Reliable Modeling and Optimization for Chemical Engineering Applications: Interval Analysis Approach

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NSF Workshop on Reliable Engineering Computing, Savannah, GA, September 15–17, 2004

Outline

- Motivation – Reliability in Computing
- Problem Solving Methodology
- Applications in Chemical Engineering
  - Overview
  - Parameter estimation in modeling of vapor-liquid equilibrium (VLE)
  - Nonlinear dynamics – ecological modeling
  - Molecular modeling – transition state analysis
- Concluding Remarks

Motivation

- Many applications in chemical engineering deal with nonlinear models of complex physical phenomena, on scales from macroscopic to molecular
- A common problem is the need to solve a nonlinear equation systems in which the variables are constrained physically within upper and lower bounds; that is, to solve:

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

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

- These problems may:
  - Have multiple solutions – Have all been found?
  - Have no solution – Can this be verified?
  - Be difficult to converge to any solution using standard methods

Motivation (Cont'd)

- Another common problem is the need to globally minimize a nonlinear function, subject to nonlinear equality and/or inequality constraints:

$$\min_{\mathbf{x}} \phi(\mathbf{x})$$

subject to

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

$$\mathbf{g}(\mathbf{x}) \geq \mathbf{0}$$

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

- These problems may:
  - Have multiple local minima – Has the global minimum been found?
  - Require finding all local minima or stationary points – Have all been found?
  - Have no solution (infeasible NLP) – Can this be verified?
  - Be difficult to converge to any local minima using standard methods

Interval Analysis

- One approach for dealing with these issues is interval analysis
- Interval analysis can
  - Provide the tools needed to solve modeling and optimization problems with complete certainty
  - Provide problem-solving reliability not available when using standard local methods
  - Deal automatically with rounding error, thus providing both mathematical and computational guarantees

Interval Methodology

- Core methodology is 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
  - IN/GB can also be extended and employed as a deterministic approach for global optimization problems
- A general purpose approach; in general requires no simplifying assumptions or problem reformulations
- No strong assumptions about functions need to be made

Interval Methodology (Cont'd)

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

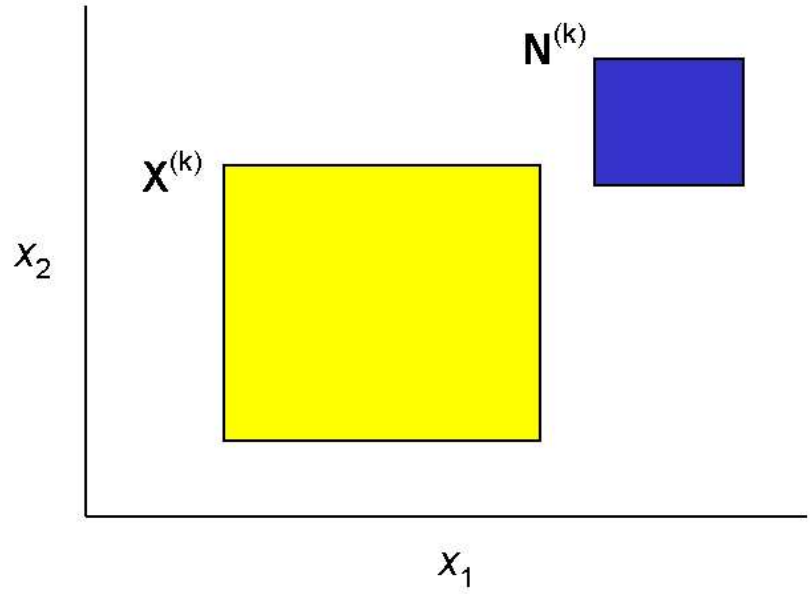
Basic iteration scheme: For a particular subinterval (box), $\mathbf{X}^{(k)}$, perform root inclusion test:

- (Range Test) Compute the interval extension $\mathbf{F}(\mathbf{X}^{(k)})$ of $\mathbf{f}(\mathbf{x})$ (this provides bounds on the range of $\mathbf{f}(\mathbf{x})$ for $\mathbf{x} \in \mathbf{X}^{(k)}$)
  - If $0 \notin \mathbf{F}(\mathbf{X}^{(k)})$, delete the box. Otherwise,
- (Interval Newton Test) Compute the *image*, $\mathbf{N}^{(k)}$, of the box by solving the linear interval equation system

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

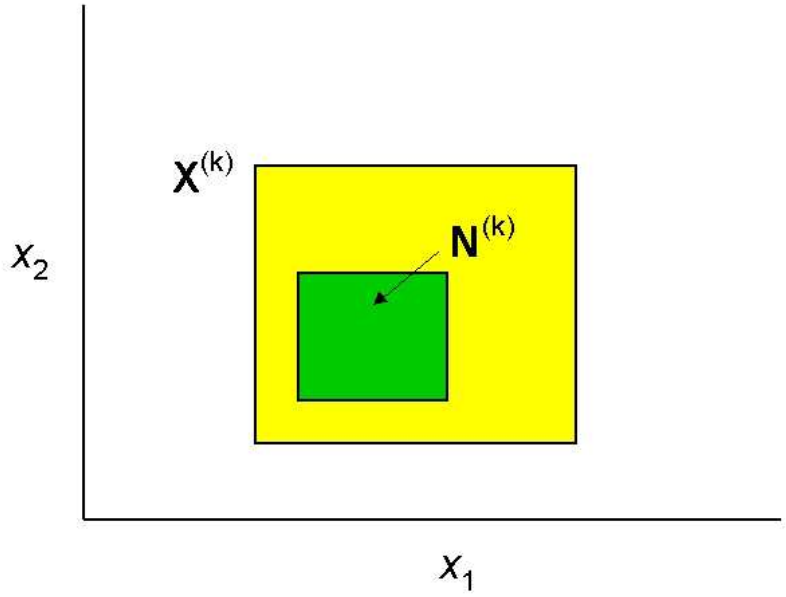
  - $\tilde{\mathbf{x}}^{(k)}$ is some point in $\mathbf{X}^{(k)}$
  - $\mathbf{F}'(\mathbf{X}^{(k)})$ is an interval extension of the Jacobian of $\mathbf{f}(\mathbf{x})$ over the box $\mathbf{X}^{(k)}$

Interval Methodology (Cont'd)



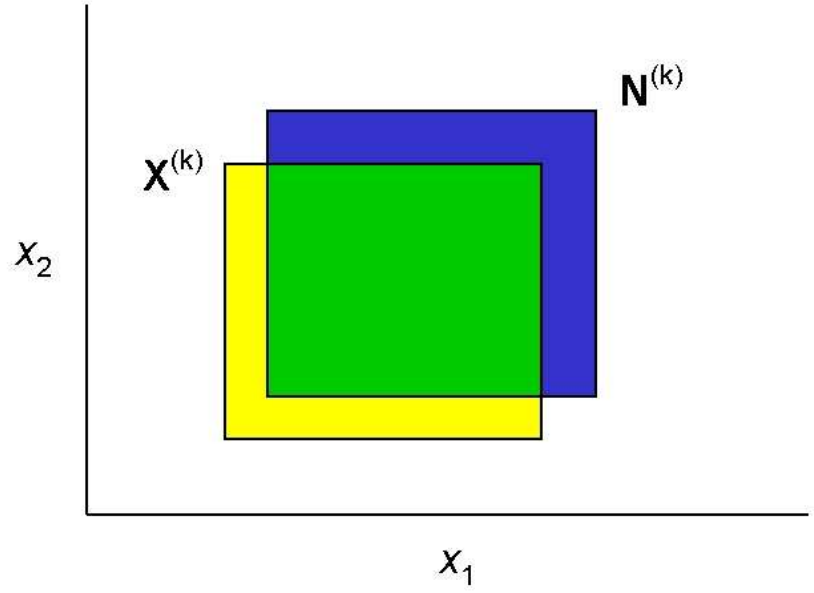
- There is no solution in $\mathbf{X}^{(k)}$

Interval Methodology (Cont'd)



- There is a *unique* solution in $\mathbf{X}^{(k)}$
- This solution is in $\mathbf{N}^{(k)}$
- Additional interval-Newton steps will tightly enclose the solution with quadratic convergence

Interval Methodology (Cont'd)



- Any solutions in $\mathbf{X}^{(k)}$ are in intersection of $\mathbf{X}^{(k)}$ and $\mathbf{N}^{(k)}$
- If intersection is sufficiently small, repeat root inclusion test
- Otherwise, bisect the intersection and apply root inclusion test to each resulting subinterval
- This is a branch-and-prune scheme on a binary tree

Interval Methodology (Cont'd)

- Can be extended to global optimization problems
- For unconstrained problems, solve for stationary points ($\boldsymbol{\nabla}\phi = \mathbf{0}$)
- For constrained problems, solve for KKT or Fritz-John points
- Add an additional pruning condition (objective range test):
  - Compute interval extension of objective function
  - If its lower bound is greater than a known upper bound on the global minimum, prune this subinterval
- This combines IN/GB with a branch-and-bound scheme on a binary tree

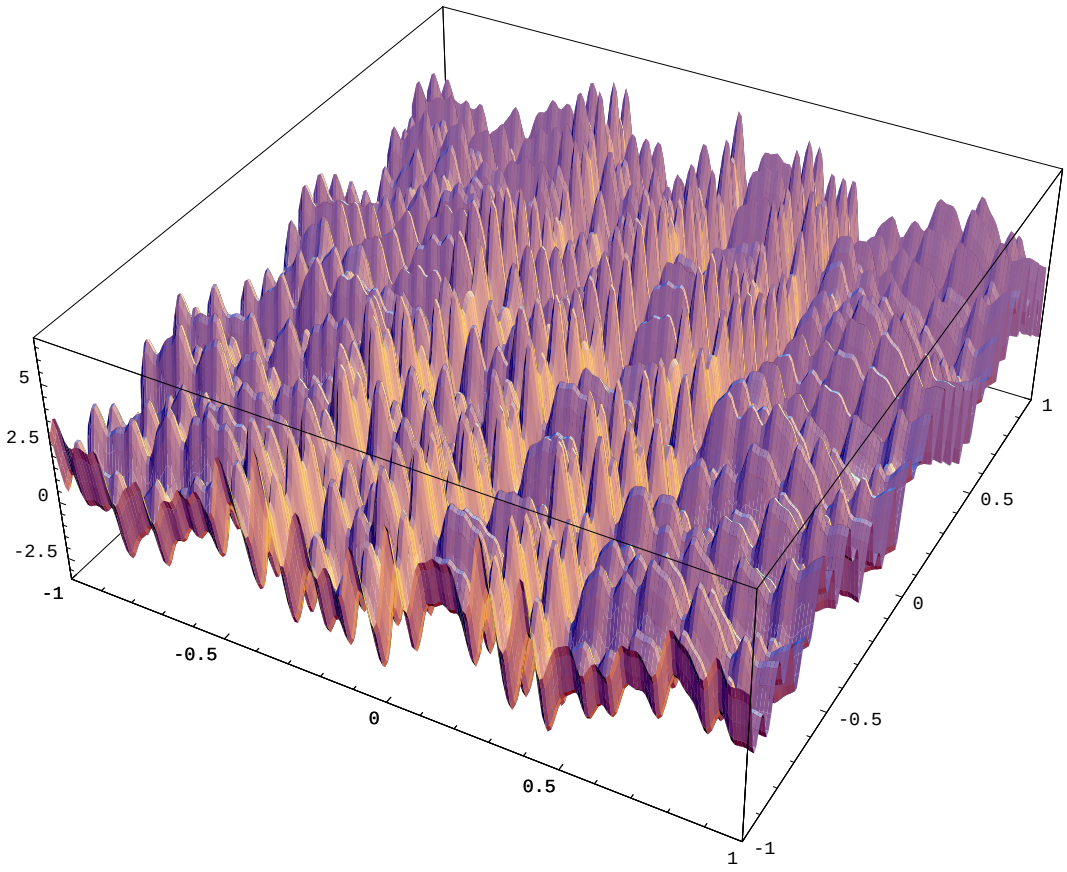
Interval Methodology (Cont'd)

Enhancements to basic methodology:

- Hybrid preconditioning strategy (HP) for solving interval-Newton equation (Gau and Stadtherr, 2002)
- Strategy (RP) for selection of the real point $\tilde{\mathbf{x}}^{(k)}$ in the interval-Newton equation (Gau and Stadtherr, 2002)
- Use of linear programming techniques to solve interval-Newton equation — LISS/LP (Lin and Stadtherr, 2003, 2004)
  - Exact bounds on $\mathbf{N}^{(k)}$ (within roundout)
- Constraint propagation (problem specific)
- Tighten interval extensions using known function properties (problem specific)

Example

- Trefethen (2002) Challenge Problem #4 — Find the Global Minimum



$$f(x,y) = \exp(\sin(50x)) + \sin(60\exp(y)) + \sin(70\sin(x)) + \sin(\sin(80y)) - \sin(10(x+y)) + (x^2+y^2)/4; \qquad x \in [-1,1]; \qquad y \in [-1,1]$$

Example (Cont'd)

- Global minimum is easily found using interval approach

$$x \in [-0.0244030796943751 7, -0.0244030796943751 6]$$

$$y \in [0.21061242715535 57, 0.21061242715535 58]$$

$$f \in [-3.30686864747524 5, -3.30686864747523 2]$$

- CPU time (LISS/LP): 0.16 seconds on SUN Blade 1000 model 1600 workstation

Another Example

- Find the global minimum of the function (Siirola et al., 2002):

$$f(\mathbf{x}) = 100 \prod_{i=1}^{N} \sum_{j=1}^{5} \left(\frac{j^5}{4425} \cos(j + j x_i) \right) + \frac{1}{N} \sum_{i=1}^{N} (x_i - x_{0,i})^2$$

  where $x_{0,i} = 3, \quad x_i \in [x_{0,i} - 20, x_{0,i} + 20], \quad i = 1, ..., N.$

- For $N = 6$, there are $\approx 10^{10}$ local optima.

- Results:

	Global Minimizer Points			
N	x_i^*	$x_{j \neq i}^*$	Global Minimum	CPU time (s)
2	4.6198510288	5.2820519601	-88.1046253312	0.07
3	4.6201099154	5.2824296177	-87.6730486951	2.12
4	4.6202393815	5.2826184940	-87.4572049443	33.95
5	4.6203170683	5.2827318347	-87.3276809494	413.61
6	4.6203688625	5.2828074014	-87.2413242244	4566.42

CPU times on Dell workstation – 1.7 GHz Xeon running Linux

Some Applications in Chemical Engineering

- Fluid phase stability and equilibrium
  - Activity coefficient models (Stadtherr *et al.*, 1995; Tessier *et al.*, 2000)
  - Cubic EOS (Hua *et al.*, 1996, 1998, 1999)
  - SAFT EOS (Xu *et al.*, 2002)
- Combined reaction and phase equilibrium (Burgos *et al.*, 2004)
- Location of azeotropes: Homogeneous, Heterogeneous, Reactive (Maier *et al.*, 1998, 1999, 2000)
- Location of mixture critical points (Stradi *et al.*, 2001)
- Solid-fluid equilibrium
  - Single solvent (Xu *et al.*, 2000, 2001)
  - Solvent and cosolvents (Scurto *et al.*, 2003)

Applications (cont'd)

- General process modeling problems (Schnepper and Stadtherr, 1996)
- Parameter estimation

$\Longrightarrow$ Relative least squares (Gau and Stadtherr, 1999, 2000)

  - Error-in-variables approach (Gau and Stadtherr, 2000, 2002)

- Nonlinear dynamics

$\Longrightarrow$ Equilibrium states and bifurcations in ecological models (Gwaltney *et al.*, 2004)

- Molecular Modeling
  - Density-functional-theory model of phase transitions in nanoporous materials (Maier *et al.*, 2001)

$\Longrightarrow$ Transition state analysis (Lin and Stadtherr, 2004)

  - Molecular conformations (Lin and Stadtherr, 2004)

Example – Parameter Estimation in VLE Modeling

- Goal: Determine parameter values $\boldsymbol{\theta}$ in activity coefficient models (e.g., Wilson, van Laar, NRTL, UNIQUAC):

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

- Use a relative least squares objective; thus, seek the minimum of:

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

- 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)

Parameter Estimation in VLE Modeling

- One binary system studied was benzene (1) and hexafluorobenzene (2)
- Ten problems, each a different data set from the DECHEMA VLE Data Collection were considered
- The model used was the Wilson equation

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]$$

- This has binary interaction parameters

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

  where v_1 and v_2 are pure component molar volumes

- The energy parameters θ_1 and θ_2 must be estimated

Results

- Each problem was solved using the IN/GB approach to determine the globally optimal values of the θ_1 and θ_2 parameters
- For each problem, the number of local minima in $\phi(\boldsymbol{\theta})$ was also determined (branch and bound steps were turned off)
- Table 1 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
- CPU times on Sun Ultra 2/1300

Table 1: 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**

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 2 shows comparison of homogeneous azeotrope prediction when the locally optimal DECHEMA parameters are used, and when the global optimal parameters are used

Table 2: 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

Example – Nonlinear Dynamics

- Nonlinear dynamic systems are of frequent interest in engineering and science

$$\dot{\mathbf{x}} = \frac{d\mathbf{x}}{dt} = \mathbf{f}(\mathbf{x}, \mathbf{p}); \qquad \mathbf{x} = \text{state variables}; \qquad \mathbf{p} = \text{parameters}$$

- Common problems include computing
  - Equilibrium states ($\dot{\mathbf{x}} = \mathbf{0}$)
  - Bifurcations of equilibria
  - Limit cycles
  - Bifurcations of cycles
- Of specific interest are food chain/web models
  - Use to predict impact on ecosystems of introducing new materials (ionic liquids) into the environment

Ionic Liquids

- Ionic liquids (ILs) are salts that are liquid at or near room temperature
- Many attractive properties
  - No measurable vapor pressure – ILs do not evaporate
  - Many potential applications, including replacement of volatile organic compounds (VOCs) currently used as industrial solvents
  - Eliminates a major source of air pollution
- Could enter the environment via aqueous waste streams
  - Very little environmental toxicity information available
  - Single species toxicity information is not sufficient to predict ecosystem impacts
- Need for ecological risk assessment – Modeling can play an important role

Finding Equilibrium States and Bifurcations

- Equilibrium states: Solve equilibrium conditions for $\mathbf{x}$

$$\dot{\mathbf{x}} = \frac{d\mathbf{x}}{dt} = \mathbf{f}(\mathbf{x}) = \mathbf{0}$$

- Bifurcations of equilibria: Solve augmented equilibrium conditions for $\mathbf{x}$ and parameter(s) of interest

- Augmenting conditions (in terms of Jacobian matrix $J = d\mathbf{f}/d\mathbf{x}$)
  - Fold and transcritical bifurcations: $\det(J(\mathbf{x}, \alpha)) = 0$
  - Hopf bifurcation: $\det(2J(\mathbf{x}, \alpha) \otimes I) = 0$
  - Fold-fold or fold-Hopf bifurcations: $\det(J(\mathbf{x}, \alpha, \beta)) = 0$ and $\det(2J(\mathbf{x}, \alpha, \beta) \otimes I) = 0$

Finding Equilibrium States and Bifurcations (cont'd)

- These equation systems commonly have multiple solutions
- Typically these systems are solved using a continuation-based strategy (e.g., Kuznetsov, 1991; AUTO software)
  - Initialization dependent
  - No guarantee of locating all solution branches
- Interval mathematics provides a method that is
  - Initialization independent
  - Capable of locating all solution branches with certainty
- As a relatively simple test problem (Gwaltney *et al.*, 2004), consider a tritrophic food chain with logistic prey and hyperbolic predator and superpredator response functions (Rosenzweig-MacArthur model)

Rosenzweig-MacArthur model

In terms of prey(1), predator(2) and superpredator(3) biomasses x_1, x_2 and x_3, the model is given by

$$\frac{dx_1}{dt} = x_1 \left[r\left(1 - \frac{x_1}{K}\right) - \frac{a_2 x_2}{b_2 + x_1} \right]$$

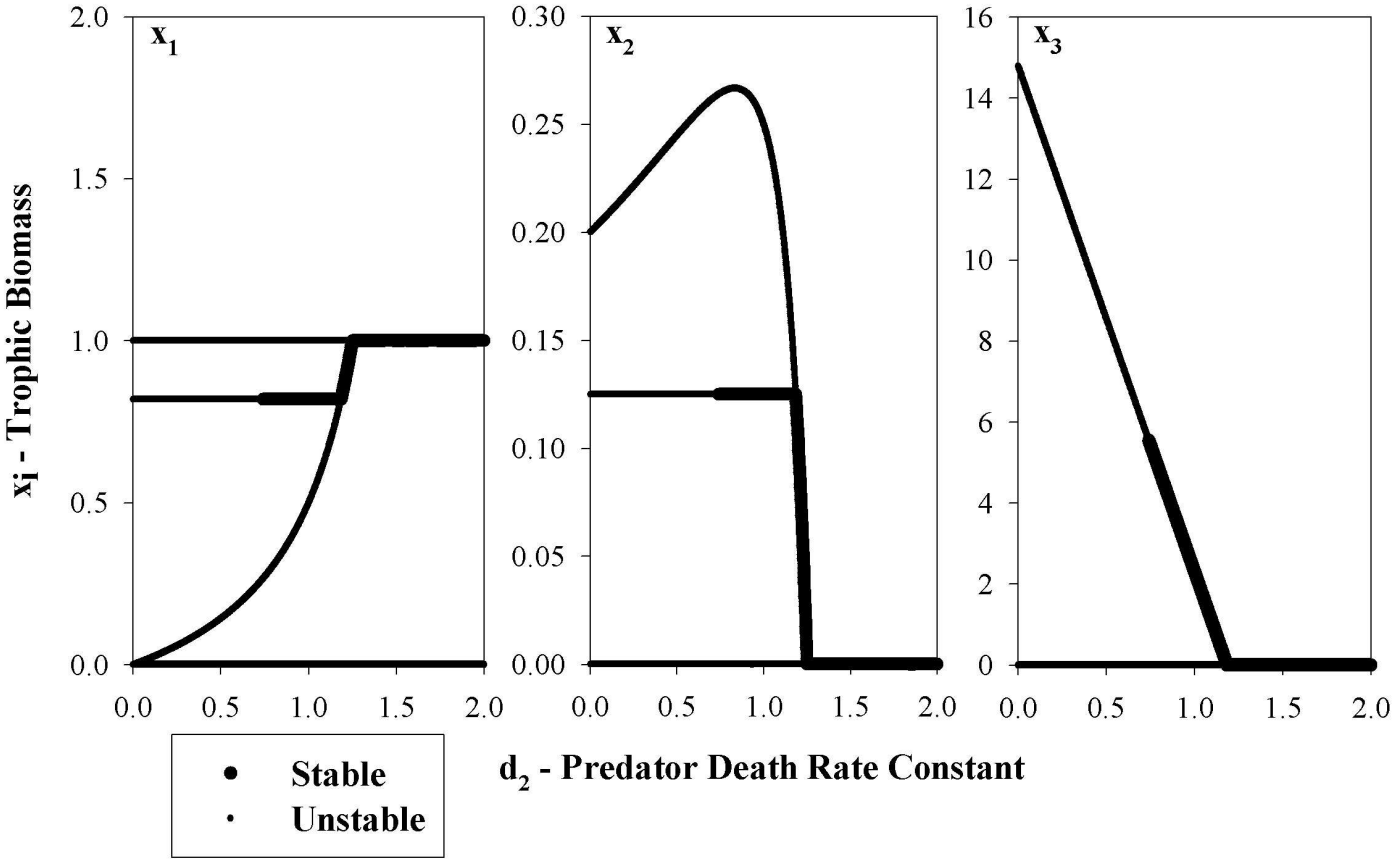
$$\frac{dx_2}{dt} = x_2 \left[e_2 \frac{a_2 x_1}{b_2 + x_1} - \frac{a_3 x_3}{b_3 + x_2} - d_2 \right]$$

$$\frac{dx_3}{dt} = x_3 \left[e_3 \frac{a_3 x_2}{b_3 + x_2} - d_3 \right]$$

Here r is the prey growth rate constant, K is the prey carrying capacity of the ecosystem, the d_i are death rate constants, the a_i represent maximum predation rates, the b_i are half-saturation constants, and the e_i are predation efficiencies

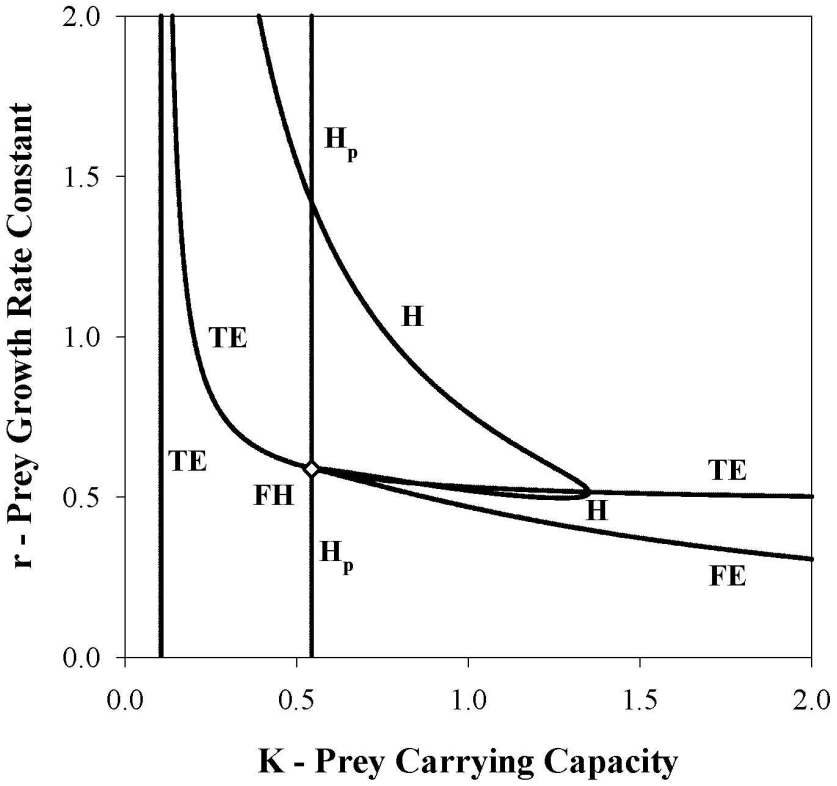
Results – Rosenzweig-MacArthur Model

Example of a solution-branch diagram (equilibrium states vs. one parameter with other parameters fixed) – here x_1, x_2 and x_3 vs. d_2



Results – Rosenzweig-MacArthur Model

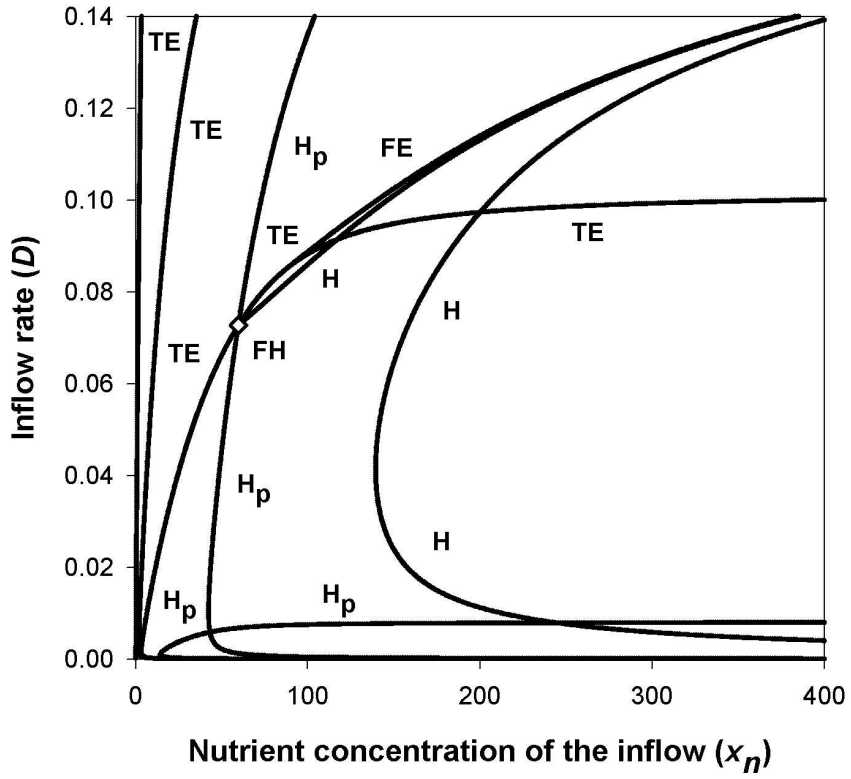
Example of a bifurcation diagram (parameter value at which bifurcation occurs vs. another parameter – here r vs. K with other parameters fixed)



TE = Transcritical of equilibrium; FE = Fold of equilibrium; H = Hopf; H_p = Planar Hopf; FH = Fold-Hopf

Results – Canale's Chemostat Model

This is a more complex model (4 state variables). This is the computed D vs. x_n bifurcation diagram



TE = Transcritical of equilibrium; FE = Fold of equilibrium; H = Hopf; H_p = Planar Hopf; FH = Fold-Hopf

Example – Transition State Analysis

- Transition state analysis is widely used in engineering and science to study the kinetics of various phenomena, e.g.,
  - Chemical reactions
  - Adsorption/desorption to/from surfaces
  - Diffusion through a porous media (e.g., zeolites)
- The key step is identifying stationary points on the potential energy surface $\mathcal{V}$ that characterizes the intermolecular and intramolecular interactions governing the system
- Motion in the system then is assumed to proceed as a series of hops from one local minimum to another, passing through a saddle point (transition state)
- Need a method that is guaranteed to find all stationary points of $\mathcal{V}$

Transition State Analysis (cont'd)

- One example problem – diffusion of xenon in silicalite (June *et al.*, 1991; Lin and Stadtherr, 2004)
- Use truncated Lennard-Jones 6-12 potential

$$\mathcal{V} = \sum_{i=1}^{N} \mathcal{V}_i$$

$$\mathcal{V}_i = \begin{cases} \frac{a}{r_i^{12}} - \frac{b}{r_i^6} & r_i < r_{\text{cut}} \\ 0 & r_i \geq r_{\text{cut}} \end{cases}$$

$$r_i^2 = (x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2$$

where (x, y, z) are the Cartesian coordinates of the xenon, and $(x_i, y_i, z_i), i = 1, \ldots, N$ are the Cartesian coordinates of the $N = 192$ oxygen atoms in a unit cell of the silicalite lattice

- Problem is to solve $\nabla \mathcal{V}(x, y, z) = 0$ for all stationary points (x, y, z)

Results using interval-Newton methodology (LISS_LP)

No.	Type	Energy(kcal/mol)	x(Å)	y(Å)	z(Å)	Connects
1	minimum	-5.9560	3.9956	4.9800	12.1340	
2	minimum	-5.8763	0.3613	0.9260	6.1112	
3	minimum	-5.8422	5.8529	4.9800	10.8790	
4	minimum	-5.7455	1.4356	4.9800	11.5540	
5	minimum	-5.1109	0.4642	4.9800	6.0635	
6	1st order	-5.7738	5.0486	4.9800	11.3210	(1, 3)
7	1st order	-5.6955	0.0000	0.0000	6.7100	(2′, 2)
8	1st order	-5.6060	2.3433	4.9800	11.4980	(1, 4)
9	1st order	-4.7494	0.1454	3.7957	6.4452	(2, 5)
10	1st order	-4.3057	9.2165	4.9800	11.0110	(3, 4)
11	1st order	-4.2380	0.0477	3.9147	8.3865	(2, 4)
12	1st order	-4.2261	8.6361	4.9800	12.8560	(3, 5′)
13	1st order	-4.1405	0.5925	4.9800	8.0122	(4, 5)
14*	2nd order	-4.1404	0.5883	4.8777	8.0138	(4,5),(4,4′)
15	2nd order	-4.1027	9.1881	4.1629	11.8720	(2,3),(4,5)

* Not found by June *et al.* (1991)

Concluding Remarks

- Interval analysis provides a powerful general purpose and model independent approach for solving a wide variety of modeling and optimization problems, giving a mathematical and computational guarantee of reliability.
- Guaranteed reliability of interval methods comes at the expense of CPU time. Thus, there is a choice between fast local methods that are not completely reliable, or a slower method that is guaranteed to give the correct answer.
- The modeler must make a decision concerning how important it is to get the correct answer.
- Continuing advances in computing hardware and software will make this approach even more attractive.
  - Compiler support for interval arithmetic (Sun Microsystems)
  - Parallel computing

Concluding Remarks (cont'd)

- With effective load management strategies, interval methods can be implemented very efficiently using MPI on a networked cluster of workstations (Gau and Stadtherr, 2002).
  - Good scalability
  - Exploit potential for superlinear speedup in optimization
- Parallel computing technology can be used not only to solve problems faster, but to solve problems more reliably.
- Reliability issues are often overlooked:

Are we just getting the wrong answers faster?