

Modeling and Computation of Phase Equilibrium Using Interval Methods

Mark A. Stadtherr

Department of Chemical and Biomolecular Engineering, University of Notre Dame

Notre Dame, IN, USA



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Outline

- Motivation and Background – [Computing Phase Equilibrium](#)
- Overview of Problem Solving Methodology
- Problem Formulation – [Asymmetric Models](#)
- Examples
- Related Problems
- Concluding Remarks

Motivation – Computing Phase Equilibrium

- At equilibrium,
 - How many phases are present?
 - What types of phases are present (vapor, liquid, solid)?
 - What is the composition of each phase?
 - How much of each phase is present?
- Typically the temperature, T , pressure, P , and overall composition (mole fraction), x_0 , are specified (but other specifications are possible)
- A **critical computation** in the simulation, optimization and design of a wide variety of industrial processes, especially those involving separation operations such as **distillation** and **extraction**
- Also important in the simulation of **enhanced oil recovery** processes, such as miscible or immiscible gas flooding
- Even when accurate models of the necessary thermodynamic properties are available, **it is often very difficult to reliably compute phase equilibrium**

Background – Computing Phase Equilibrium

- For phase equilibrium at constant temperature and pressure, **the total Gibbs energy of the system is minimized.**
- Gibbs energy models are available (equations of state, activity coefficient models, etc.)
 - **Symmetric approach:** Same model for all types of phases
 - **Asymmetric approach:** Different models for different types of phases
- Computation generally done in two (possibly alternating) phases:
 - **Phase stability problem**
 - **Phase split problem**

Background – Phase Stability Problem

- Determine if a given mixture (test phase) can **split into multiple phases**
- Can be interpreted as a **global optimality test** that determines whether the phase being tested corresponds to a global optimum in the total Gibbs energy of the system.
- Can be formulated as an optimization problem or equivalent nonlinear equations solving problem
- **Must be solved globally** to assure correct solution to the overall phase equilibrium problem

Background – Phase Split Problem

- Determine amounts and compositions of phases **assumed** to be present
- Can be interpreted as finding a **local minimum** in the total Gibbs energy, either by direct minimization, or by solving an equivalent nonlinear equation system (equipotential equations)
- This local minimum can then be **tested for global optimality** using phase stability analysis
- If necessary, the phase split calculation must then be **repeated**, perhaps changing the number and/or type of phases assumed to be present, until a solution is found that meets the global optimality test.
- **The correct global solution of the phase stability problem is the key in this two-stage global optimization procedure for phase equilibrium**
- Conventional solution methods for phase stability are initialization dependent, and may fail by converging to trivial or nonphysical solutions, or to a point that is a local but not a global minimum: **NEED FOR INTERVAL METHODS**

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

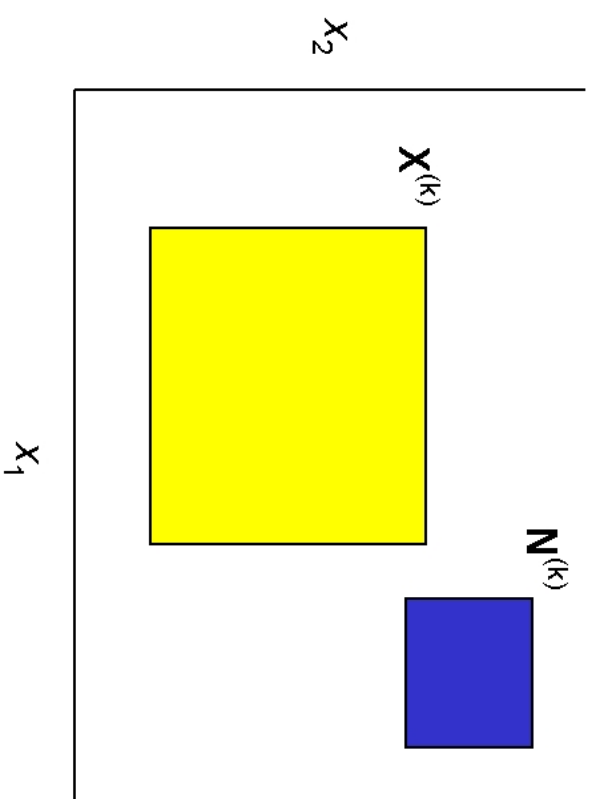
inclusion test:

- (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 $\mathbf{0} \notin \mathbf{F}(\mathbf{X}^{(k)})$, delete the box. Otherwise,
- (Interval Newton Test) Compute the *image*, $\mathbf{N}^{(k)}$, of the box by solving the linear interval equation system

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

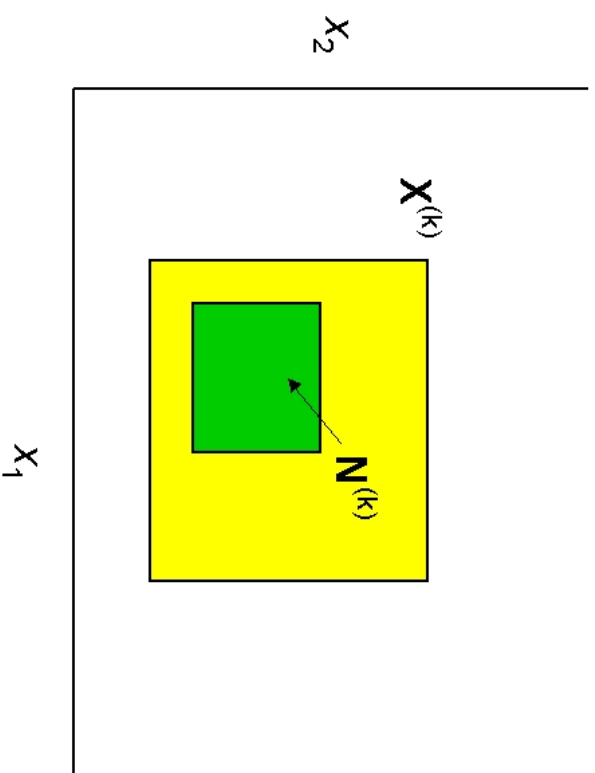
- $\tilde{\mathbf{x}}^{(k)}$ is some point in $\mathbf{X}^{(k)}$
- $\mathbf{F}'(\mathbf{X}^{(k)})$ is an interval extension of the Jacobian of $\mathbf{f}(\mathbf{x})$ over the box $\mathbf{X}^{(k)}$

Interval Methodology (Cont'd)



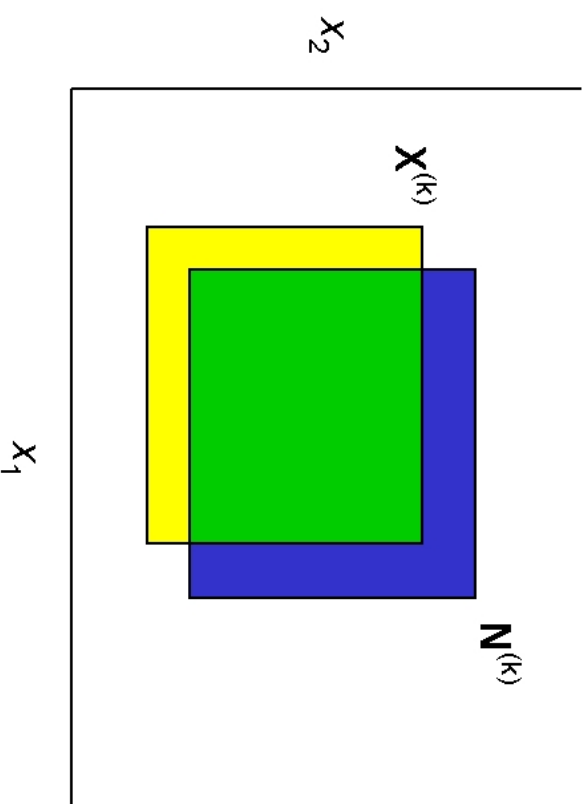
- There is no solution in $X^{(k)}$

Interval Methodology (Cont'd)



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

Interval Methodology (Cont'd)



- 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 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** ($\nabla \phi = \mathbf{0}$)
- 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)

Application to Phase Stability Analysis

- Will a mixture (feed) at a given T , P , and composition \mathbf{x}_0 split into multiple phases?
- Using **tangent plane analysis**, can be formulated as a minimization problem, or as an equivalent nonlinear equation solving problem.
- A phase at given T , P , and feed composition \mathbf{x}_0 is not stable (and may split) if the Gibbs energy vs. composition surface $g(\mathbf{x})$ ever falls below a plane tangent to the surface at \mathbf{x}_0

$$g_{tan}(\mathbf{x}) = g(\mathbf{x}_0) + \nabla g(\mathbf{x}_0)^T (\mathbf{x} - \mathbf{x}_0)$$

- That is, if the *tangent plane distance*
$$D(\mathbf{x}) = g(\mathbf{x}) - g_{tan}(\mathbf{x})$$
is negative for any composition \mathbf{x} , the phase is not stable.
- To prove stability, must show **global minimum** of D is zero.

Illustration

- Liquid-liquid equilibrium for the mixture of *n*-Butyl Acetate (1) and Water (2).
- Symmetric model using NRTL activity coefficient model to obtain the Gibbs energy.
- Gibbs energy (of mixing) vs. x_1

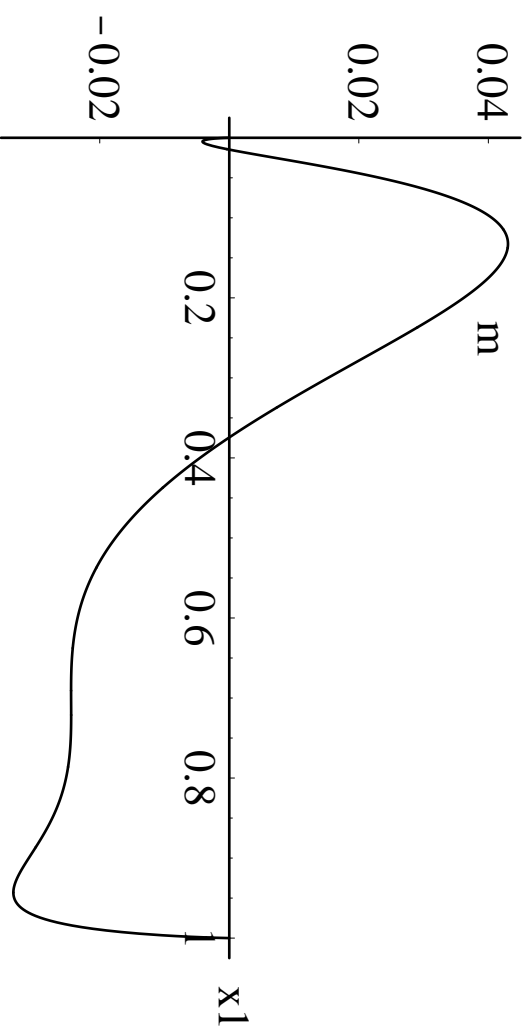
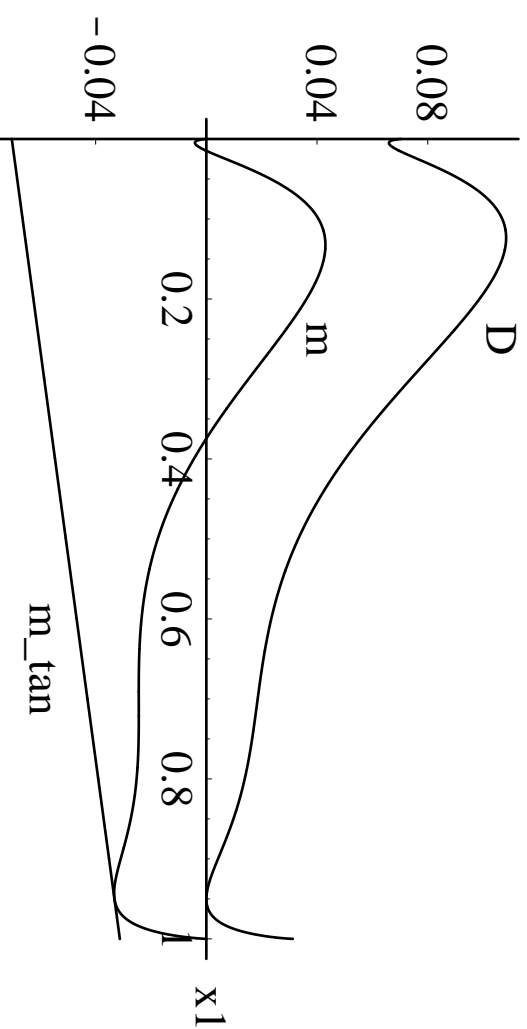


Illustration (cont'd)

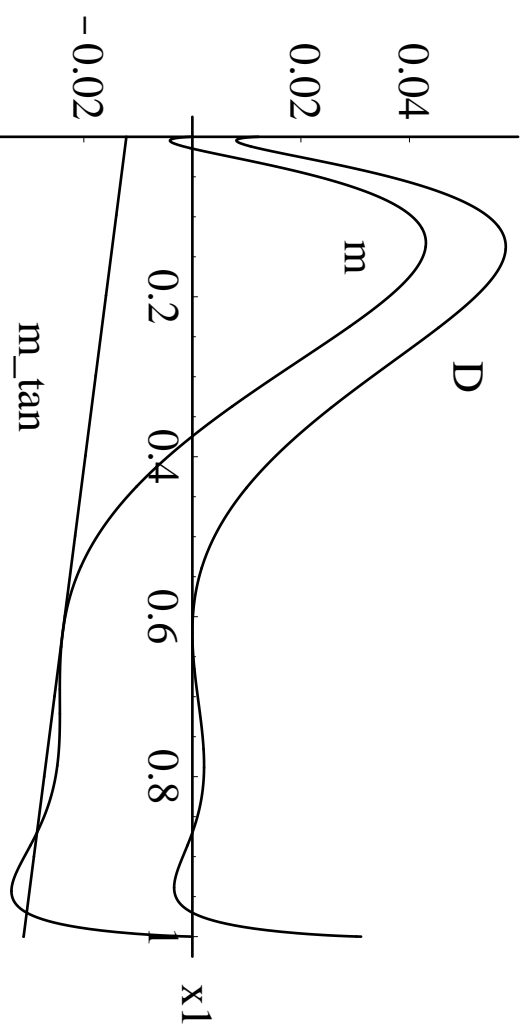
- For feed (test phase) composition $x_{0,1} = 0.95$



- A liquid phase of this composition is stable, since D is never negative (m_{tan} never crosses m .)

Illustration (cont'd)

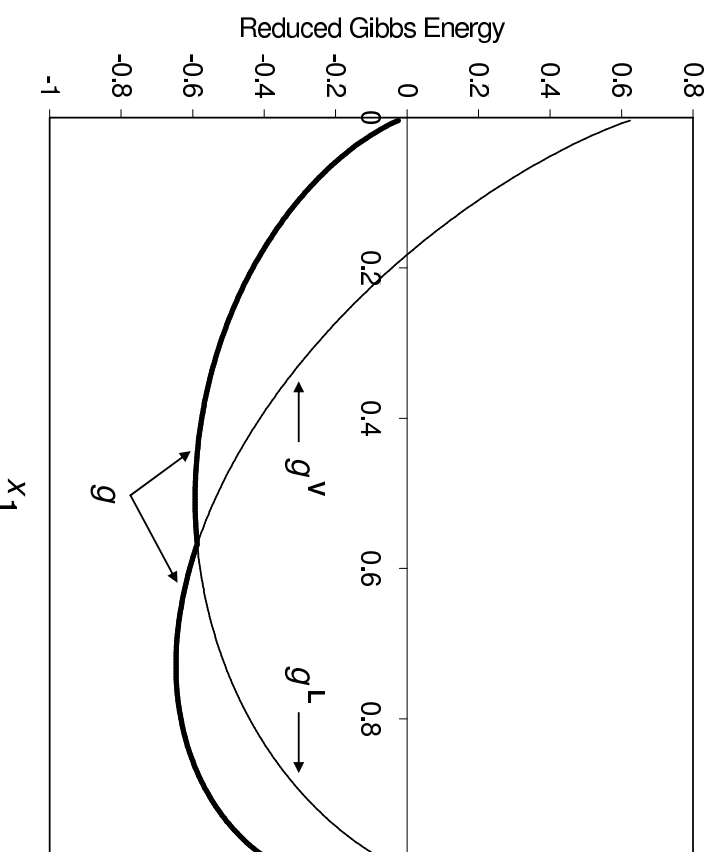
- For feed (test phase) composition $x_{0,1} = 0.62$



- A liquid phase of this composition is not stable and will split, since D becomes negative (m_{tan} crosses m .)
- At liquid-liquid equilibrium, m_{tan} touches m at two points (the phase compositions), and $D = 0$ at these points. These points are found in a phase split calculation.

Asymmetric Model

- Different Gibbs energy models for different types of phases
- Often used in the case of **vapor-liquid equilibrium** at low/moderate pressures.
 - Vapor phase model $g^V(\mathbf{x})$: Equation of state (e.g., Peng-Robinson, SRK)
 - Liquid phase model $g^L(\mathbf{x})$: Activity coefficient (e.g., NRTL)
- The system model is then $g(\mathbf{x}) = \min\{g^V(\mathbf{x}), g^L(\mathbf{x})\}$

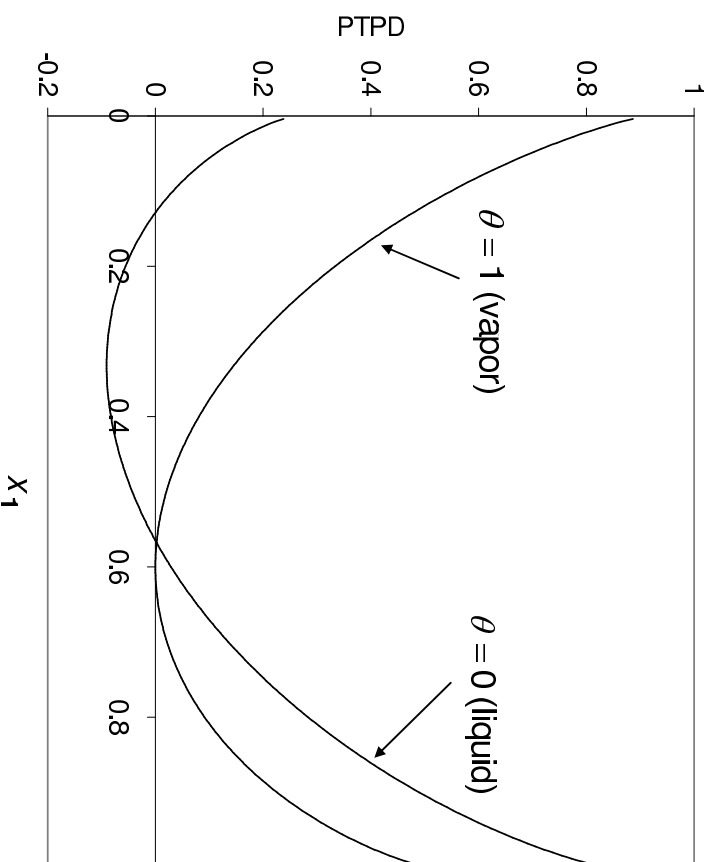


Asymmetric Model (cont'd)

- Tangent plane distance function is now

$$\begin{aligned} D(\mathbf{x}) &= \min[g^V(\mathbf{x}), g^L(\mathbf{x})] - g(\mathbf{x}_0) + \nabla g(\mathbf{x}_0)^T(\mathbf{x} - \mathbf{x}_0) \\ &= \min[D^V(\mathbf{x}), D^L(\mathbf{x})] \end{aligned}$$

- Objective in stability analysis is $\min_{\mathbf{x}} D(\mathbf{x}) = \min_{\mathbf{x}} \min[D^V(\mathbf{x}), D^L(\mathbf{x})]$



Asymmetric Model (cont'd)

- To deal with slope discontinuity, define a “pseudo tangent plane distance” objective function

$$\tilde{D}(\mathbf{x}) = \theta D^V(\mathbf{x}) + (1 - \theta) D^L(\mathbf{x})$$

with binary variable $\theta \in \{0, 1\}$ or $\theta(1 - \theta) = 0$

- Complete optimization problem, using cubic equation of state (EOS), is

$$\min_{\mathbf{x}, \theta, Z} \tilde{D}(\mathbf{x}, \theta, Z)$$

subject to

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

$$\text{EOS: } f(Z, \mathbf{x}) = Z^3 + b(\mathbf{x})Z^2 + c(\mathbf{x})Z + d(\mathbf{x}) = 0$$

$$\theta \in \{0, 1\} \quad \text{or} \quad \theta(1 - \theta) = 0$$

Asymmetric Model (cont'd)

- Usually the **stationary points** in this optimization problem are sought, since they can be used as **good initializations** in the phase split calculation
- Find stationary points by solving the nonlinear equation system

$$\frac{\partial \tilde{D}}{\partial x_i} - \frac{\partial \tilde{D}}{\partial x_n} = 0, \quad i = 1, \dots, n-1$$

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

$$f(Z, \mathbf{x}) = Z^3 + b(\mathbf{x})Z^2 + c(\mathbf{x})Z + d(\mathbf{x}) = 0$$

$$\theta \in \{0, 1\} \quad \text{or} \quad \theta(1 - \theta) = 0$$

- An $(n+2) \times (n+2)$ equation system to be solved using an interval Newton approach

Example

- Consider the binary mixture of 2,3-dimethyl-2-butene (component 1) and methanol (component 2)
- Vapor-liquid equilibrium measurements were made by Uusi-Kyyry et al. (2004) at atmospheric pressure
- The data was modeled using the NRTL activity coefficient model for the liquid phase and the SRK equation-of-state model for the vapor phase
- At $T = 325.243$, Uusi-Kyyry et al. (2004) use their model to compute phase equilibrium at $x_1 = 0.6233$ (liquid) and $y_1 = 0.4684$ (vapor). This is a close match to experimental data.
- Use interval method to test this result: Do stability analysis for $x_{1,0} = 0.6233$

Results

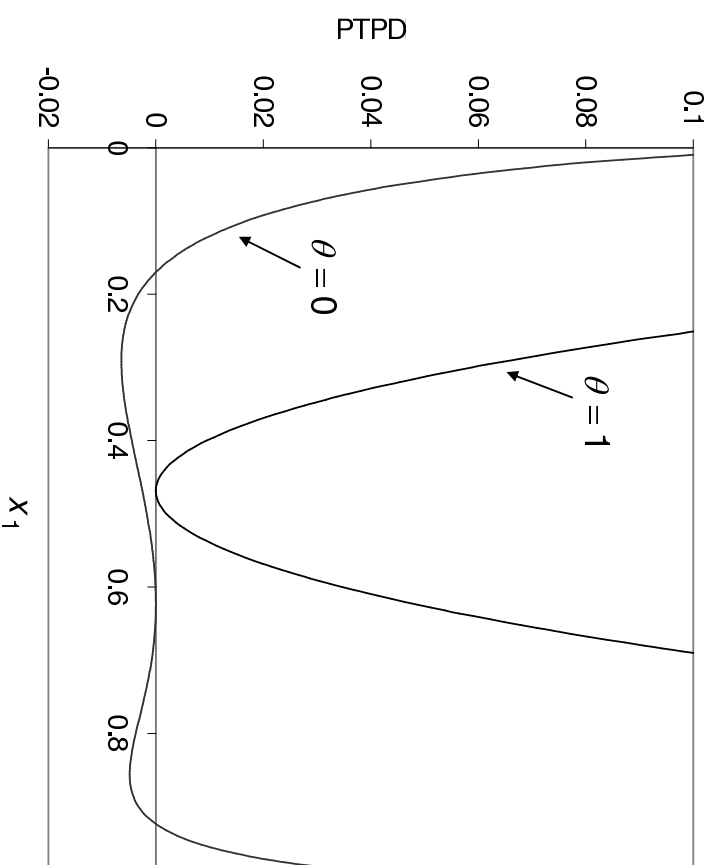
- For feed (test phase) composition $x_{1,0} = 0.6233$
- Computed stationary points are

x_1	θ	\ddot{D}
0.6233	0	0
0.4684	1	0
0.2914	0	-0.006428
0.8559	0	-0.004878

- A liquid with $x_1 = 0.6233$ is **not a stable phase**.
- Phase equilibrium calculation by Uusi-Kyyry et al. (2004) is **wrong!**

Results (cont'd)

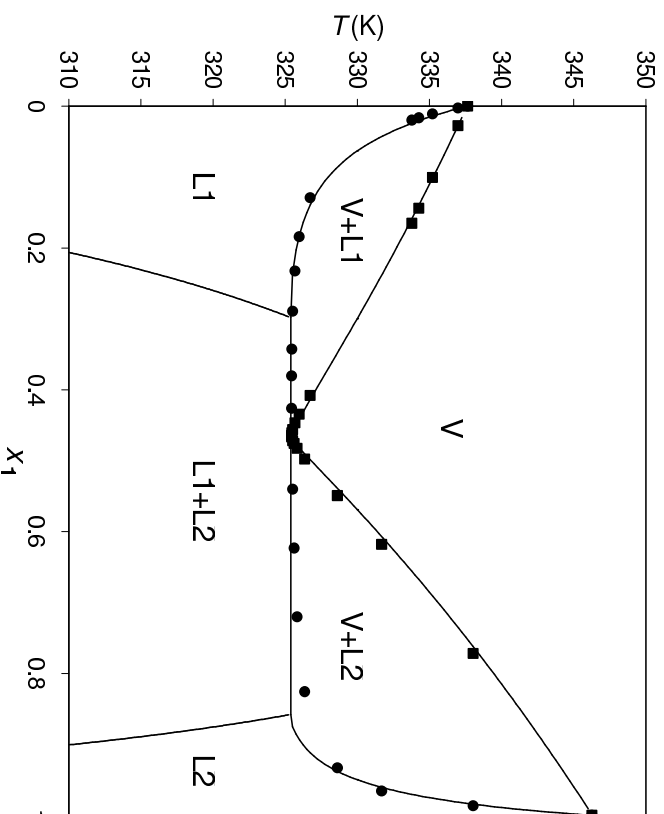
- Tangent plane distances curves are



- The correct phase equilibrium is liquid-liquid equilibrium with one phase at $x_1 = 0.29703$ and the other at $x_1 = 0.85822$.
- This is **not** what is observed experimentally.

Results (cont'd)

- Phase diagram computed using interval method vs. experimental data



- The model predicts a **heterogeneous azeotrope** (VLE line). Experimentally it is a **homogeneous azeotrope**.
- The model predicts **liquid-liquid** phase splits. This is not observed experimentally
- The model of Uusi-Kyyry et al. (2004) is poor.

Results (cont'd)

- **Q:** How did Uusi-Kyyny et al. (2004) go wrong?
- **A1:** In parameter estimation, they fit their experimental data to an **unstable solution** of the phase split problem, obtaining a poor model
- **A2:** In solving for phase equilibrium, they either did not check phase stability, or used a method that did not work correctly. Thus they obtained an **unstable solution** to the phase split problem
- **Second mistake cancels the first mistake**—experimental results successfully matched and model apparently validated
- **Incorrect solution of incorrect model** = match of experimental data = validated model
- Many such “validated” models exist in the literature

Another Example

- Consider the binary mixture of dichlorodifluoromethane (CFC-12) (component 1) and hydrogen fluoride (component 2)
- Vapor-liquid equilibrium measurements were made by Kang (1998) at $T = 303.15$ K. A liquid-liquid phase split was observed.
- The data was modeled using the NRTL activity coefficient model for the liquid phase and the Peng-Robinson equation-of-state model (with association terms) for the vapor phase.
- For overall composition $z_1 = 0.54$, Kang (1998) uses his to model to compute a liquid-liquid equilibrium with $x_1 = 0.0652$ for one phase and $x_1 = 0.8993$ for the second phase. This is a close match to the experimental observation.
- Use interval method to test this result: Do stability analysis for $x_{1,0} = 0.0652$

Results

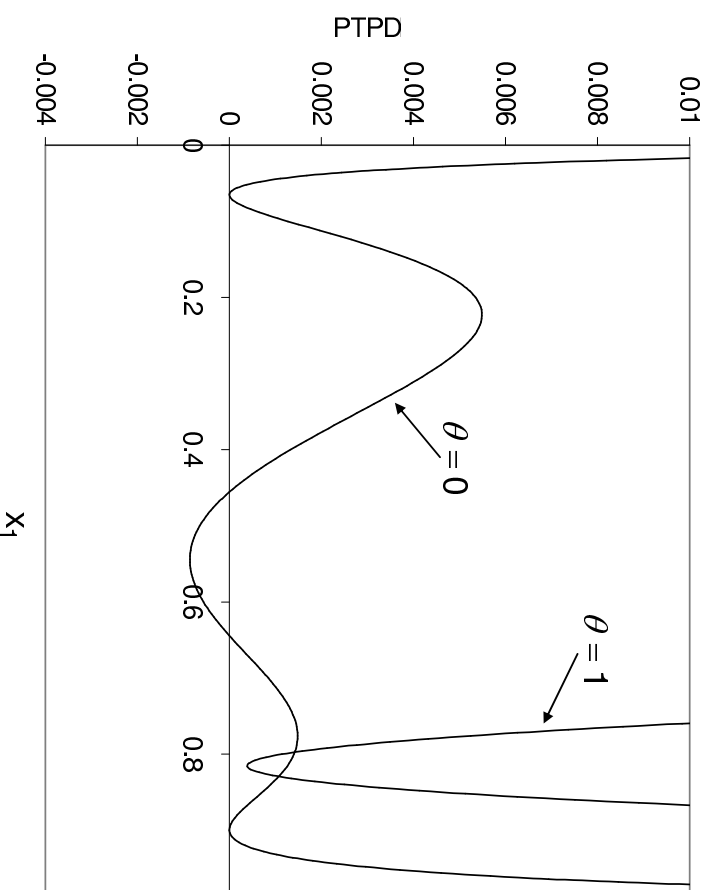
- For feed (test phase) composition $x_{1,0} = 0.0652$
- Computed stationary points are

x_1	θ	\tilde{D}
0.0652	0	0
0.8993	0	0
0.8152	1	0.0001724
0.2228	0	0.005488
0.5446	0	-0.0008581
0.7762	0	0.001485

- A liquid with $x_1 = 0.0652$ is **not a stable phase**.
- Phase equilibrium calculation by Kang (1998) is **wrong!**

Results (cont'd)

- Tangent plane distances curves are



- For overall composition of 0.54, the correct result is only a **single liquid phase**; this is **not** what is observed experimentally
- As in previous example, Kang (1998) fit his model parameters to an unstable solution of the phase split problem, then obtained match of experimental data by **incorrect solution of incorrect model**

Combining with Standard Software for Phase Equilibrium

- There are many **existing methods and software packages** for phase and chemical equilibrium
- Many are **very reliable** and fail to find the correct answer only occasionally
- We can use interval methods for phase stability to **validate correct results** from these codes and **identify incorrect results**
- **Corrective feedback** can be provided until a result that is correct is found and validated
- You can use your **favorite software package** for phase equilibrium, but still have validated result

Combining Interval Method with CHASEOS

- **CHASEOS** is a code for phase and chemical equilibrium using cubic equation-of-state models (symmetric)
 - Based on reactive phase split method of Castier et al. (1989) and Myers and Myers (1986)
 - Incorporates phase stability method of Michelsen (1982)
 - Very reliable, but can fail to get correct result in some cases
- Combine with **INTSTAB**, our code for phase stability analysis based on interval Newton approach
- Results from CHASEOS are passed to INTSTAB for validation
- If result is incorrect, then stationary points from INTSTAB are passed back to CHASEOS to get a new initialization for the phase split calculation
- The result is **V-CHASEOS** (Burgos et al., 2004)

Example: Using V-CHASEOS

- Consider system of acetic acid, ethanol, water, ethyl acetate and CO₂ at $T = 60\text{ C}$ and $P = 57.8\text{ atm}$.
- This problem arises in studying the esterification of acetic acid with ethanol using supercritical CO₂ as a solvent



- This is a reactive system. Want to consider both phase and reaction equilibrium.
- Apply V-CHASEOS

Example: Using V-CHASEOS (cont'd)

- For one set of model parameters:
- Initial run of CHASEOS computes a **vapor-liquid** equilibrium state
- INTSTAB determines that this is **not a stable state**. A new phase split initialization is returned to CHASEOS
- Next run of CHASEOS computes a **liquid-liquid** equilibrium state
- INTSTAB determines that this is **not a stable state**. A new phase split initialization is returned to CHASEOS
- Third run of CHASEOS computes a **vapor-liquid-liquid** equilibrium state (three phases)
- INTSTAB validates this result as a **stable equilibrium** state

Many 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)
- ⇒ Asymmetric models (Xu *et al.*, 2005)
- 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**
 - ⇒ **Relative least squares** (Gau and Stadtherr, 1999, 2000)
 - **Error-in-variables approach** (Gau and Stadtherr, 2000, 2002)
- **Nonlinear dynamics**
 - **Equilibrium states and bifurcations in ecological models** (Gwaltney *et al.*, 2004, 2005)
- **Molecular Modeling**
 - **Density-functional-theory model of phase transitions in nanoporous materials** (Maier *et al.*, 2001)
 - **Transition state analysis** (Lin and Stadtherr, 2004)
 - ⇒ **Molecular conformations** (Lin and Stadtherr, 2005)

Example – Parameter Estimation in VLE Modeling

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

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

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

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

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

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

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

- This has binary interaction parameters

$$A_{12} = (v_2/v_1) \exp(-\theta_1/RT)$$

$$A_{21} = (v_1/v_2) \exp(-\theta_2/RT)$$

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 $\phi(\theta)$ 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
- CPU times on Sun Ultra 2/1300

Table 1: IN/GB results vs. DECHEMA values

Data Set	Data points	T ($^{\circ}C$)	DECHEMA			IN/GB			No. of Minima	CPU time(s)
			θ_1	θ_2	$\phi(\theta)$	θ_1	θ_2	$\phi(\theta)$		
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	$\phi(\theta)$	θ_1	θ_2	$\phi(\theta)$		
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	$T(^{\circ}C)$ 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	0.9342	0.0658	121
2	40	0.0315	0.9685	168	0.0761	0.9239	168
		0.9244	0.0756	185	0.9244	0.0756	185
3	50	NONE			0.0988	0.9012	255
		NONE			0.9114	0.0886	275
4	50	NONE			0.0588	0.9412	256
		NONE			0.9113	0.0887	274
7	$P=300$	NONE			0.1612	0.8388	$T=54.13$
		NONE			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 – Molecular Conformations

- For a given molecule, there are typically many possible **conformational geometries** (structures)
- The conformation corresponding to the global minimum of the molecular potential energy surface (PES) is of particular importance, since it dictates both the **physical and chemical properties** of the molecule in the great majority of cases.
- The existence of a **very large number of local minima**, the number of which often increases exponentially with the size of the molecule, makes this global minimization problem extremely difficult.
- **Stochastic** methods for optimization typically used (SA, GA, MC, etc.)
- Interval methods provide a **deterministic** approach.

Molecular Conformations (cont'd)

- Consider the problem described by Lavor (2003): This is a linear chain of N atoms (crude model of an n -alkane)
- There is a known analytical solution, so this is a good test problem
- Lavor (2003) determined the global minimum in the PES using **interval branch-and-bound**
- The PES is given by

$$\mathcal{V} = \sum_{(i,j) \in M_3} [1 + \cos(3\omega_{ij})] + \sum_{(i,j) \in M_3} \frac{(-1)^i}{r_{ij}},$$

where

$$r_{ij} = \sqrt{10.60099896 - 4.14720682 \cos(\omega_{ij})} \quad (i, j) \in M_3.$$

- Determine the dihedral angles ω_{ij} , $(i, j) \in M_3$ that give the global minimum

Results

- Results using [interval-Newton-based approach](#) on Pentium 4 3.2GHz workstation

N	Global Minimum	CPU time(s)
5	-0.08224	0.0009
10	-0.58939	0.02
15	-0.49342	0.16
20	-1.00057	1.53
25	-0.90460	8.31
30	-1.41175	76.02
35	-1.31579	396.2
40	-1.82294	3499.5

- The largest problem solved by Lavor (2003) was for $N = 25$, which required about 5800 s (adjusted for speed difference in machines used)
- For a realistic model of an n -alkane, the largest problem we have solved is $N = 11$ (n -undecane)

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.
- In computing phase equilibrium, can **combine with standard codes** (Burgos *et al.*, 2004)
 - Use interval methods for phase stability analysis as a **final verification step**
 - Provide **corrective feedback** to the standard code
 - Symmetric and asymmetric models
- 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.**

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