Reliable Calculation of Phase Stability using Asymmetrical Modeling

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Presenter: Gang Xu, SimSci-Esscor/Invensys
W. Haynes, NFS Inc
M.A.Stadtherr, U.Notre Dame

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

$$y_i \phi_i P = x_i \gamma_i \phi_i^{sat} P_i^{sat} Poyn_i$$

Asymmetrical modeling

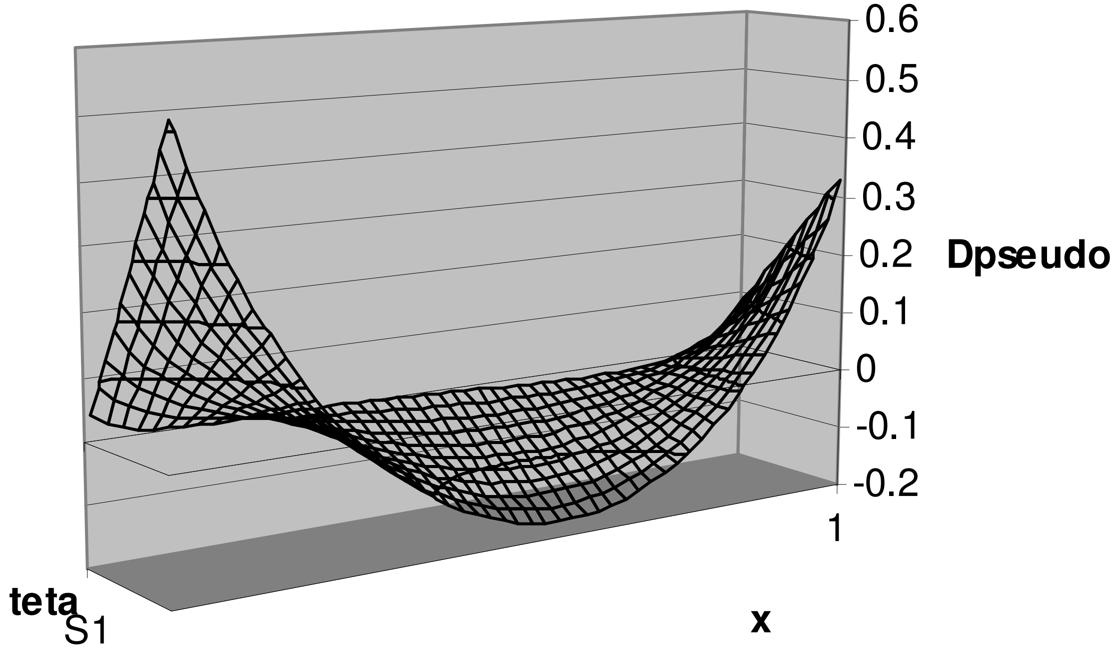
- Phase stability: Tangent-Plane-Distance analysis function based on the Gibbs energy of mixing
- New approach→ Pseudo-Tangent-Plane-Distance analysis function (PTPDF):

minimize $\tilde{D} = \theta D_1 + (1-\theta) D_2$

s.t. $\theta(\theta - 1) = 0$

Asymmetrical modeling

- Pseudo-Tangent-Plane-Distance Function



Optimization problem for PTPD

- Ideal gas (D_1)/Activity Coefficient(D_2)

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

- Cubic EOS(D_1)/Activity Coefficient(D_2)

$$\begin{aligned} \text{minimize} \quad & \tilde{D} = \theta D_1 + (1-\theta) D_2 \\ \text{s.t.} \quad & \sum_{i=1}^{n} x_i - 1 = 0, \\ & \theta(\theta - 1) = 0 \\ & f(Z,x) = Z^3 + b(x)Z^2 + c(x)Z + d(x) = 0 \end{aligned}$$

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

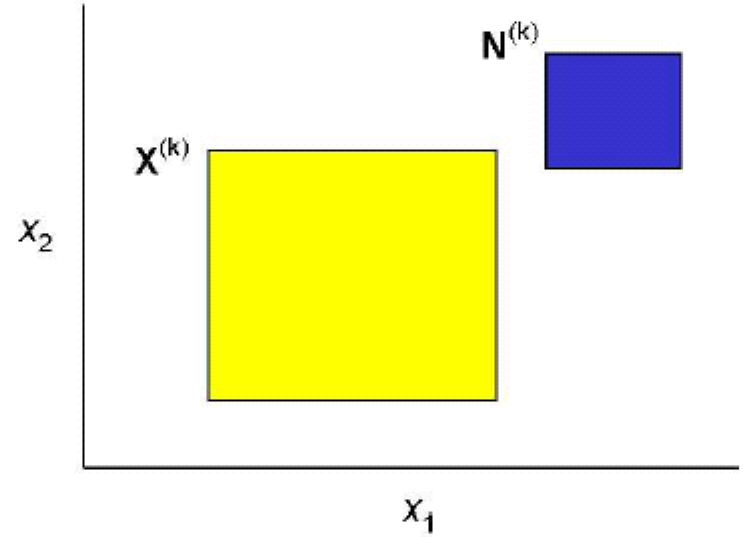
Basic iteration scheme: For a particular subinterval (box), $\mathbf{X}^{(k)}$, perform root inclusion test:

- (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

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

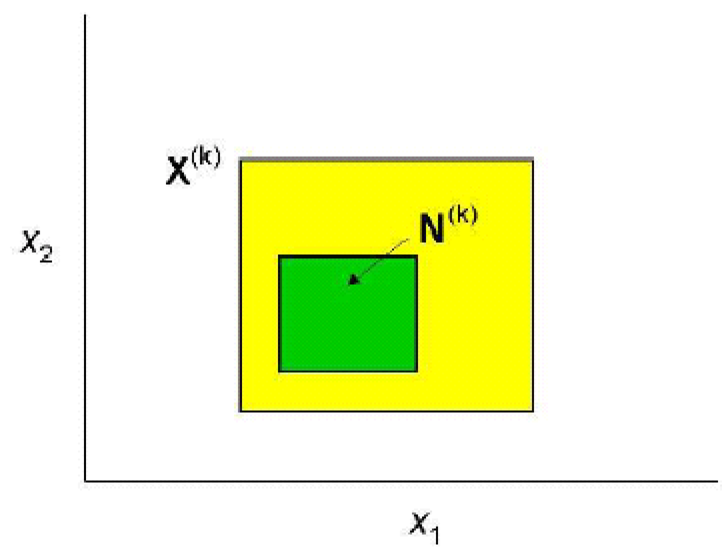
  - $\tilde{\mathbf{x}}^{(k)}$ is some point in $\mathbf{X}^{(k)}$
  - $\mathbf{F}'(\mathbf{X}^{(k)})$ is an interval extension of the Jacobian of $\mathbf{f}(\mathbf{x})$ over the box $\mathbf{X}^{(k)}$

Interval Methodology (Cont'd)



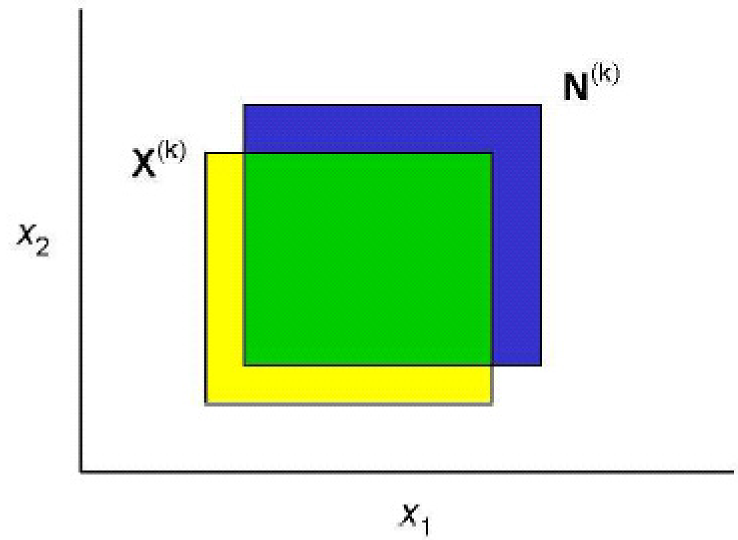
- There is no solution in $\mathbf{X}^{(k)}$

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

For objective function

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

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

$$s.t.\ \theta(\theta - 1) = 0,$$

$$s.t.\ f(Z, x) = Z^3 + b(x)Z^2 + c(x)Z + d(x) = 0$$

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,

$$\frac{\partial L}{\partial x_i} = \frac{\partial \tilde{D}}{\partial x_i} + \lambda_1 + \lambda_3 \frac{\partial f(Z,x)}{\partial x_i} = 0 \qquad (\ i = 1,\ldots n\ )$$

$$\frac{\partial L}{\partial \theta} = \frac{\partial \tilde{D}}{\partial \theta} + \lambda_2 (2\theta - 1) = 0$$

$$\frac{\partial L}{\partial Z} = \frac{\partial \tilde{D}}{\partial Z} + \lambda_3 \frac{\partial f(Z,x)}{\partial Z} = 0$$

$$\frac{\partial \tilde{D}}{\partial Z} = \theta \frac{\partial D_1}{\partial Z} + (1-\theta)\frac{\partial D_2}{\partial Z} = \theta \frac{\partial D_1}{\partial Z},$$

$$\frac{\partial D_1}{\partial Z} = \frac{\partial}{\partial Z}\left(\sum_{i=1}^{n} x_i \ln x_i + \sum_{i=1}^{n} x_i \ln \phi_i\right) = \sum_{i=1}^{n} x_i \frac{\partial \ln \phi_i}{\partial Z}$$ ==0

After applying Lagrange multipliers, nonlinear equation below is obtained:

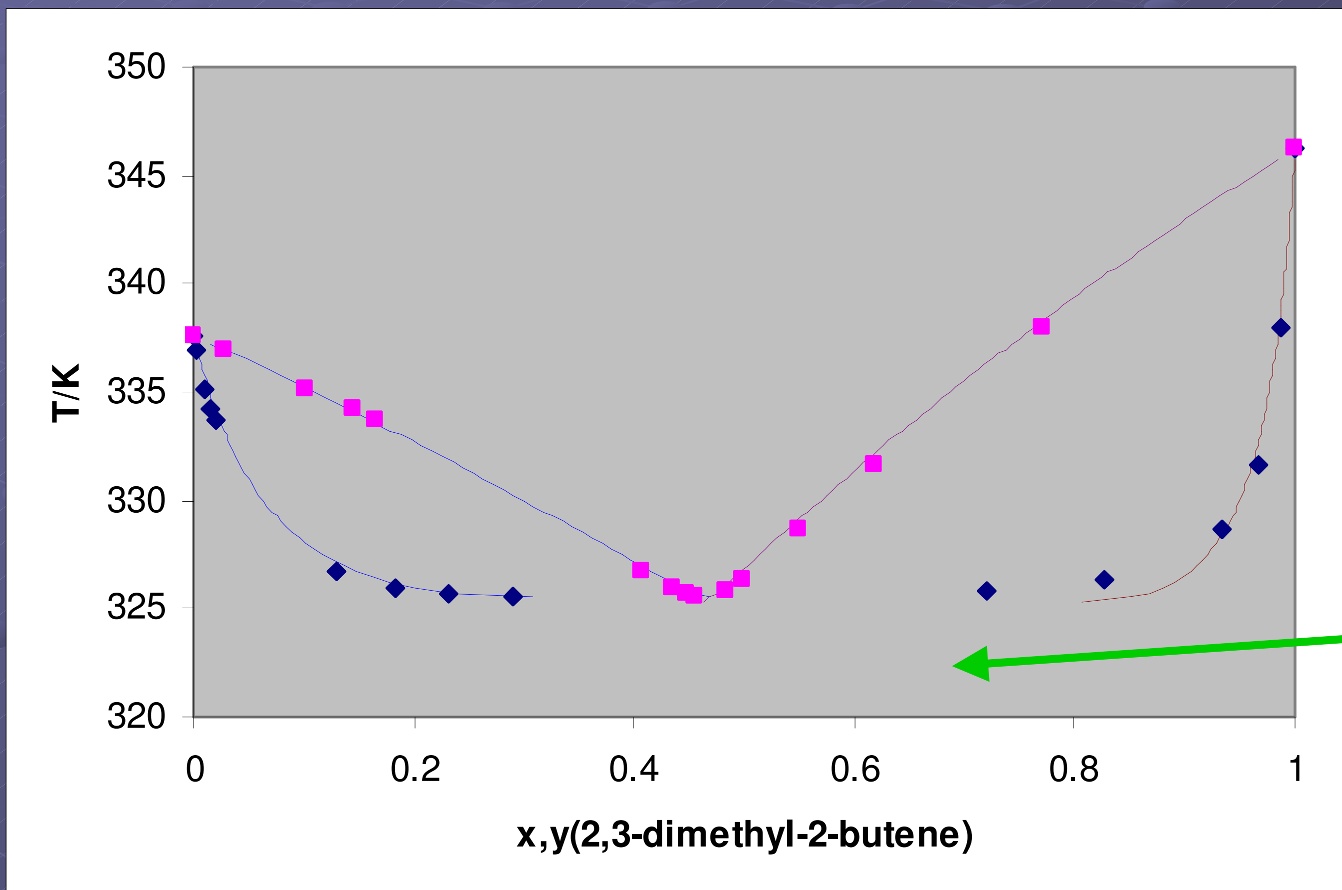
$$\frac{\partial \tilde{D}}{\partial x_i} - \frac{\partial \tilde{D}}{\partial x_n} = 0, \qquad i = 1,\dots n-1$$

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

$$\theta(\theta - 1) = 0,$$

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

Example: T-xy diagram of 2,3-dimethyl-2-butene + methanol at 1 atmosphere (SRK/NRTL)

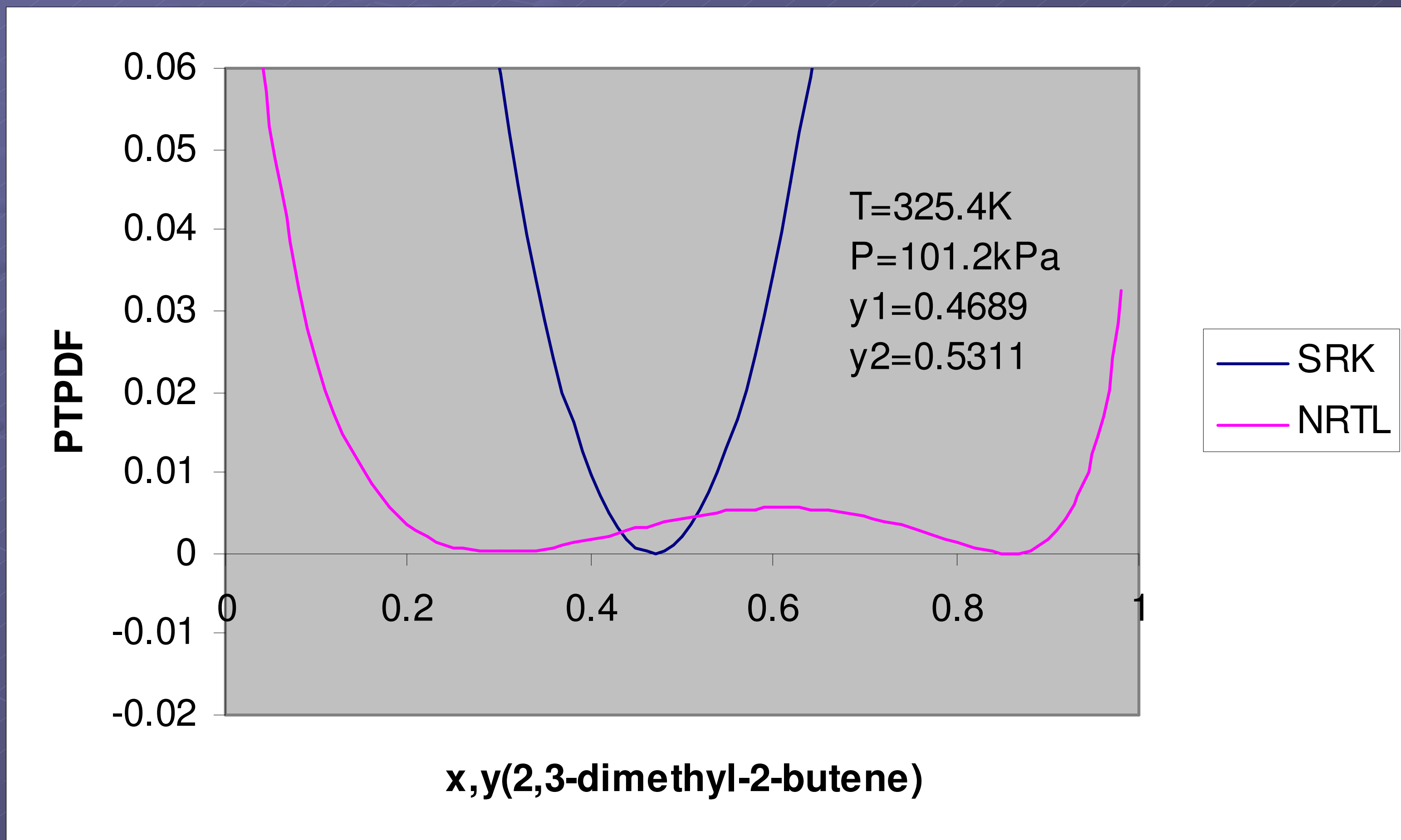


Area where phase stability is unknown

Feed(z1,z2) T(K)	# of roots	PTPD	Stability & potential split
(0.999,0.001) 330	2	0.0 0.5031	Stable no split
(0.8,0.2) 330	4	0.0 0.0001332 -0.01544 -0.1839	Not stable VLE split
(0.5,0.5) 330	2	0.0 0.1108	Stable no split
(0.2,0.8) 330	2	0.0 -0.1083	Not stable VLE split
(0.01,0.99) 330	2	0.0 0.2271	Stable No split

Feed(z1,z2) T(K)	# of roots	PTPD	Stability & potential split
(0.999,0.001) 320	2	0.0 0.8578	Stable no split
(0.5,0.5) 320	4	0.0 -0.01415 -0.0005353 0.2066	Not stable LLE split
(0.01,0.99) 320	2	0.0 0.6402	Stable no split

A three phase line must exist between 320 and 330 K:



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.