Interval Analysis for Thermodynamic Calculations in Process Design: A Novel and Completely Reliable Approach

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Summary

• In modeling phase behavior for process design, computational problems due to multiple roots or multiple local optima are well known (e.g., convergence to trivial or incorrect roots; convergence to a local but not global optimum).

• Many clever techniques have been devised to alleviate such difficulties, but there has been no general-purpose, model-independent, and completely reliable method for solving all phase behavior problems.

• Interval analysis provides a mathematically and computationally guaranteed method for reliably solving phase behavior problems.

• This is demonstrated using example problems in phase stability analysis and in finding homogeneous azeotropes, and can be applied to a variety of other problems.
Background—Interval Analysis

• A real interval $X = [a, b] = \{ x \in \mathbb{R} \mid a \leq x \leq b \}$ is a segment on the real number line and an interval vector $X = (X_1, X_2, ..., X_n)^T$ is an $n$-dimensional rectangle or “box”.

• Basic interval arithmetic for $X = [a, b]$ and $Y = [c, d]$ is $X \text{ op } Y = \{ x \text{ op } y \mid x \in X, y \in Y \}$ where $\text{op} \in \{+, -, \times, \div\}$. 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 $F(X)$ encloses all values of $f(x)$ for $x \in X$. That is, $F(X) \supseteq \{ f(x) \mid x \in X \}$.

• Interval extensions can be computed using interval arithmetic (the “natural” interval extension), or with other techniques.
Interval Newton Method

• For a system of nonlinear equations $f(x) = 0$, find (enclose) all roots in a given initial interval $X^{(0)}$ or determine that there are none.

• At iteration $k$, given the interval $X^{(k)}$, if $0 \in F(X^{(k)})$ solve the linear interval equation system

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

for the “image” $N^{(k)}$, where $F'(X^{(k)})$ is an interval extension of the Jacobian of $f(x)$ over the current interval $X^{(k)}$, and $x^{(k)}$ is a point inside $X^{(k)}$.

• Any root $x^* \in X^{(k)}$ is also contained in the image $N^{(k)}$, suggesting the iteration scheme $X^{(k+1)} = X^{(k)} \cap N^{(k)}$ (Moore, 1966).

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

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

- If a unique root cannot be confirmed ($N^{(k)} \subset X^{(k)}$) or ruled out ($X^{(k)} \cap N^{(k)} = \emptyset$), then either:
  - Continue with the next iterate $X^{(k+1)}$ if it is sufficiently smaller than $N^{(k)}$, or
  - Bisect $X^{(k+1)}$ 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 $f(x) = 0$, 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 $N^{(k)}$ (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 $z$ 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 $z$ is unstable if the Gibbs energy of mixing vs. composition surface

$$m(x, v) = \Delta g_{mix} = \Delta \hat{G}_{mix} / RT$$

ever falls below a plane tangent to the surface at $z$

$$m_{tan}(x) = m(z, v_z) + \sum_{i=1}^{n} \left( \frac{\partial m}{\partial x_i} \right) \bigg|_z (x_i - z_i)$$

- That is, if the tangent plane distance

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

is negative for any composition $x$, 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

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

subject to

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

$$EOS(x, v) = 0$$

• Trivial local optimum (minimum or maximum) at the feed composition $x = z$; 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 by solving the nonlinear equation system

\[
\left[ \left( \frac{\partial m}{\partial x_i} \right) - \left( \frac{\partial m}{\partial x_n} \right) \right] - \left[ \left( \frac{\partial m}{\partial x_i} \right) - \left( \frac{\partial m}{\partial x_n} \right) \right]_z = 0,
\]

\[i = 1, \ldots, n - 1\]

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

\[EOS(x, v) = 0\]

- Trivial root at the feed composition \(x = z\); may be multiple nontrivial roots. Need technique guaranteed to find all the roots.
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.
Example 1

CO$_2$ (1), *trans*-2-hexen-1-ol (2), $T = 303.15$ K, $P = 69.7016$ bar, $z_1 = 0.9991$, PR EOS model (standard mixing rules). Tangent plane distance $D$ vs. $x_1$:

region near $x_1 = 1$ (has multiple real $v$ roots):
Example 1 (continued)

- Five stationary points (four minima, one maximum).

- Standard local methods (e.g. Michelsen, 1982) known to fail (predict stability when system is actually unstable) because global minimum is not found.

- Easily solved (see Table 1) using interval method. Initial interval includes all physically feasible values of mole fraction and molar volume (no point initialization needed).

- Many other problems (two to five components) also easily solved using either EOS or excess Gibbs energy models (NRTL, UNIQUAC).

- Easily combined with fast, local flash algorithms to perform reliable phase equilibrium (split) calculations. Several two or three phase problems easily solved.
Example 1 — Phase Stability

$\text{CO}_2$ (1), \textit{trans}-2-hexen-1-ol (2), $T = 303.15$ K, $P = 69.7016$ bar, $z_1 = 0.9991$, PR EOS model

Table 1

<table>
<thead>
<tr>
<th>Feed ($z_1, z_2$) and CPU time</th>
<th>Stationary Points (roots) $(x_1, x_2, v$ [cm$^3$/mol])</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.9991, 0.0009) 0.71 sec</td>
<td>(0.9991, 0.0009, 160.8)</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>(0.9968, 0.0032, 106.1)</td>
<td>0.0020</td>
</tr>
<tr>
<td></td>
<td>(0.9728, 0.0272, 61.59)</td>
<td>-0.004</td>
</tr>
<tr>
<td></td>
<td>(0.8428, 0.1572, 57.97)</td>
<td>0.0030</td>
</tr>
<tr>
<td></td>
<td>(0.7018, 0.2982, 65.53)</td>
<td>$3.6 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

- 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.
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; can use sequential or simultaneous approach to formulate problem.
  – These equation system(s) often have multiple and/or trivial roots, or may have no solutions.
  – Account for temperature dependence using Antoine equation (ideal vapor phase) and temperature dependent activity coefficient model parameters (or evaluate parameters at a guessed “reference temperature” $T_{REF}$ assumed close to the azeotropic $T$).
Formulation: Sequential Approach

- \( \ln P - \ln P_i^{sat}(T) - \ln \gamma_i^L(T) = 0, \quad i \in C_{nz} \)

\[
1 - \sum_{i \in C_{nz}} x_i = 0
\]

- \( C_{nz} \) is a set of \( k \) nonzero components out of \( N \) total components.

- All \( k \)-ary azeotropes (\( k \leq N \)) for the chosen \( C_{nz} \) 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.
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 $\gamma_i$.
  - Improved reliability but no guarantee that all roots are found.

- Harding et al. (1997) use a branch and bound method.
  - Simultaneous and sequential approaches; $T_{REF}$ approach for T-dependence of $\gamma_i$.
  - Reformulation as a global optimization problem using convex underestimating functions.
  - Mathematical guarantee that all roots are found in $T_{REF}$ approach.
Example 2 — Homogeneous Azeotropes

UNIQUAC, Benzene(B), Ethanol(E) and Water(W), $P = 1.0$ atm. CPU time is on a Sun Ultra 1/140.

<table>
<thead>
<tr>
<th>Comps.</th>
<th>Mole Fr. (B E W)</th>
<th>$T$ (°C)</th>
<th>CPU (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE</td>
<td>0.552 0.448 0.000</td>
<td>67.66</td>
<td>0.036</td>
</tr>
<tr>
<td>BW</td>
<td>(0.572 0.000 0.428)*</td>
<td>(61.98)*</td>
<td>0.037</td>
</tr>
<tr>
<td>EW</td>
<td>0.000 0.886 0.115</td>
<td>78.11</td>
<td>0.041</td>
</tr>
<tr>
<td>BEW</td>
<td>no azeotrope</td>
<td></td>
<td>1.21</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td></td>
<td>1.32</td>
</tr>
</tbody>
</table>

* This is a solution to the equifugacity condition, but is not a homogeneous azeotrope since the liquid phase will split.

- Explicit $T$-dependence of activity coefficient model parameters accounted for (no $T_{REF}$ needs to be guessed).

- Many other problems (two to five components) easily solved, using Wilson, NRTL or UNIQUAC models, finding all azeotropes.
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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• For more information:
  – Contact Prof. Stadtherr at markst@nd.edu
  – See
    http://www.nd.edu/~markst/preprints.html
    http://www.nd.edu/~markst/presentations.html