Reliable Calculation of Phase Stability using Asymmetrical Modeling

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Outline:

- Motivation
- Asymmetrical modeling in phase equilibrium calculation, and a new scheme to test the phase stability using Pseudo-Tangent-Plane-Distance Function
- Solution method: Interval analysis
- Calculation examples
- Conclusion
Motivation:

- Asymmetrical modeling is widely used in thermodynamic problems (like DECHEMA data series), but phase stability tests are rare except for ideal gas vapor phase.
- Asymmetrical modeling brings additional difficulties to phase stability test, which is already a complicated problem.
Asymmetrical modeling

Apply different thermodynamic model to different phase, for example, using ideal gas model for vapor phase and activity coefficient model for liquid phase.

For general case of VLE

\[ y_i \phi_i P = x_i \gamma_i \phi_i^{sat} P_i^{sat} P_{oyn_i} \]
Asymmetrical modeling

Phase stability: Tangent-Plane-Distance analysis function based on the Gibbs energy of mixing

New approach ➔ Pseudo-Tangent-Plane-Distance analysis function (PTPDF):

\[
\text{minimize} \quad \tilde{D} = \theta D_1 + (1 - \theta) D_2
\]

s.t. \( \theta(\theta - 1) = 0 \)
Asymmetrical modeling

Pseudo-Tangent-Plane-Distance Function

\[ D_{\text{pseudo}} \]

\[ x \]

\[ \theta_{S_1} \]
Optimization problem for PTPD

**Ideal gas \((D_1)\)/Activity Coefficient\((D_2)\)**

\[
\begin{align*}
\text{minimize} & \quad \tilde{D} = \theta D_1 + (1 - \theta) D_2 \\
\text{s.t.} & \quad \sum_{i=1}^{n} x_i - 1 = 0, \\
& \quad \theta (\theta - 1) = 0
\end{align*}
\]

**Cubic EOS\((D_1)\)/Activity Coefficient\((D_2)\)**

\[
\begin{align*}
\text{minimize} & \quad \tilde{D} = \theta D_1 + (1 - \theta) D_2 \\
\text{s.t.} & \quad \sum_{i=1}^{n} x_i - 1 = 0, \\
& \quad \theta (\theta - 1) = 0 \\
& \quad f(Z, x) = Z^3 + b(x)Z^2 + c(x)Z + d(x) = 0
\end{align*}
\]
Solution Method: Interval Analysis

- Interval Newton Generalized Bisection (INGB): a global solution solver;
- INGB is able to find all the stationary points of an objective function;
- INGB is able to solve all solutions of non-linear equation system with mathematical and computational guarantees;
Interval Methodology (Cont’d)

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

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

- (Range Test) Compute the interval extension $F(X^{(k)})$ of $f(x)$ (this provides bounds on the range of $f(x)$ for $x \in X^{(k)}$)
  - If $0 \notin F(X^{(k)})$, delete the box. Otherwise,

- (Interval Newton Test) Compute the image, $N^{(k)}$, of the box by solving the linear interval equation system

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

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

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

\[ \tilde{D} = \theta D_1 + (1-\theta) D_2 \]

\[ \text{s.t. } \sum_{i=1}^{n} x_i - 1 = 0, \]

\[ \text{s.t. } \theta (\theta - 1) = 0, \]

\[ \text{s.t. } f(Z, x) = Z^3 + b(x)Z^2 + c(x)Z + d(x) = 0 \]

Apply Lagrange to above objective function,

\[ L = \tilde{D} + \lambda_1 \left( \sum_{i=1}^{n} x_i - 1 \right) + \lambda_2 \theta (\theta - 1) + \lambda_3 f(Z, x) \]
at stationary points, \( \int \) 

\[
\begin{align*}
\frac{\partial L}{\partial x_i} &= \tilde{D}_i + \lambda_1 + \lambda_3, \\
\frac{\partial L}{\partial \theta} &= \frac{\partial f(Z,x)}{\partial \theta}, \\
\frac{\partial L}{\partial Z} &= \frac{\partial f(Z,x)}{\partial Z}.
\end{align*}
\]
After applying Lagrange multipliers, nonlinear equation below is obtained:

\[
\frac{\partial \tilde{D}}{\partial x_i} - \frac{\partial \tilde{D}}{\partial x_n} = 0, \quad i = 1, \ldots, n - 1
\]

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

\[
\theta(\theta - 1) = 0,
\]

\[
f(Z, x) = Z^3 + b(x)Z^2 + c(x)Z + d(x) = 0.
\]
Example: T-xy diagram of 2,3-dimethyl-2-butene + methanol at 1 atmosphere (SRK/NRTL)

Area where phase stability is unknown
<table>
<thead>
<tr>
<th>Stability &amp; potential split</th>
<th>PTPD</th>
<th>Feed(z1,z2)</th>
<th>T(K)</th>
<th># of roots</th>
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</thead>
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<tr>
<td>Stable</td>
<td>0.0</td>
<td>(0.999, 0.001)</td>
<td>330</td>
<td>2</td>
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<tr>
<td>not split</td>
<td>0.5031</td>
<td>(0.8, 0.2)</td>
<td>330</td>
<td>4</td>
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<tr>
<td>VLE split</td>
<td>0.0001332</td>
<td>(0.5, 0.5)</td>
<td>330</td>
<td>2</td>
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<tr>
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<td>0.0</td>
<td>(0.5, 0.5)</td>
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<td>0.5031</td>
<td>(0.999, 0.001)</td>
<td>330</td>
<td>2</td>
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<tr>
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<td>(0.5, 0.5)</td>
<td>330</td>
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<td>(0.5, 0.5)</td>
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<tr>
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<td>(0.01, 0.99)</td>
<td>330</td>
<td>2</td>
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<tr>
<td>Feed(z1,z2) T(K)</td>
<td># of roots</td>
<td>PTPD</td>
<td>Stability &amp; potential split</td>
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<td>(0.999,0.001) 320</td>
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<td>0.0</td>
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A three phase line must exist between 320 and 330 K:

T=325.4 K
P=101.2 kPa
y1=0.4689
y2=0.5311
Conclusion:
The introduction of the Pseudo-Tangent-Plane-Distance function significantly reduced the complex of the phase stability analysis for asymmetrical modeling; no further complexity was added to the Tangent-Plane-Distance function (objective function), so that even local solver would solve the new PTPD objective easily with multiple initials.