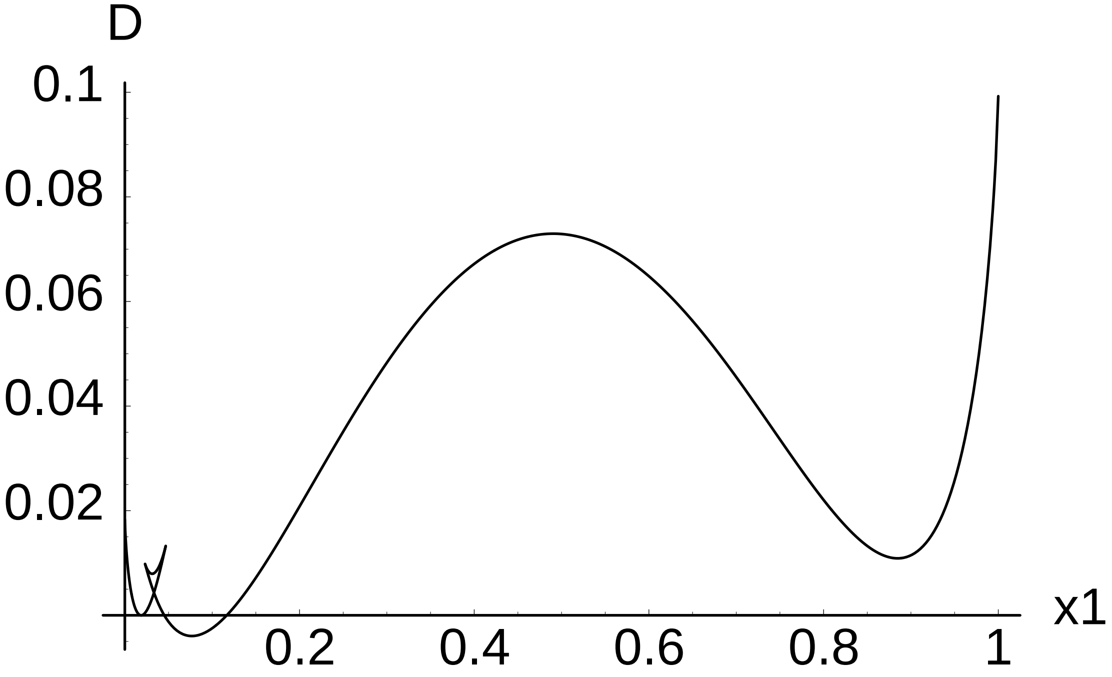
$$1 - \sum_{i=1}^{n} x_i = 0$$

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

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

Example 1

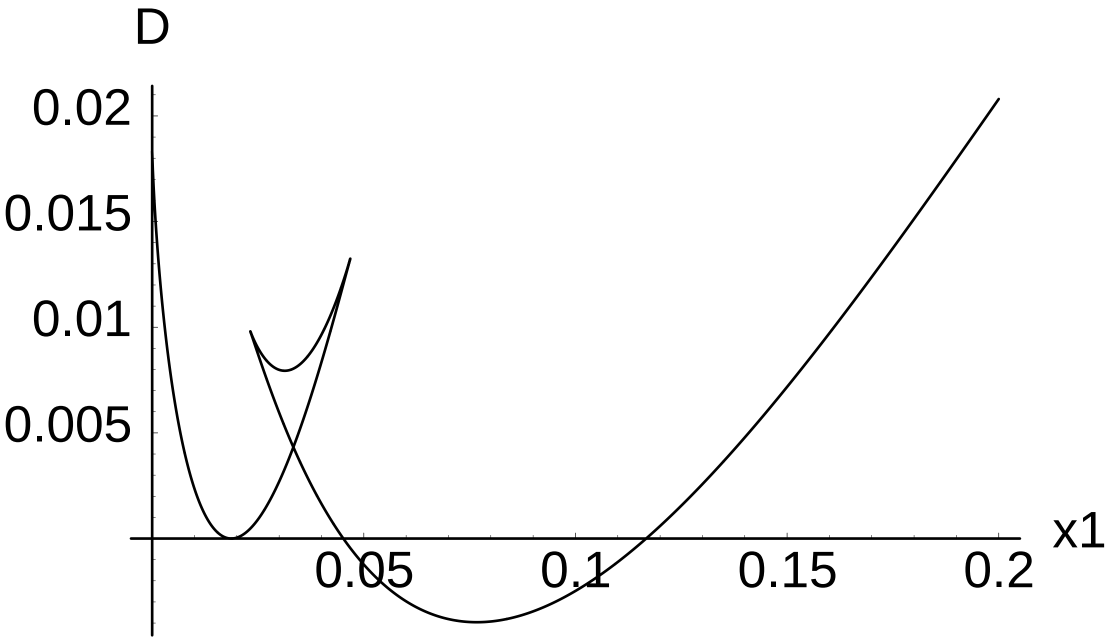
CH_4, H_2S, $T = 190$ K, $P = 40$ atm, $z_1 = 0.0187$, SRK model. Tangent plane distance D vs. x_1



- 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_2S, $T = 190$ 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): 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

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:
  - Identify and use function monotonicity
  - Let monotonicity information be inherited when an interval is bisected
  - Use special properties of mole fraction weighted averages

- "Standard" mixing rules used
  - Quadratic for a
  - Linear for b

Example 1 — Phase Stability

CH_4, H_2S, $T = 190$ 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

CO_2, CH_4, $T = 220$ K, $P = 60.8$ bar, PR model

Feed (z_1, z_2)	Number of Stationary Points	D_{min}	CPU time (sec)
(0.10, 0.90)	1	0.0	0.11
(0.20, 0.80)	3	-0.007	0.33
(0.30, 0.70)	3	-0.0002	0.36
(0.43, 0.57)	3	-0.001	0.35
(0.60, 0.40)	1	0.0	0.29

CPU times on Sun Ultra 2/1300.

Example 3 — Phase Stability

Green et al. (1993) ternary, $T = 400$ K, $P = 80$ atm, VDW model

Feed (z_1, z_2, z_3)	Number of Stationary Points	D_{min}	CPU time (sec)
(0.83,0.085,0.085)	3	-0.0099	0.70
(0.77,0.115,0.115)	3	-0.0036	0.76
(0.72,0.14,0.14)	3	-0.0036	0.83
(0.69,0.155,0.155)	3	0.0	0.85

CPU times on Sun Ultra 2/1300.

Example 4 — 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.

Example 5 — Phase Stability

CH_4, CO_2, H_2S, H_2O, PR model

Feed	Number of Stationary Points	D_{min}	CPU time (sec)
A	3	-0.027	60.4
B	3	-1.201	9.8
C	3	-0.295	10.2
D	3	-0.027	129.2

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.

Finding the global minimum

- Requires evaluation of an interval extension of the objective function D. This extra expense does not pay off on small problems.
- There is a known upper bound of zero (the tangent point) on the global minimum of D.
- If interval extension of D has positive lower bound over some interval, that interval cannot contain the global minimum and can be discarded.
- If interval extension of D has negative upper bound over some interval, global minimum will be negative, proving instability
- This is a special form of interval branch and bound combined with interval Newton
- For feed D in Problem 5, CPU time reduced from 129.2 sec to 2.9 sec.

Incorporating Local Techniques

- If a local method indicates instability then this is the correct answer as it means a point at which $D < 0$ has been found.

- If a local method indicates stability, however, this may not be the correct answer since the local method may have missed the global minimum in D.

- Combined local/global approach:
  - Use local methods to try to demonstrate instability.
  - If instability not found, only then use global interval method to confirm stability or identify instability.

Approach Used

- If $m(\mathbf{z}, v_{\mathbf{z}}) > 0 \Rightarrow$ unstable

- Evaluate D at pure components. If any $D < 0 \Rightarrow$ unstable

- For a number of randomly chosen compositions:
  - If $D < 0 \Rightarrow$ unstable
  - If $D \geq 0$, then start a local solver (Newton) and try to converge to a stationary point. If at termination $D < 0 \Rightarrow$ unstable

- If still not shown unstable, then apply interval approach to confirm stability or find instability missed by local techniques.

- This approach is implemented in the code INTSTAB (Hua *et al.*, 1997)

Effect of Local Approach

- Typical results comparing combined local/global approach with global only approach

Example Problem	Stable?	CPU time (sec) Global	CPU time (sec) Local/Global
1	N	0.20	0.002
3 (feed 1)	N	0.70	0.001
3 (feed 4)	Y	0.85	0.88
4 (feed 1)	N	1.3	0.002
4 (feed 4)	Y	0.54	0.58

- CPU times on Sun Ultra 2/1300 using INTSTAB.
- For unstable mixtures, instability generally detected in milliseconds.
- For stable mixtures, negligible increase in computation time.

Phase Equilibrium Problem

- Can formulate as global minimization of total Gibbs energy, subject to material balance constraints. May have multiple local minima.

- Can also formulate as equation solving problem: equifugacity equations and material balances. May have multiple solutions.

- Need to seek global solution, but local methods can be applied since phase stability analysis can be used as a global optimality test that can be applied to any local solution (Baker *et al.*, 1982).

- Correct solution of the phase stability problem is thus the key to correct solution of the phase equilibrium problem.

- Interval analysis guarantees correct solution of the phase stability problem, and so can also guarantee correct solution of the phase equilibrium (split) problem.

Global Solution of Phase Equilibrium Problem

- Can combine the global stability analysis with any standard phase split (or flash) algorithm.

- One approach
  - Perform global stability analysis. If unstable, use the local minima in D to generate initial guesses for the solution to the phase split problem.
  - For each such initial guess, use a local optimizer (SQP) to solve the phase split problem and then test for stability.
  - If global solution not found increase number of phases and continue.

- This approach is implemented in the code INTFLASH (Hua *et al.*, 1997)

Example 6 — Phase Equilibrium

CH_4, CO_2, H_2S, $T = 282.15$ K, $P = 59.5$ bar, PR model, $z_1 = 0.4995$, $z_2 = 0.0977$, $z_3 = 0.4028$

Phase I (L)	β^I	0.1748
	v^I	41.95 cm^3/mol
	$\mathbf{x}^I$	(0.1047,0.0727,0.8226)
Phase II (V)	β^{II}	0.8352
	v^{II}	280.1 cm^3/mol
	$\mathbf{x}^{II}$	(0.5832,0.1030,0.3138)
CPU	2.05 sec	

CPU times on Sun Ultra 2/1300 using INTFLASH.

Example 7 — Phase Equilibrium

CH_4, CO_2, H_2S, $T = 208$ K, $P = 54.9$ bar, PR model, $z_1 = 0.4989$, $z_2 = 0.0988$, $z_3 = 0.4023$

Phase I (V)	β^I	0.0702
	v^I	141.9 cm^3/mol
	$\mathbf{x}^I$	(0.9120,0.0417,0.0463)
Phase II (L)	β^{II}	0.3816
	v^{II}	53.46 cm^3/mol
	$\mathbf{x}^{II}$	(0.7539,0.0848,0.1613)
Phase III (L)	β^{III}	0.5482
	v^{III}	35.69 cm^3/mol
	$\mathbf{x}^{III}$	(0.2685,0.1158,0.6157)
CPU	9.0 sec	

CPU times on Sun Ultra 2/1300 using INTFLASH.

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
  - These equation system(s) often have multiple and/or trivial roots, or may have no solutions

Formulation : Simultaneous Approach

$$x_i \left(\ln P - \ln P_i^{sat} - \ln \gamma_i\right) = 0,\ i \in \mathcal{C}$$

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

- $\mathcal{C}$ is the set of all N components
- Ideal vapor phase
- P_i^{sat} and γ_i are functions of T
- All k-ary azeotropes $(k \leq N)$ are solutions, as are all of the pure components (trivial roots)
- Need solution method guaranteed to find all solutions

Formulation : Sequential Approach

- If $x_i \neq 0$

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

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

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

Formulation : Other Issues

- T dependence of γ_i
  - Treat explicitly using T-dependent parameters in γ_i model
  - Guess a reference temperature T_{ref} and treat T-dependent parameters as constants evaluated at T_{ref} $\Rightarrow$ No guarantee all azeotropes will be found, even if equations solved correctly

- Solutions of equifugacity equations may not be stable phases (liquid may split)
  - Need to check stability of liquid phase at azeotropic composition and temperature
  - Interval analysis also provides guaranteed method to determine stability

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, but 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

Example Problems

- Solved using both simultaneous and sequential approaches (with same results for azeotropic composition and temperature)

- Solved for case of T-dependent γ_i-model parameters and for the case of constant γ_i-model parameters

- Problem A1
  - Ethanol, Methyl Ethyl Ketone, Water
  - 1 atm, 10-100 °C, Wilson Equation

- Problem A2
  - Acetone, Chloroform, Methanol
  - 16.8 atm, 100-200 °C, NRTL Equation

- Problem A3
  - Acetone, Methyl Acetate, Methanol
  - 1 atm, 10-100 °C, Wilson Equation

- Have solved many other problems using Wilson, NRTL and UNIQUAC activity coefficient models with up to N=5

Results - Problem A1

Azeotropes

γ_i parameters	E	MEK	W	T (°C)
Constant (T_{ref}=73.7 °C)	0.49	0.51	0.00	74.1
	0.90	0.00	0.10	78.1
	0.00	0.68	0.32	73.7
	0.23	0.54	0.23	72.8
T-dependent	0.49	0.51	0.00	74.1
	0.91	0.00	0.09	78.2
	0.00	0.68	0.32	73.7
	0.23	0.54	0.23	72.8

CPU Times (Sun Ultra 1/140, sec)

	Constant	T dependent
Sequential	0.21	0.34
Simultaneous	0.90	4.62

E = Ethanol; MEK = Methyl Ethyl Ketone
W = Water

Results - Problem A2

Azeotropes

γ_i parameters	A	C	M	T (°C)
Constant	0.33	0.67	0.00	181.8
(T_{ref}=152.4°C)	0.29	0.00	0.71	155.3
	0.00	0.41	0.59	151.6
T-dependent	0.32	0.68	0.00	181.2
	0.29	0.00	0.71	155.4
	0.00	0.41	0.59	151.6

CPU Times (sec)

	Constant	T dependent
Sequential	0.51	0.82
Simultaneous	0.94	6.15

A = Acetone; C = Chloroform; M = Methanol

Results - Problem A3

Azeotropes

γ_i parameters	A	MA	M	T (°C)
Constant*	0.53	0.47	0.00	55.7
	0.75	0.00	0.25	54.5
	0.00	0.68	0.32	54.4
	0.27	0.47	0.26	54.3
T dependent	0.66	0.34	0.00	55.6
	0.79	0.00	0.21	55.4
	0.00	0.66	0.34	53.6

CPU Times (sec)

	Constant	T dependent
Sequential	0.40	1.04
Simultaneous	1.63	6.36

A = Acetone(1); MA = Methyl Acetate(2)
M=Methanol(3)

* $\Lambda_{12} = 0.480$, $\Lambda_{21} = 1.550$, $\Lambda_{13} = 0.768$
$\Lambda_{31} = 0.566$, $\Lambda_{23} = 0.544$, $\Lambda_{32} = 0.650$

Other Process Modeling Problems

1. Simple ethylene plant
2. Mixer/divider network
3. Adiabatic CSTR
4. Flash with recycle
5. Ammonia plant

Problem	Number of Equations	Number of Roots	CPU time (sec)
1	163	1	3.1
2	146	1	21.8
3	11	3	12.9
4	50		MAX
		1	4.0
5	177	1	1003

CPU times on BBN TC2000 (1 processor).

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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