Combined Local and Global Approach to Reliable Computation of Phase Equilibria

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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.

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

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

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

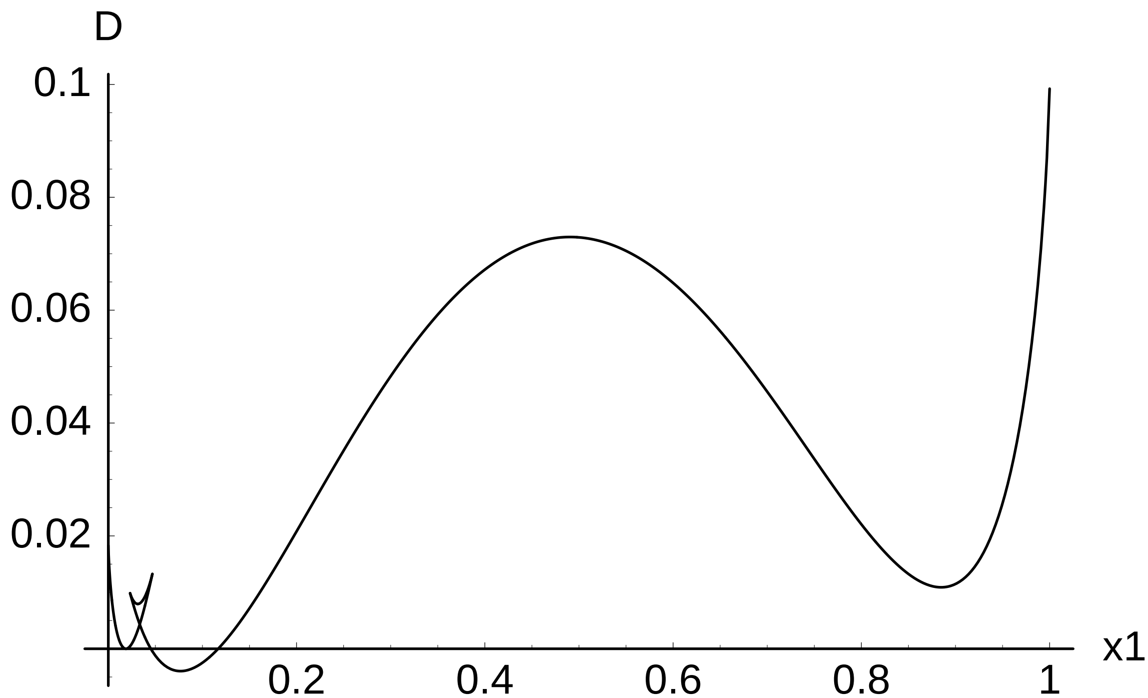
$$1 - \sum_{i=1}^{n} x_i = 0$$

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

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

Example 1

CH_4, H_2S, $T = 190$ K, $P = 40$ atm, $z_1 = 0.0187$, SRK model



- Five stationary points (four minima, one maximum).
- Standard local methods (e.g. Michelsen, 1982) known to fail (predict stability when system is actually unstable).

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 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
  - Can find with mathematical and computational certainty either all the solutions or that no solutions exist. (e.g., Kearfott 1987,1996; Neumaier 1990)

- A general purpose and model-independent approach
  - Requires no simplifying assumptions or problem reformulations
  - Can use for EOS models (with any mixing rule) or with activity coefficient models

- Details of algorithm given by Schnepper and Stadtherr (1996)

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

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.

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 (available from the authors)

Effect of Local Approach

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

Example Problem	Stable?	CPU time (sec)	
		Global	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 Split 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 split problem.
- Interval analysis guarantees correct solution of the phase stability problem, and so can also guarantee correct solution of the phase split problem.

Global Solution of Phase Split 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 (available from the authors)

Example 5 — Phase Split

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 6 — Phase Split

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.

Concluding Remarks

- Can combine speed of local methods with reliability of global interval analysis to compute multicomponent, multiphase equilibria with complete certainty.

- Have solved many other problems using VDW, PR and SRK equation of state models, as well as problems using NRTL and UNIQUAC activity coefficient models.

- Interval analysis provides a general-purpose and model-independent approach for solving phase stability and phase split problems, providing a mathematical and computational guarantee of reliability.

- Interval analysis provides powerful problem solving techniques with many other applications in the modeling of phase behavior and in other process modeling problems.

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