Recent Advances in Reliable Nonlinear Equation Solving

Mark A. Stadtherr*

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

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*Phone: (219)631-9318; Fax: (219)631-8366; E-mail: markst@nd.edu

Background

- In steady-state process modeling, the central problem is the solution of a system of nonlinear equations (NLE):

$$\mathbf{f}(\mathbf{x}) = \mathbf{0}$$

- Solution of NLE problems is also the basis for many optimization methods.

- In engineering problems, the variables in an NLE solving problem are typically constrained physically within upper and lower bounds; that is:

$$\mathbf{x}^L \leq \mathbf{x} \leq \mathbf{x}^U$$

- These problems may:
  - Have multiple solutions
  - Have no solution
  - Be difficult to converge to any solution

Selected Recent Advances in NLE Solving

- Methods for parallel computation
- Tensor methods

$\Longrightarrow$ • Methods for finding (enclosing) all solutions

Methods for Parallel Computation

- Most methods are block oriented: decompose problem into disjoint or loosely coupled blocks
- May employ some multilevel iteration strategy
- Asynchronous vs. synchronous techniques

Tensor Methods

- Developed by Schnabel and colleagues.
- Based on quadratic model of the nonlinear function.
- Second order term based on a three-dimensional "tensor" which is computed from past function values.
- Computational tests indicate this approach is very well suited for problems with ill-conditioned or singular Jacobian, and is at least as efficient as "standard" methods on other problems.
- Has been extended to large, sparse problems.
- Has been extended to constrained optimization and compares favorably to SQP.

Methods for enclosing *all* solutions

- Global optimization approach
  - Developed by Floudas and colleagues
  - Reformulate the NLE solving problem as a minimization problem
  - Find global minimum (minima) deterministically using a branch-and-bound strategy with convex underestimating functions

$\Longrightarrow$ • Interval analysis approach

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, 1996; Neumaier, 1990)

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

- We have applied IN/GB successfully to several types of problems in chemical engineering

Interval Approach (Cont'd)

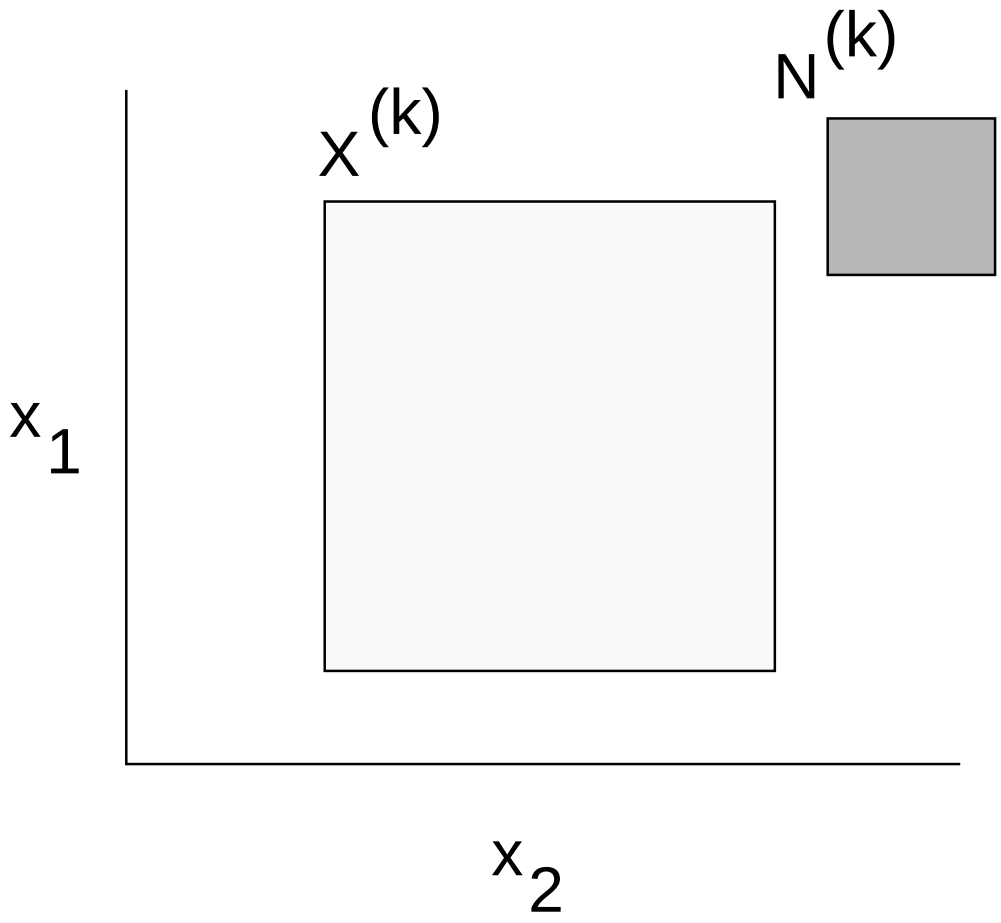
Problem: Solve $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ for all roots in interval $\mathbf{X}^{(0)}$.

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

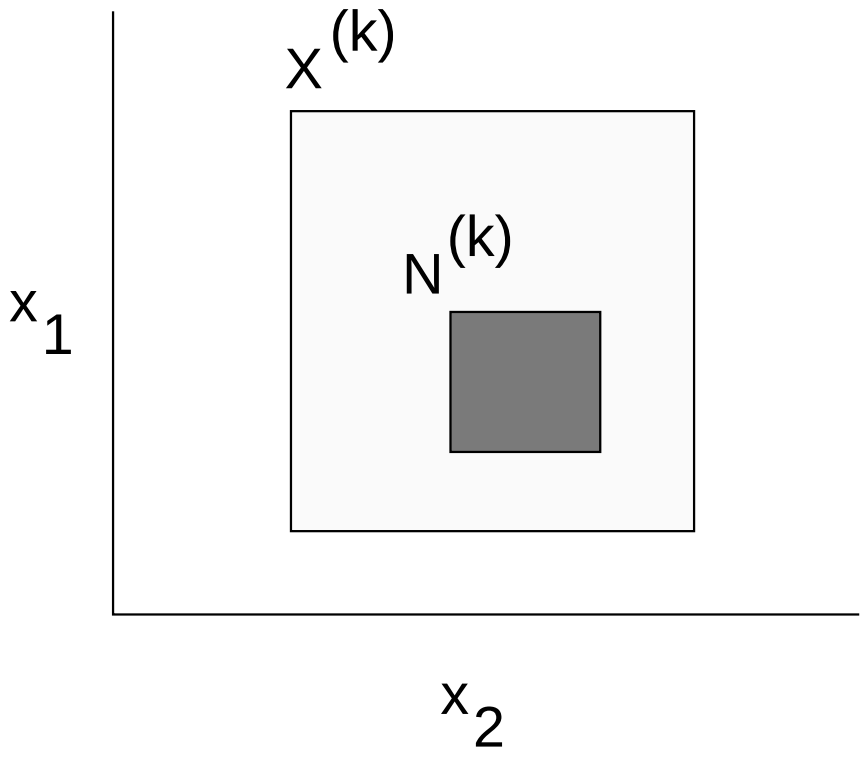
- Compute the interval extension (range) of each function in the system.
- If 0 is not an element of each range, delete the box.
- If 0 is an element of each range, then compute the $image$, $\mathbf{N}^{(k)}$, of the box by solving the interval Newton equation

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

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



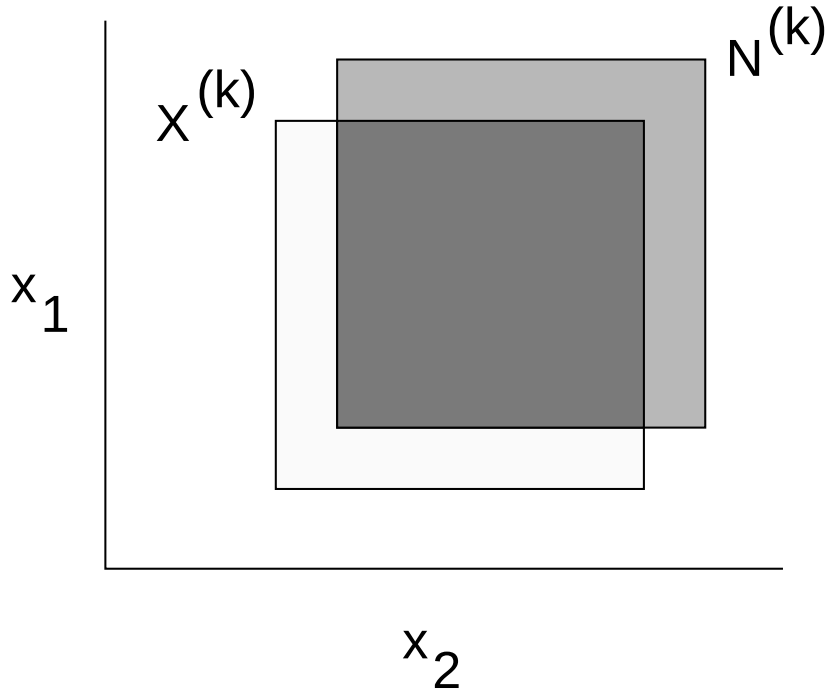
There was no solution in $X^{(k)}$



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.

Interval Approach (Cont'd)

- Can be extended to global optimization problems.
- No strong assumptions about the function $\mathbf{f}(\mathbf{x})$ need be made.
- The problem $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ must have a finite number of real roots in the given initial interval.
- The method is not suitable if $\mathbf{f}(\mathbf{x})$ is a "black-box" function.
- If there is a solution at a singular point, then existence and uniqueness cannot be confirmed. The eventual result of the IN/GB approach will be a very narrow enclosure that may contain one or more solutions.

Example – 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

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

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

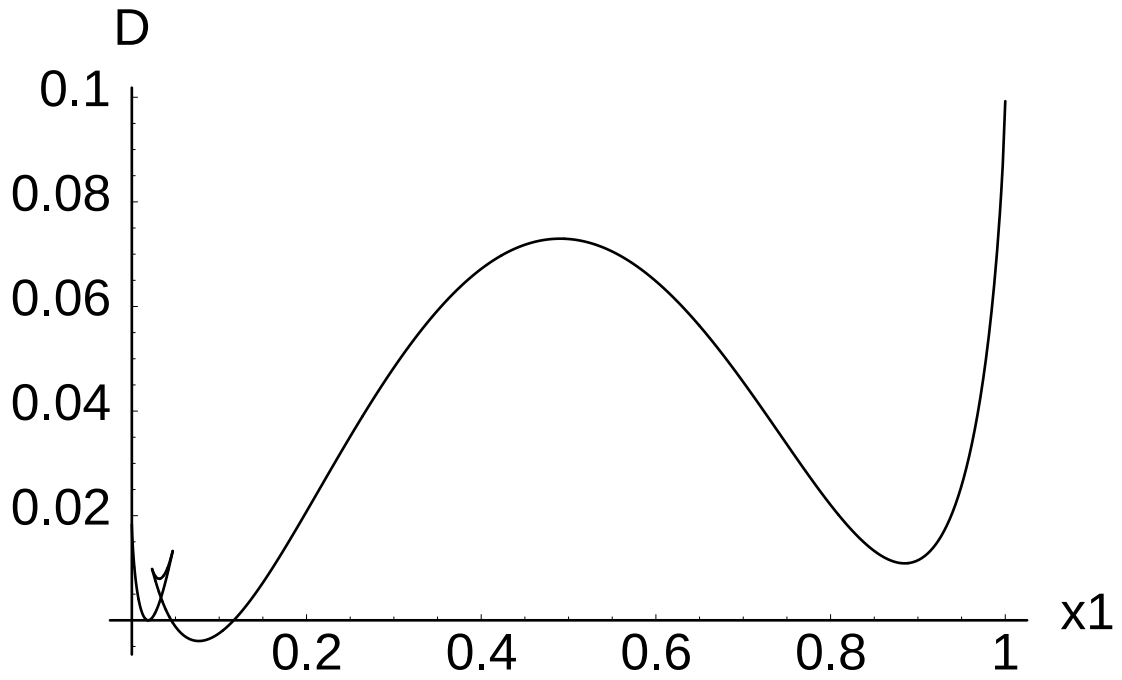
$$1 - \sum_{i=1}^{n} x_i = 0$$

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

- Trivial root at the feed composition $\mathbf{x} = \mathbf{z}$; may be multiple nontrivial roots. Need technique guaranteed to either find all the roots or find the root that corresponds to the global minimum in D.

Example 1 – Phase Stability

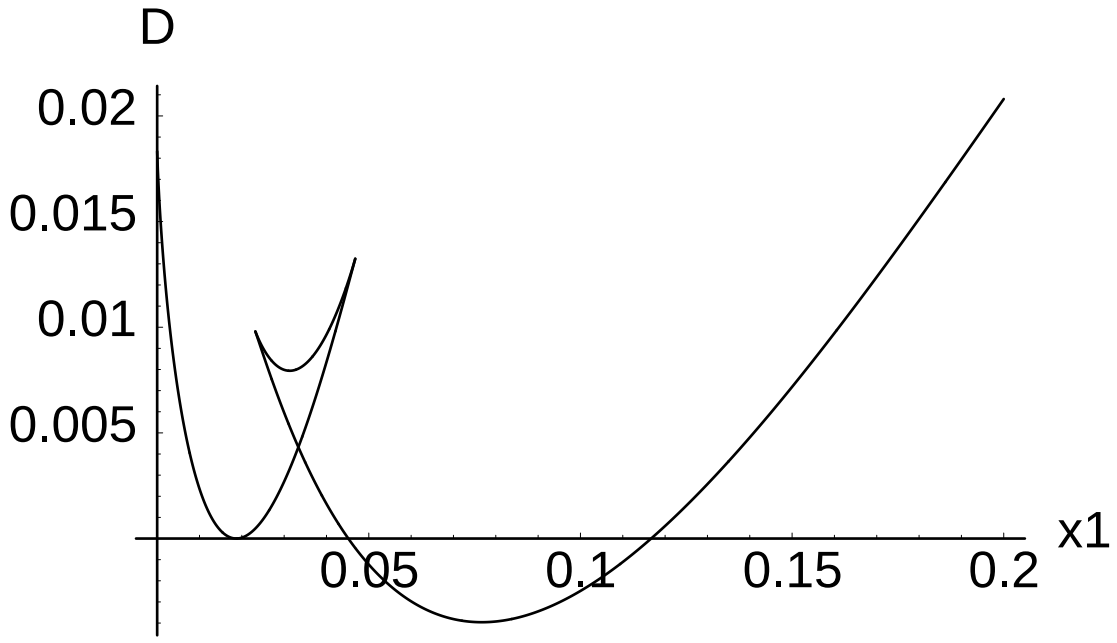
CH_4, H_2S, $T = 190$ K, $P = 40$ atm, $z_1 = 0.0187$, SRK EOS model. Tangent plane distance D vs. x_1



- 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 EOS model. Tangent plane distance D vs. x_1 (region near origin)



Example 1 (continued)

- Use interval method to solve the NLE system, finding all the stationary points
- Initial interval includes all physically feasible values of mole fraction and molar volume

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

CH_4, CO_2, H_2S, H_2O, PR EOS 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 stationary point that is the global minimum. The method can be implemented so that this is done.

Finding the Global Minimum Only

- Requires evaluation of an interval extension of the objective function D. This extra expense does not pay off on small problems.

- Can take advantage of the knowledge that there is a known upper bound of zero (the tangent point) on the global minimum of D.

- Technique used is a special form of interval branch and bound combined with interval Newton

- For feed D in Example 2, CPU time reduced from 129.2 sec to 2.9 sec.

- Interval method can be combined with local solvers to further increase efficiency (for unstable feeds) while maintaining rigor.

Example – Parameter Estimation

- Assuming a relative least squares objective and using an unconstrained formulation, the problem is

$$\min_{\boldsymbol{\theta}} \phi(\boldsymbol{\theta}) = \sum_{i=1}^{q} \sum_{\mu=1}^{p} \left[\frac{y_{\mu i} - f_i(\mathbf{x}_\mu, \boldsymbol{\theta})}{y_{\mu i}} \right]^2$$

- A common approach for solving this problem is to use the gradient of $\phi(\boldsymbol{\theta})$ and to seek the stationary points of $\phi(\boldsymbol{\theta})$ by solving $\mathbf{g}(\boldsymbol{\theta}) \equiv \nabla\phi(\boldsymbol{\theta}) = \mathbf{0}$. This system may have many roots, including local minima, local maxima and saddle points.

- To insure that the global minimum of $\phi(\boldsymbol{\theta})$ is found, the capability to find *all* the roots of $\mathbf{g}(\boldsymbol{\theta}) = \mathbf{0}$ is needed. This is provided by the interval technique (IN/GB).

- Interval Newton can be combined with branch-and-bound so that roots of $\mathbf{g}(\boldsymbol{\theta}) = \mathbf{0}$ that cannot be the global minimum need not be found.

Parameter Estimation in VLE Modeling

- Goal: Determine parameter values in liquid phase activity coefficient models (e.g. Wilson, van Laar, NRTL, UNIQUAC):

$$\gamma_{\mu i,\mathrm{calc}} = f_i(\mathbf{x}_\mu, \boldsymbol{\theta})$$

- The relative least squares objective is:

$$\phi(\boldsymbol{\theta}) = \sum_{i=1}^{n} \sum_{\mu=1}^{p} \left[\frac{\gamma_{\mu i,\mathrm{calc}}(\boldsymbol{\theta}) - \gamma_{\mu i,\mathrm{exp}}}{\gamma_{\mu i,\mathrm{exp}}} \right]^2 .$$

- Experimental values $\gamma_{\mu i,\mathrm{exp}}$ of the activity coefficients are obtained from VLE measurements at compositions $\mathbf{x}_\mu, \mu = 1, \ldots, p$.

- This problem has been solved for many models, systems, and data sets in the DECHEMA VLE Data Collection (Gmehling *et al.*, 1977-1990).

Example 3 – Parameter Estimation

- The binary system water (1) and formic acid (2) was studied.

- Eleven problems, each a different data set from the DECHEMA VLE Data Collection were considered.

- The model used was the Wilson equation. This has binary interaction parameters

$$\Lambda_{12} = (v_2/v_1)\exp(-\theta_1/RT) \text{ and}$$
$$\Lambda_{21} = (v_1/v_2)\exp(-\theta_2/RT)$$

  where v_1 and v_2 are pure component molar volumes.

- The energy parameters θ_1 and θ_2 must be estimated.

- Parameter estimation results for θ_1 and θ_2 are given in the DECHEMA Collection for all eleven problems.

Results–Example 3

- Each problem was solved using the IN/GB approach to determine the globally optimal values of the θ_1 and θ_2 parameters.

- These results were compared to those presented in the DECHEMA Collection.

- For each problem, the number of local minima in $\phi(\boldsymbol{\theta})$ was also determined (branch and bound steps were turned off).

- Table 1 presents a summary of these results and comparisons. CPU times are on a Sun Ultra 2/1300 workstation.

Table 1: Example 3 – IN/GB results vs. DECHEMA values

Data Set	Data points	P (mmHg)	DECHEMA			IN/GB			No. of Minima	CPU time(s)
			θ_1	θ_2	$\phi(\boldsymbol{\theta})$	θ_1	θ_2	$\phi(\boldsymbol{\theta})$		
1	15	760	-195	759	0.0342	-195	759	0.0342	2	14.7
2	15	760	-278	1038	0.0106	-278	1038	0.0106	2	12.9
3	12	760	-310	1181	0.0151	-308	1167	0.0151	2	17.4
4	28	760	-282	985	0.353	-282	984	0.353	2	22.0
5	12	760	-366	1513	0.0257	-365	1509	0.0257	3	16.0
6	15	760	1067	-1122	0.0708	1065	-1120	0.0708	2	21.7
7*	14	200	892	-985	0.1410	**-331**	**1250**	**0.0914**	2	19.5
8*	11	200	370	-608	0.0459	**-340**	**1404**	**0.0342**	3	17.8
9*	16	100	539	-718	0.1650	**-285**	**996**	**0.1114**	2	24.4
10*	19	100	450	-663	0.1510	**-329**	**1394**	**0.0819**	3	27.4
11*	9	70	558	-762	0.0399	**-330**	**1519**	**0.0372**	3	16.4

*:New globally optimal parameters found.

- Detailed results (Figure 1 and Figure 2) will be shown for Data Set 10.

Figure 1: Data Set 10 – Comparison of Relative Deviation in γ_1

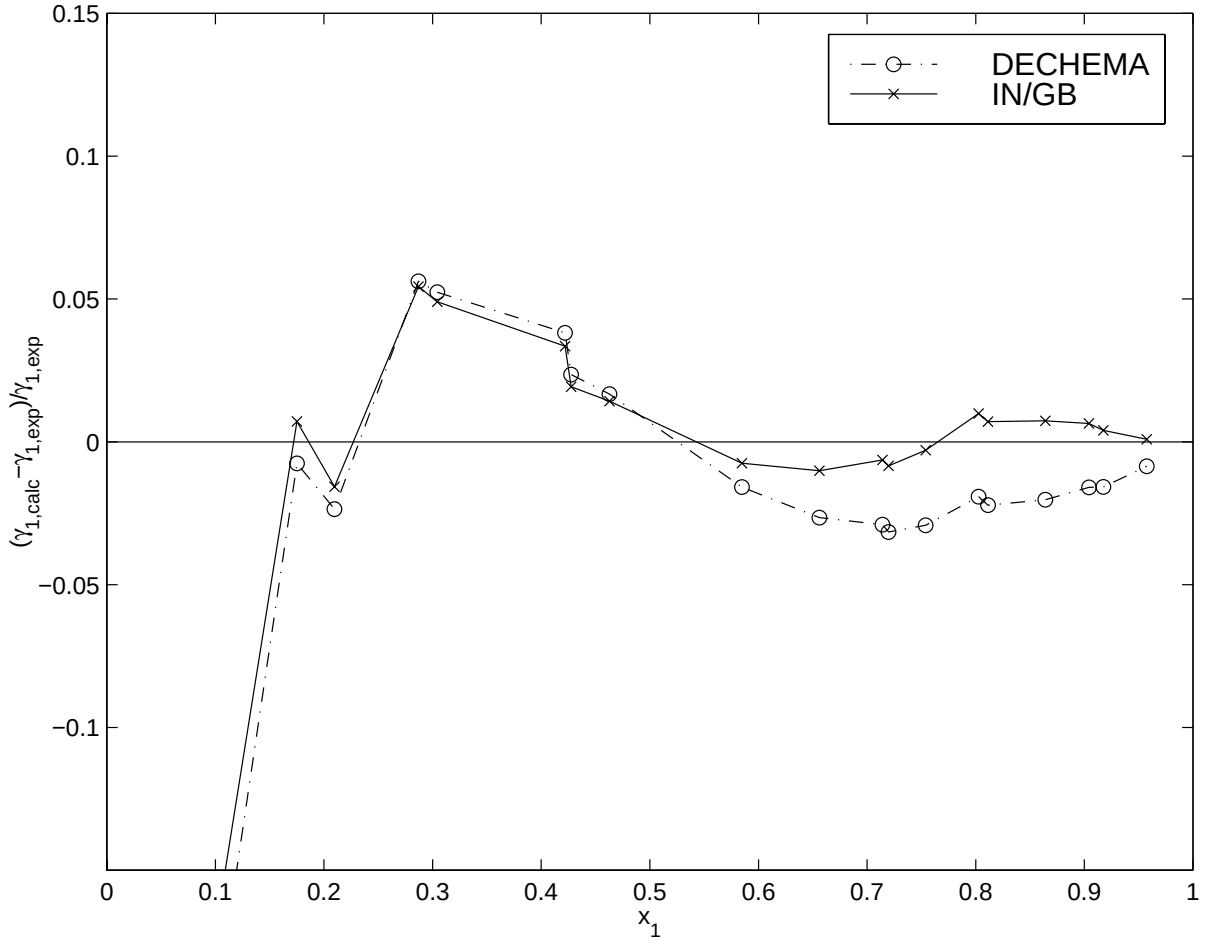
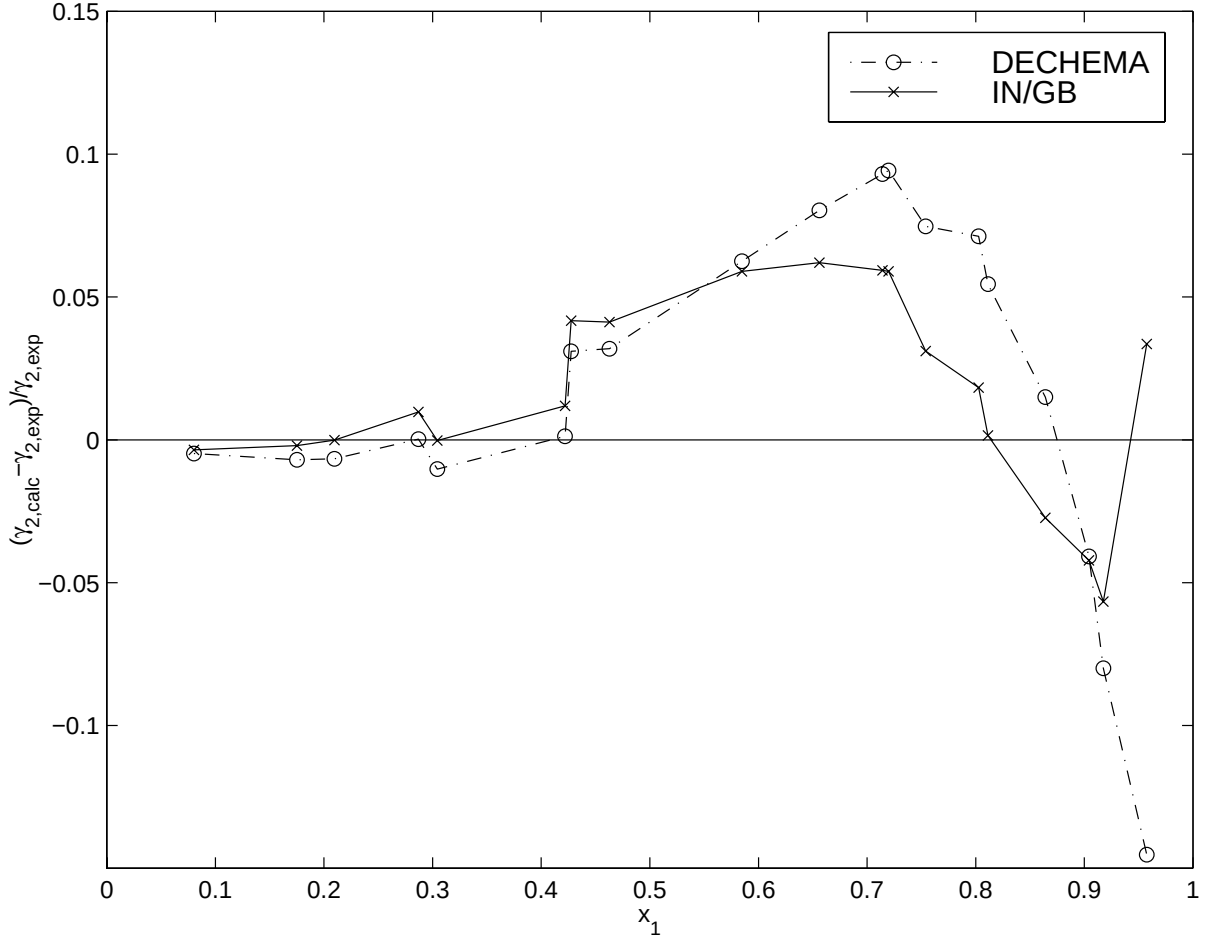


Figure 2: Data Set 10–Comparison of Relative Deviation in γ_2



Example 4 – Parameter Estimation

- The binary system benzene (1) and hexafluorobenzene (2) was studied.
- Ten problems, each a different data set from the DECHEMA VLE Data Collection were considered.
- The model used was the Wilson equation.
- Table 2 compares parameter estimation results for θ_1 and θ_2 with those given in the DECHEMA Collection. New globally optimal parameter values are found in five cases.

Table 2: Example 4 – IN/GB results vs. DECHEMA values

Data Set	Data points	T (^oC)	DECHEMA			IN/GB			No. of Minima	CPU time(s)
			θ_1	θ_2	$\phi(\boldsymbol{\theta})$	θ_1	θ_2	$\phi(\boldsymbol{\theta})$		
1*	10	30	437	-437	0.0382	**-468**	**1314**	**0.0118**	2	15.1
2*	10	40	405	-405	0.0327	**-459**	**1227**	**0.0079**	2	13.7
3*	10	50	374	-374	0.0289	**-449**	**1157**	**0.0058**	2	12.3
4*	11	50	342	-342	0.0428	**-424**	**984**	**0.0089**	2	10.9
5	10	60	-439	1096	0.0047	-439	1094	0.0047	2	9.7
6	9	70	-424	1035	0.0032	-425	1036	0.0032	2	7.9

Data Set	Data points	P (mmHg)	DECHEMA			IN/GB			No. of Minima	CPU time(s)
			θ_1	θ_2	$\phi(\boldsymbol{\theta})$	θ_1	θ_2	$\phi(\boldsymbol{\theta})$		
7*	17	300	344	-347	0.0566	**-432**	**993**	**0.0149**	2	17.4
8	16	500	-405	906	0.0083	-407	912	0.0083	2	14.3
9	17	760	-407	923	0.0057	-399	908	0.0053	1	13.9
10	17	760	-333	702	0.0146	-335	705	0.0146	2	20.5

*:New globally optimal parameters found.

Example 4 – Discussion

- Does the use of the globally optimal parameters make a significant difference when the Wilson model is used to predict vapor-liquid equilibrium (VLE)?

- A common test of the predictive power of a model for VLE is its ability to predict azeotropes.

- Experimentally this system has two homogeneous azeotropes.

- Table 3 shows comparison of homogeneous azeotrope prediction when the locally optimal DECHEMA parameters are used, and when the global optimal parameters are used.

Table 3: Example 4 – Homogeneous azeotrope prediction

Data Set	$T(^oC) or$ P (mmHg)	DECHEMA			IN/GB		
		x_1	x_2	P or T	x_1	x_2	P or T
1	T=30	0.0660	0.9340	P=107	0.0541	0.9459	P=107
					0.9342	0.0658	121
2	40	0.0315	0.9685	168	0.0761	0.9239	168
					0.9244	0.0756	185
3	50	NONE			0.0988	0.9012	255
					0.9114	0.0886	275
4	50	NONE			0.0588	0.9412	256
					0.9113	0.0887	274
7	P=300	NONE			0.1612	0.8388	T=54.13
					0.9315	0.0685	52.49

- Based on DECHEMA results, one would conclude Wilson is a poor model for this system. But actually Wilson is a reasonable model if the parameter estimation problem is solved correctly.

Other Types of Problems Solved

- Location of azeotropes (Maier $et\ al.$, 1998, 1999, 2000)
  - Homogeneous
  - Heterogeneous
  - Reactive
- Location of mixture critical points (Stradi $et\ al.$, 1999)
- Solid-fluid equilibrium (Xu $et\ al.$, 2000)
- General process modeling problems – up to 163 equations (Schnepper and Stadtherr, 1996)

Concluding Remarks

- Interval analysis is a powerful *general-purpose* and *model-independent* approach for solving a variety of process modeling problems, providing a *mathematical and computational guarantee* of reliability.

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

- The guaranteed reliability of interval methods comes at the expense of a significant CPU requirement. Thus, there is a choice between fast local methods that are not completely reliable, or a slower method that is guaranteed to give the complete and correct answer.

- The modeler must make a decision concerning how important it is to get the correct answer.

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- For more information:
  - Contact Mark Stadtherr at markst@nd.edu