

Reliable Computation of Solid-Supercritical Fluid Equilibria Using Interval Analysis

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Motivation

- Industrial applications of Supercritical Fluids for extraction of solutes from solids are important;
- Challenges remain for the measurement and modeling of phase behavior at supercritical conditions;
- Need methodology for reliably computing **Solid-Supercritical Fluid Equilibria (SSFE)**.

A typical binary solvent-solute system

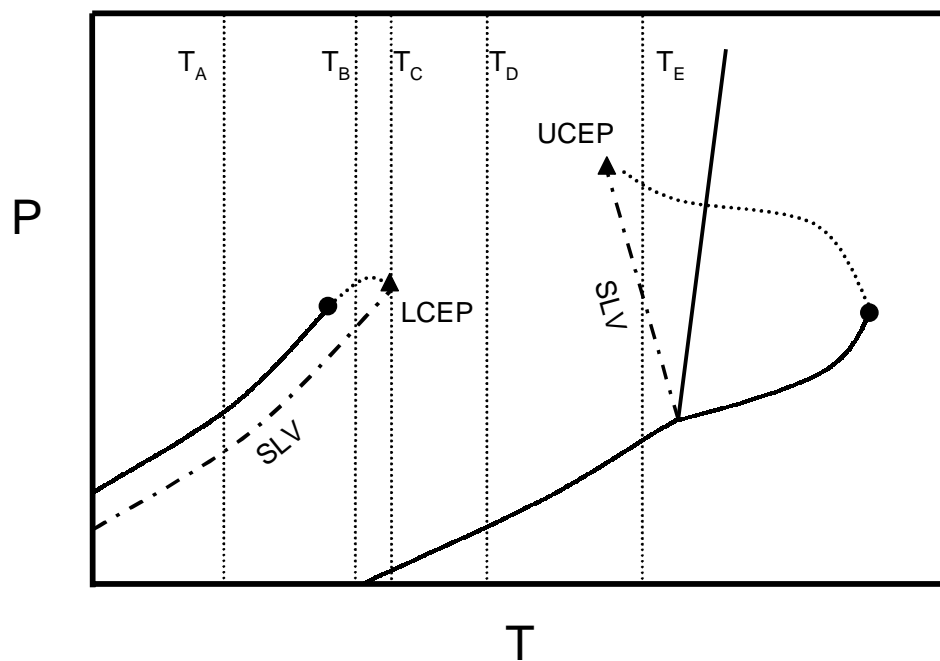


Figure 1: The pressure-temperature projection of a typical binary solvent-solute system

Difficulties

- Equifugacity Equation
 - Multiple roots may exist, but this may not be realized by the modeler
- Equifugacity is a necessary but not sufficient condition for **SSFE**
 - Need a global thermodynamic phase stability test that is guaranteed to be reliable : no such method has yet appeared in **SSFE** research area
- These difficulties have led in some cases to misinterpretation of experimental **SSFE** data (e.g., CO₂/Naphthalene in McHugh and Paulaitis, 1980)

New Reliable Strategy for Modeling **SSFE**

- Here we provided a new general-purpose method for reliably computing **SSFE** at constant T and P.
- Based on this method, a totally clear understanding of **SSFE** phase behavior can be drawn from a model.
- This understanding may improve the design of processes that use supercritical fluids to selectively extract solid solutes.

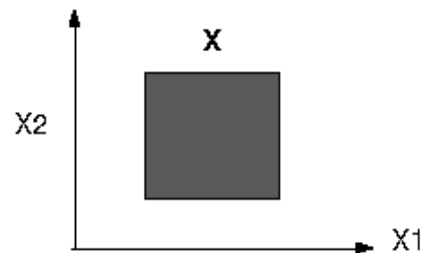
Interval Analysis

- Definition of a real interval

$$X = [a, b] = \{x \in \mathbb{R} \mid a \leq x \leq b\}, \quad a, b \in \mathbb{R}, \text{ and } a \leq b \quad (1)$$

- Definition of interval vector

$$\mathbf{X} = (X_i) = (X_1, X_2, \dots, X_n)^T \quad (2)$$



Interval Analysis – Continued

- Definition of interval operators (if we have intervals $\mathbf{X} = [a, b]$, $\mathbf{Y} = [c, d]$)

$$\mathbf{X} + \mathbf{Y} = [a + c, b + d] \quad (3)$$

$$\mathbf{X} - \mathbf{Y} = [a - d, b - c] \quad (4)$$

$$\mathbf{X} \times \mathbf{Y} = [\min(ac, ad, bc, bd), \max(ac, ad, bc, bd)] \quad (5)$$

$$\mathbf{X} \div \mathbf{Y} = [a, b] \times [1/d, 1/c], \quad 0 \notin \mathbf{Y} \quad (6)$$

For other interval operators (log, sin, etc), see *Interval Arithmetic Specification*, Chiriaev and Walster, *Sun Microsystems*, **1998**.

Interval Analysis – Continued

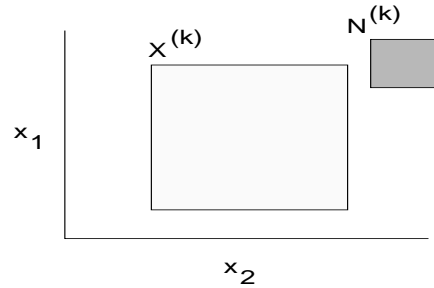
- Root inclusion test for solving $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ by interval Newton/generalized bisection (IN/GB).

$$\mathbf{F}'(\mathbf{X}^{(k)})(\mathbf{N}^{(k)} - \mathbf{x}^{(k)}) = -\mathbf{f}(\mathbf{x}^{(k)}) \quad (7)$$

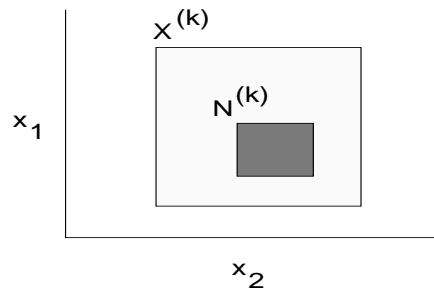
Given $\mathbf{X}^{(k)}$ solve for $\mathbf{N}^{(k)}$.

- $\mathbf{X}^{(k)}$ is the current box, and $\mathbf{x}^{(k)}$ is a point inside the current box.
- $\mathbf{F}'(\mathbf{X}^{(k)})$ is the interval extension of the Jacobian of $\mathbf{f}(\mathbf{x})$.
- $\mathbf{N}^{(k)}$ is the image of current box, $\mathbf{X}^{(k)}$.
- The relation between $\mathbf{X}^{(k)}$ and $\mathbf{N}^{(k)}$ gives information about the roots of $\mathbf{f}(\mathbf{x}) = \mathbf{0}$.

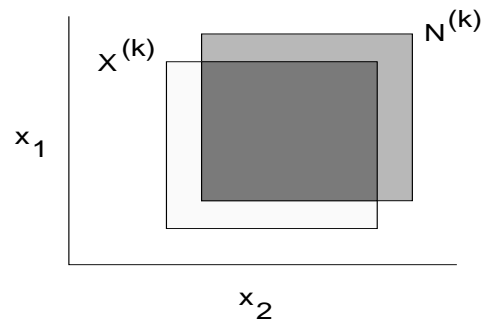
- If $\mathbf{X}^{(k)} \cap \mathbf{N}^{(k)} = \emptyset$, then there is no root in $\mathbf{X}^{(k)}$.



- If $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then there is exactly one root in $\mathbf{X}^{(k)}$, and this root is also in $\mathbf{N}^{(k)}$.



- If $\mathbf{X}^{(k)} \cap \mathbf{N}^{(k)} \neq \emptyset$, then any solutions in $\mathbf{X}^{(k)}$ are in the intersection of $\mathbf{X}^{(k)}$ and $\mathbf{N}^{(k)}$



If the intersection is sufficiently small, repeat root inclusion test; otherwise bisect the result of the intersection and apply root inclusion test to each resulting subinterval.

- For mathematical proofs, see Kearfott, *Rigorous Global Search: Continuous Problems*, Kluwer (1996)

Modeling of SSFE – Equifugacity Eq.

- Single component solvent (1), pure solute (2)

$$\ln f_2^S = \ln f_2^F(y_1, y_2, v) \quad (8)$$

$$y_1 + y_2 = 1$$

$$\mathbf{EOS}(y_1, y_2, v) = 0 \quad (\text{Peng-Robinson})$$

Initial interval $y_2 \in [0, \psi_2], \quad (0 < \psi_2 < 1)$

ψ_2 is the overall mole fraction in solid-fluid system

$$y_1 \in [0, 1]$$

$$v \in [b_{min}, \frac{2RT}{P}]$$

Tangent Plane Distance Analysis – TPDA

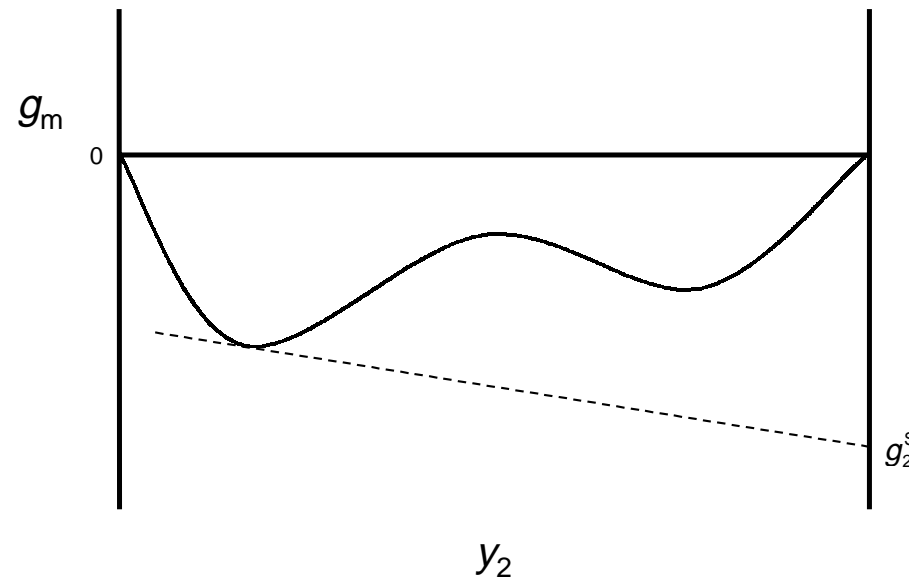


Figure 2: Single root for equifugacity eq. (Solid-Fluid-Equilibrium.)

$$g_2^S = RT \ln f_2^S / f_2^F$$

g_2^S indicates the molar Gibbs energy of the pure solid phase relative to a pure fluid phase ($y_2 = 1$) at given T and P.

Tangent Plane Distance Analysis – TPDA

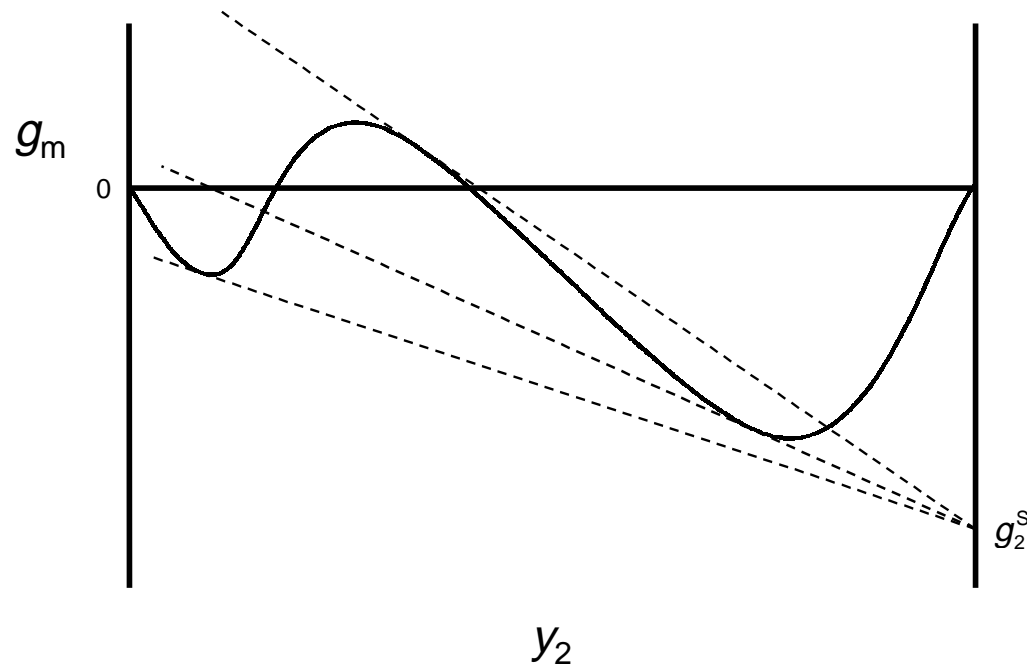


Figure 3: Multiple roots for equifugacity eq. (Solid-Fluid-Equilibrium)

Tangent Plane Distance Analysis – TPDA

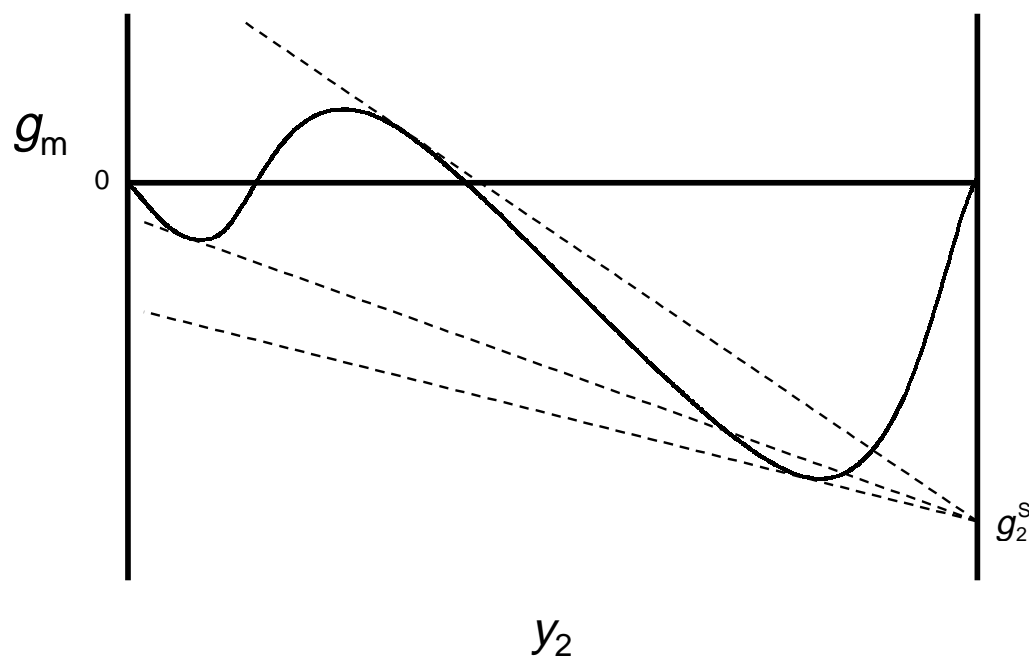


Figure 4: Multiple roots for equifugacity eq. (Solid-Liquid-Equilibrium)

Tangent Plane Distance Analysis – TPDA

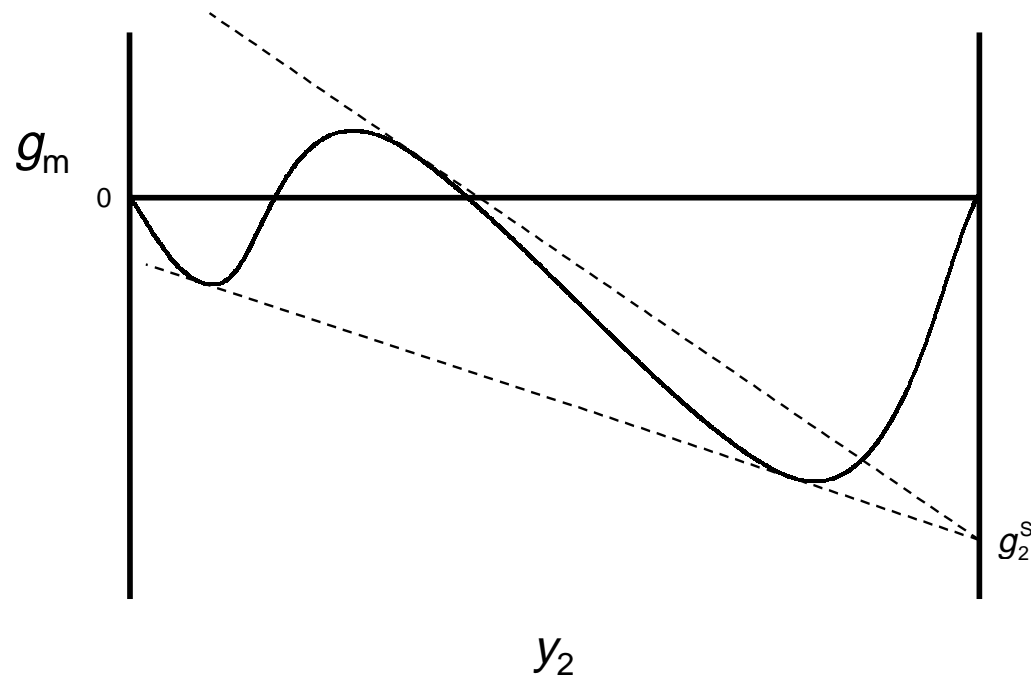


Figure 5: Multiple roots for equifugacity eq. (Solid-Fluid-Liquid-Equilibrium)

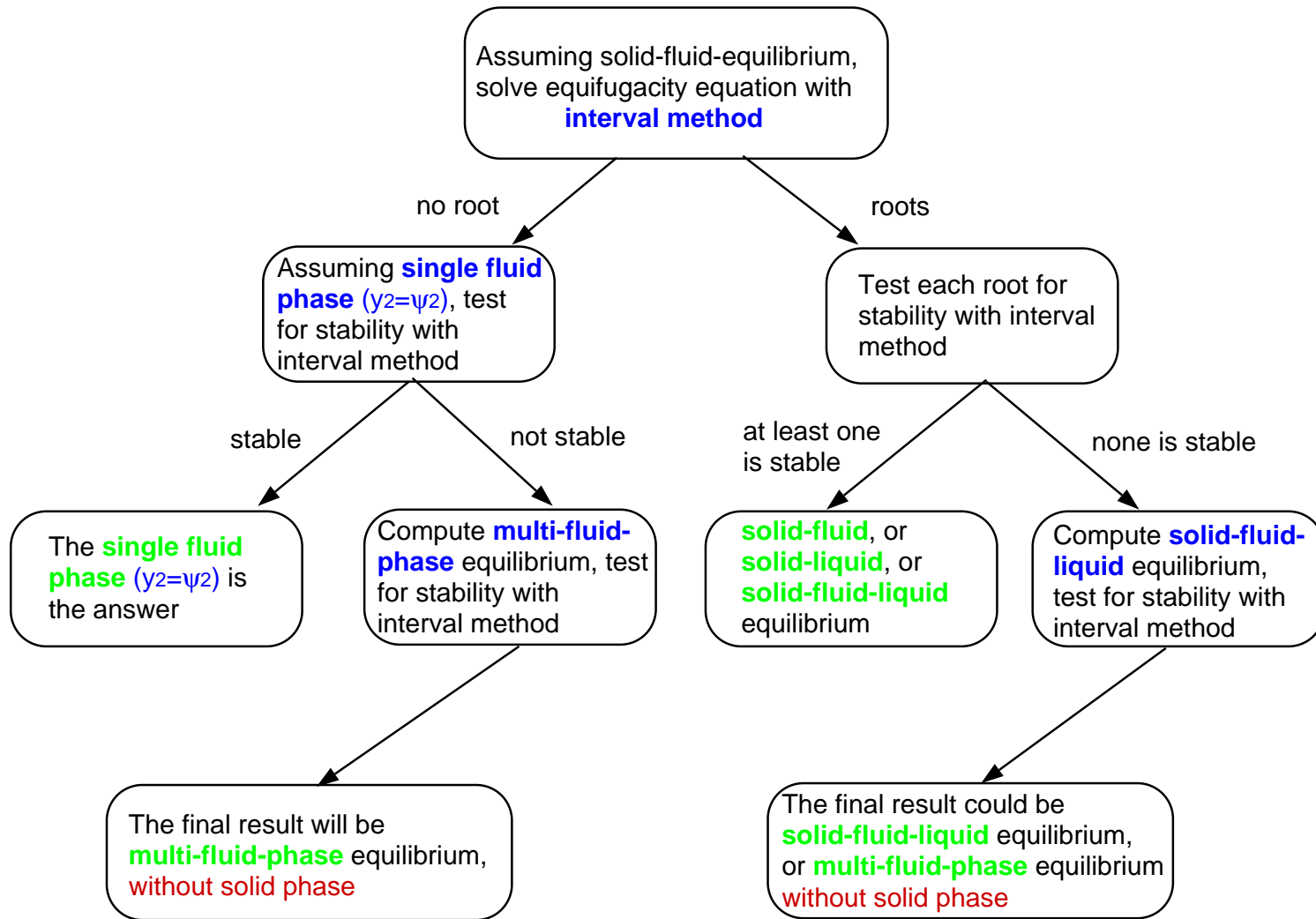
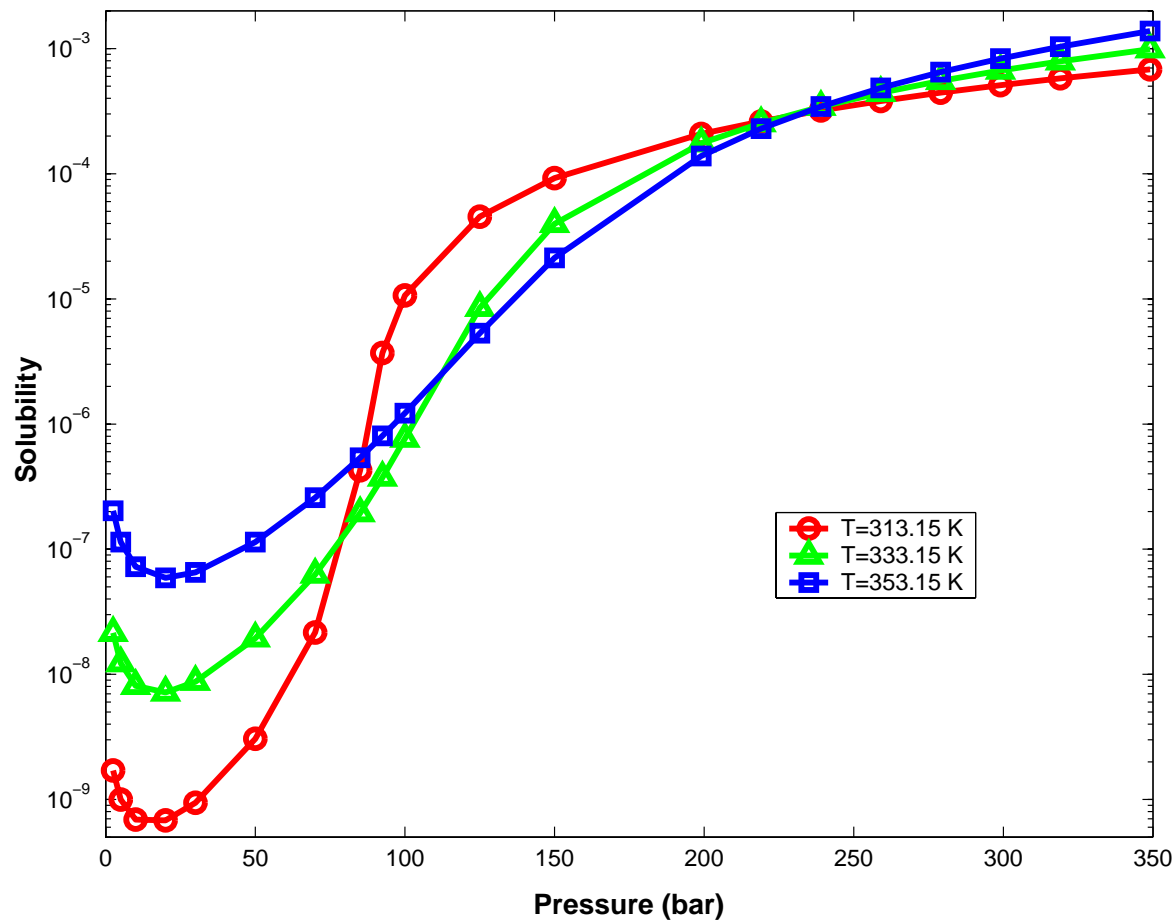


Figure 6: Calculation strategy for **SSFE**

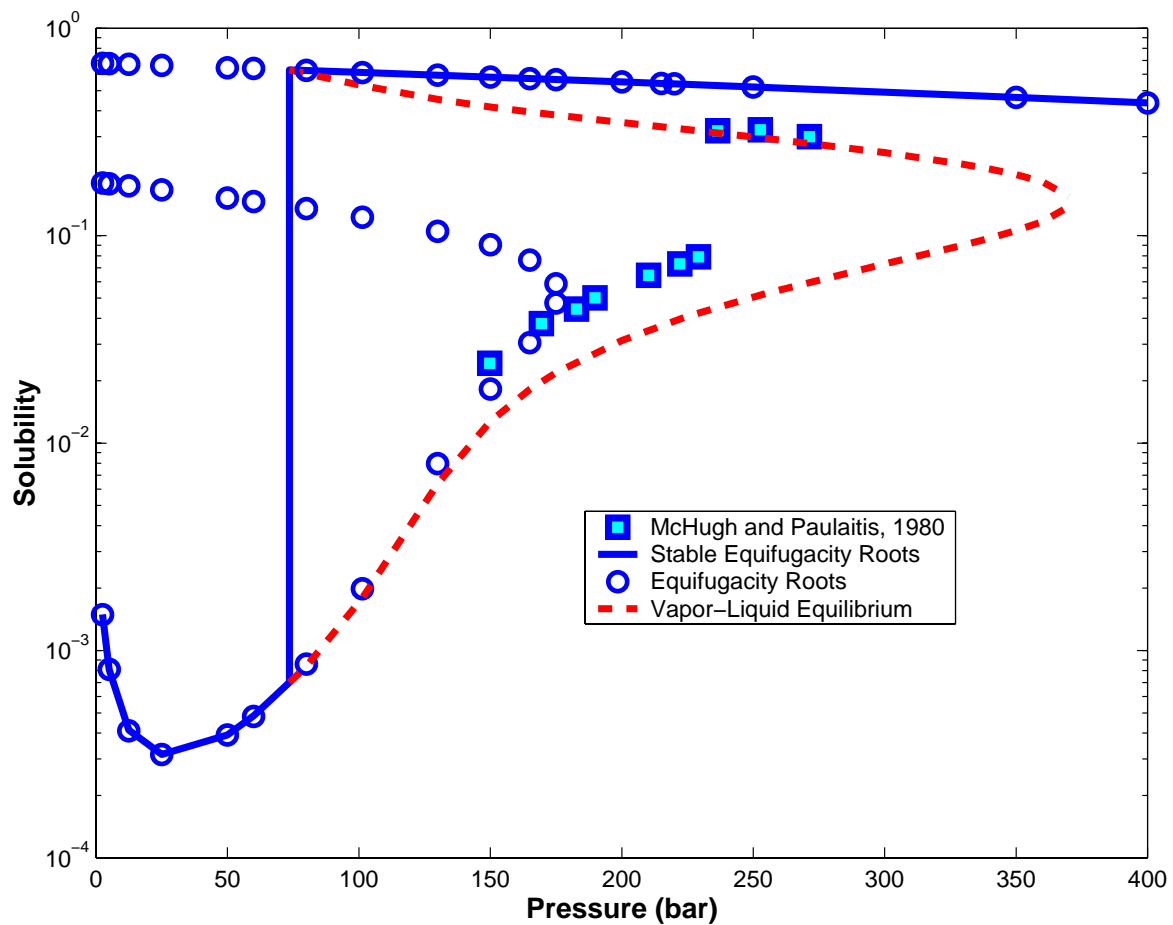
Results from our method

- Systems studied are CO₂/caffeine, CO₂/anthracene, CO₂/naphthalene, and CO₂/biphenyl;
- Samples like caffeine and anthracene that have melting points far away from UCEP have only one root to the equifugacity equation; if $\psi_2 \rightarrow 1$, this root is stable **SSFE**;
- Samples like naphthalene and biphenyl that have melting points near to UCEP show multiple roots for equifugacity equation near UCEP region. Those roots need to be tested with stability analysis.

Results

Figure 7: Calculated solubility of caffeine in supercritical CO_2

Results

Figure 8: Solubility of naphthalene in supercritical CO₂ at 65°C

Analysis of Fig. 8

- Experimental data of McHugh and Paulaitis (1980) was reported as Solid-Fluid-Equilibrium; Yet, our method finds that their data **does not correspond to the stable fluid phase** in equilibrium with the solid;
- Later studies by McHugh and Yogan (1984) and Lamb and coworkers (1986) measured the UCEP of CO₂/naphthalene, and realized that the measurements by McHugh and Paulaitis (1980) were **VLE** without solid phase;
- To replicate computationally the experiments of McHugh and Paulaitis, we performed calculations at 338.05 K with
 - pressure up to 400 bar with $\psi_2 \rightarrow 1$;
 - both $\psi_2 = 0.05$ and $\psi_2 = 0.0001$ at 150 bar.
- We found the stable Solid-Fluid-Equilibrium, and explained in which condition the solid phase is absent.

Modeling of Multi-component-solvent

- Multi-component-solvent (1,3,4,...), pure solute (2)

$$\ln f_2^S = \ln f_2^F(y_1, y_2, \dots, y_{nc}, v) \quad (9)$$

$$\sum_{i=1}^{nc} y_i = 1$$

$$\mathbf{EOS}(y_1, y_2, \dots, y_{nc}, v) = 0$$

$$y_1 = a_j y_j \quad j = 3, \dots, nc$$

The last equation here is the material balance equation, which refers to the fixed ratio of solvent species.

The material balance equation for ternary system

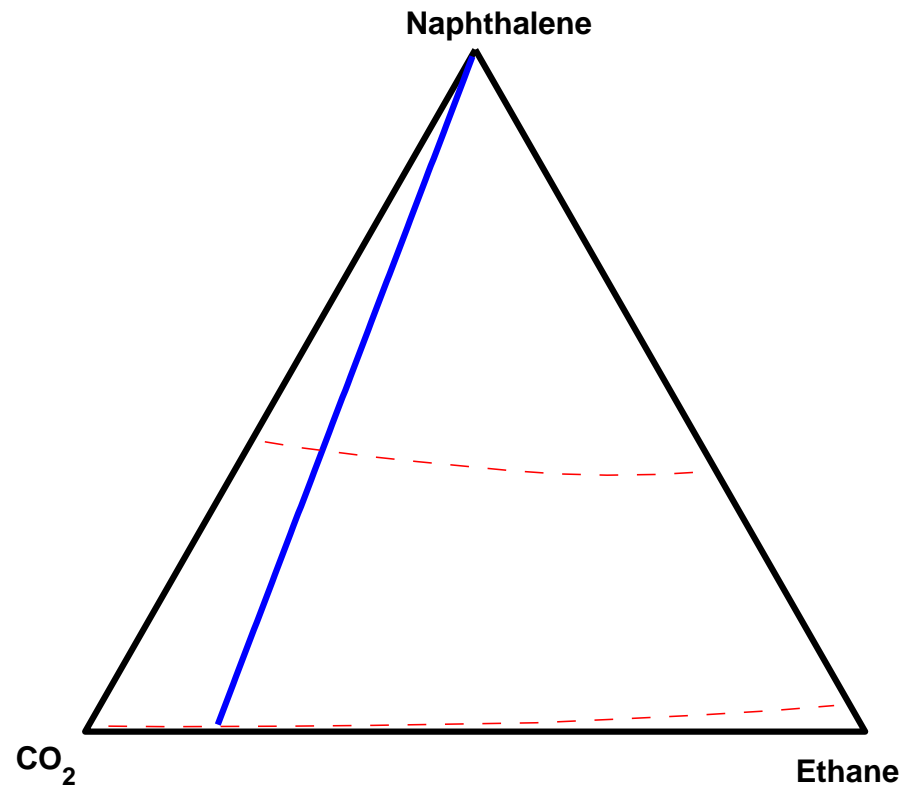


Figure 9: The blue line is the material balance equation ($\text{CO}_2/\text{ethane} = 5 : 1$)

Overall Strategy for Multi-Component-Solvent SSFE

- Same as figure 6.
- If the final equilibrium is solid-fluid equilibrium, then the fluid phase is on the material balance (MB) line.
- If the final equilibrium involves a solid phase and multi-fluid phases, then those fluid phases may not be on the MB line.

Sample Result

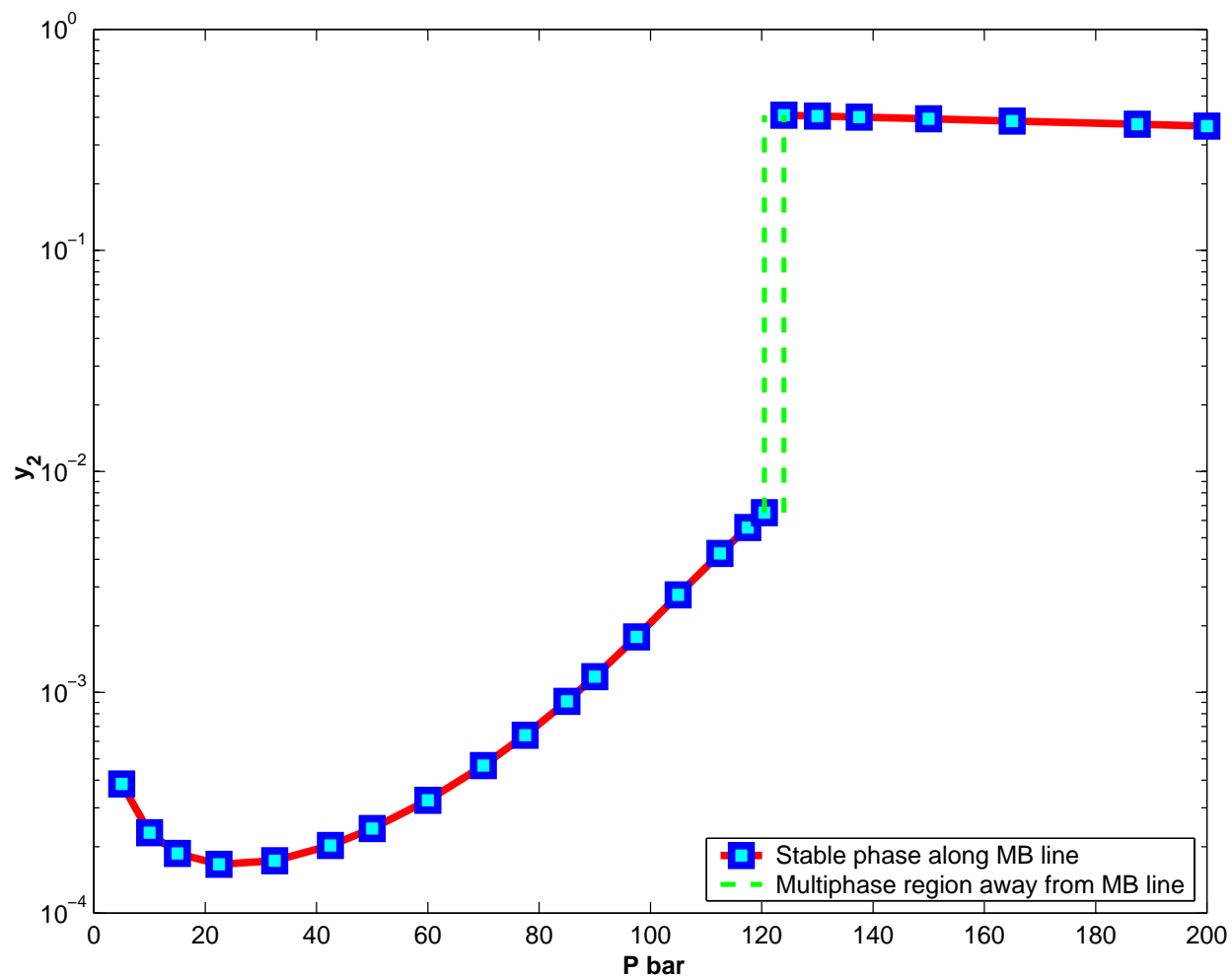


Figure 10: Calculated solubility of naphthalene in CO₂/ethane (5:1) at 328.15 K

Sample Result

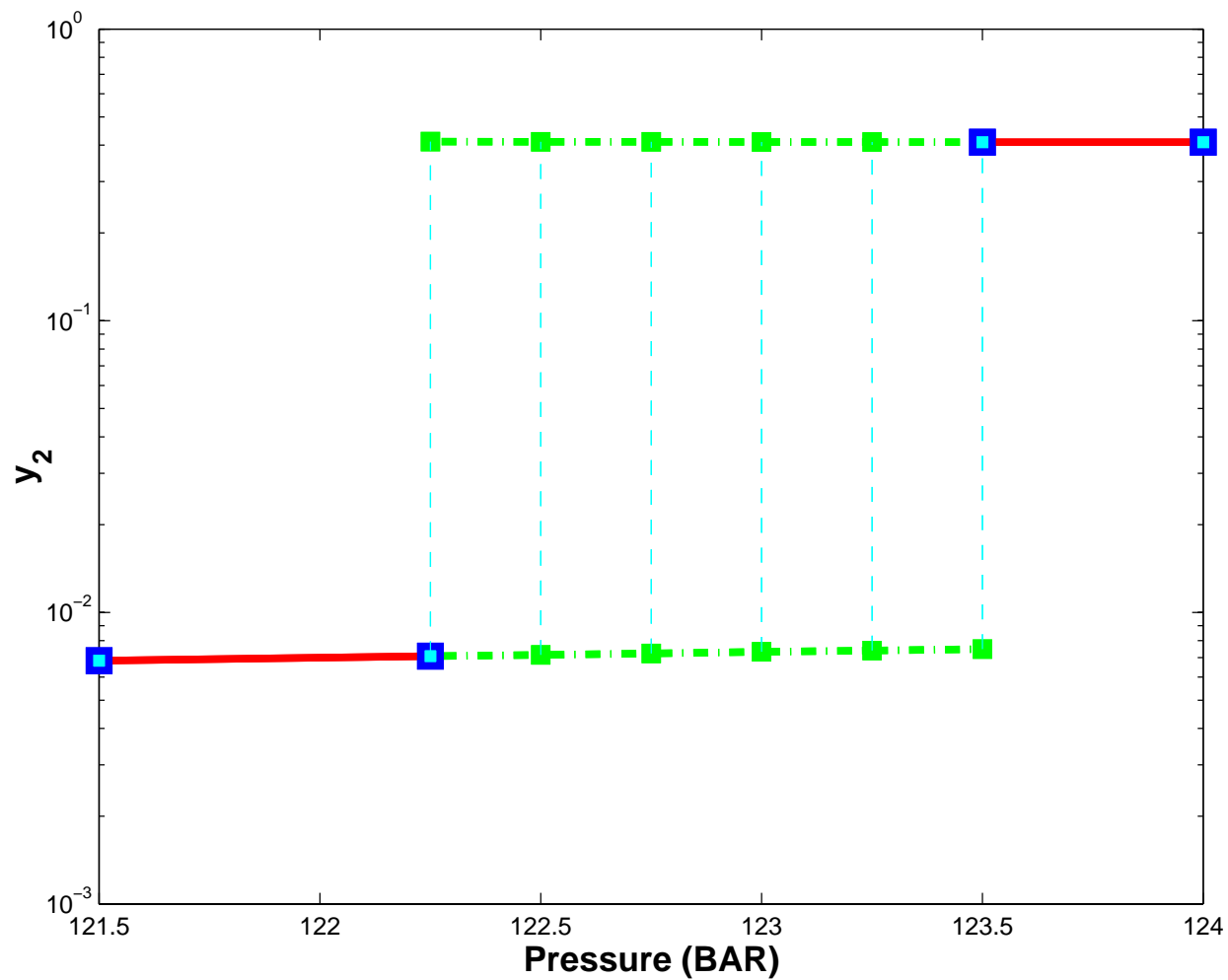


Figure 11: Close-up of Solid-Fluid-Liquid region in Fig. 10 (328.15 K)

Pressure values from Fig. 12 at multi-phase region

Assuming $3/4$ mole Naphthalene and $1/4$ mole mixed solvents in overall mixture
with CO₂/ethane 5 : 1 at 328.15 K

Pressure	122.25 bar	122.75 bar	123.5 bar
Fluid Phase Frac.	0.24680	0.15605	0.02641
Naphthalene	0.00708	0.00723	0.00748
Ethane	0.16517	0.15935	0.15112
CO ₂	0.82776	0.83342	0.84140
Liquid Phase Frac.	0.00841	0.16134	0.37908
Naphthalene	0.41134	0.41067	0.40966
Ethane	0.10748	0.10414	0.09939
CO ₂	0.48117	0.48519	0.49096
Solid Phase Frac.	0.74479	0.68261	0.59451

Summary

- This is the first application of interval analysis to **SSFE** problems.
- Results can be used to correctly interpret the experimental data from previous studies.
- Our new method for computing **SSFE** will be very useful in process design involving solids and supercritical fluids.
- Our methodology is general purpose and can be applied to a wide variety of problems.

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