An enhanced branch and bound algorithm for phase stability testing of multicomponent mixtures

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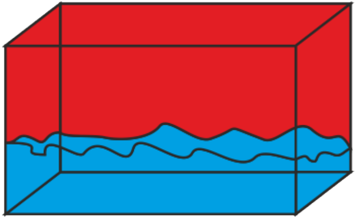
Introduction - VTN-phase stability testing

Basic introduction

- Stability of matter is one of the fundamental problems in physics.
- This problem is important for storing gasses and liquids.
- We want to predict whether the mixture is stable or a splitting into more phases occurs



Stating of the problem

- We examine the mixture under fixed volume, temperature, total concentration $\sum_{i=1}^{N} c_i$ and mole fractions.
- Helmholtz free energy density

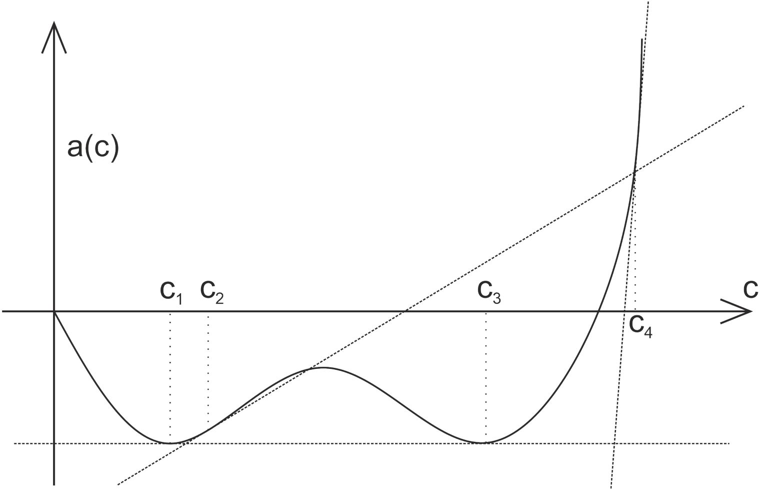
$$a(\mathbf{c}) = RT \sum_{i=1}^{N} c_i \ln \frac{c_i}{c_0} - RT \left(\sum_{i=1}^{N} c_i \right) \ln \left(1 - \sum_{i=1}^{N} b_i c_i \right) - \frac{\sum_{i,j=1}^{N} a_{ij} c_i c_j}{2\sqrt{2} \sum_{i=1}^{N} b_i c_i} \ln \left(\frac{1 + (1+\sqrt{2}) \sum_{i=1}^{N} b_i c_i}{1 + (1-\sqrt{2}) \sum_{i=1}^{N} b_i c_i} \right)$$

TPD-function

$$TPD(\mathbf{c}, \mathbf{c}^*) = a(\mathbf{c}) - a(\mathbf{c}^*) - \sum_{i=1}^{n} \frac{\partial a}{\partial c_i}(\mathbf{c}^*)(c_i^* - c_i)$$

- TPD function is nonnegative in the whole feasible set, if and only if the mixture is stable.
- TPD function has a geometric interpretation.
- Our problem can be solved by optimising the TPD function.
- There are 3 possible outcomes in relation to the character of the global minima of the TPD function.

Geometric interpretation of the TPD function



Formulation as an optimisation problem

$$\begin{aligned} \min_{\mathbf{c}} \quad & TPD(\mathbf{c}, \mathbf{c}^*) \\ \text{s.t.} \quad & c_i \geq 0; \quad i = 1, \dots, n \\ & \sum_{i=1}^{n} b_i c_i < 1 \end{aligned}$$

- We need to solve optimisation of nonconvex function over convex set.

Computational algorithm

Convex-concave split

- Algorithm is based on dividing the feasible set and solving the underestimated problem.

Theorem (Convex-concave split)

Let f be a function of several real variables, for which $f = gh$ holds. If g and h are convex, nonnegative, functions of several real variables. Then we can rewrite

$$f = \frac{1}{2}(g+h)^2 - \frac{1}{2}(g^2+h^2).$$

Furthermore functions

$$\frac{1}{2}(g+h)^2 \text{ and } \frac{1}{2}(g^2+h^2)$$

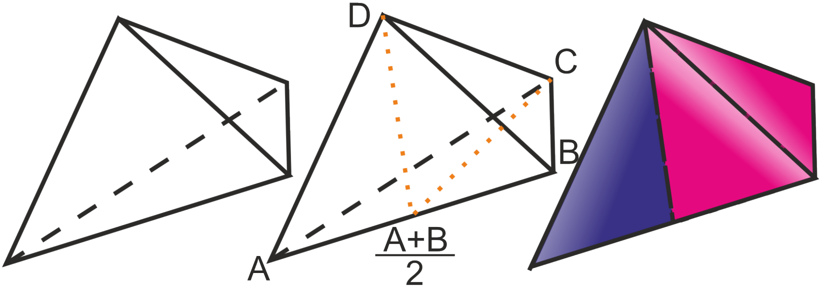
are convex.

$$a(\mathbf{c}) = a_c(\mathbf{c}) + a_{nc}(\mathbf{c}) \geq a_c(\mathbf{c}) + \sum_{i=1}^{n+1} \alpha_i a_{nc}(\mathbf{c}^{(i)}) = a^{\text{under}}(\mathbf{c})$$

$$TPD(\mathbf{c}, \mathbf{c}^*) = \sum_{i=1}^{n} \frac{\partial a}{\partial c_i}(\mathbf{c}^*)(c_i^* - c_i) - (a(\mathbf{c}^*) - a(\mathbf{c}))$$

Dividing a simplex

- Feasible set is interior of the simplex
- If we divide the simplex in such a way that a new vertex is created in the middle of the longest edge, we will end up with two simplices.



Main cycle of the algorithm

- 1) Choose simplex $\mathbf{S}$.
- 2) Find a minimum of the
original problem on $\mathbf{S}$,
if $U < UB$; $UB = U$.
- 3) Divide $\mathbf{S}$ to $\mathbf{S}_1$ and $\mathbf{S}_2$.
- 4) Find minimum of
the relaxed problem on $\mathbf{S}_1$ and $\mathbf{S}_2$.
If $L > UB$,
exclude simplex.
Otherwise place L to the queue LB.
- 5) Repeat, until UB is not sufficiently close to LB.

Necessary condition of optimality

- Necessary condition of optimality leads us to the following equation.

$$TPD(\mathbf{c},\mathbf{c}^*) = \sum_{i=1}^{n} \frac{\partial a}{\partial c_i}(\mathbf{c}^*)(c_i^* - c_i) - (a(\mathbf{c}^*) - a(\mathbf{c}))$$

$$\nabla a(\mathbf{c}^*) = \nabla a(\mathbf{c})$$

- With few operations we get the following inequality in the stationary points.

$$TPD(\mathbf{c},\mathbf{c}^*) = -\left(-P^{EOS}(T,\mathbf{c}^*) + P^{EOS}(T,\mathbf{c})\right)$$

$$P^{EOS}(T,\mathbf{c}^*) \leq \max_{\mathbf{c}\in\mathbf{S}} P^{EOS}(T,\mathbf{c})$$

Equations of pressure

$$P^{EOS}(T,\mathbf{c}) = \frac{\left(\sum_{i=1}^{N} c_i\right) RT}{1-\sum_{i=1}^{N} b_i c_i} - \frac{\sum_{i,j=1}^{N} a_{ij} c_i c_j}{1+2\sum_{i=1}^{N} b_i c_i - \left(\sum_{i=1}^{N} b_i c_i\right)^2}$$

Bounding conditions

- We exclude the parts of the simplex where the following inequality holds.

$$P^{EOS}(T, \mathbf{c}^*) \geq \max_{\mathbf{c}\in\mathbf{S}} P^{EOS}_{upper}(T, \mathbf{c})$$

- Estimate is found by comparing the values of tangent hyperplane in the vertices of the simplex

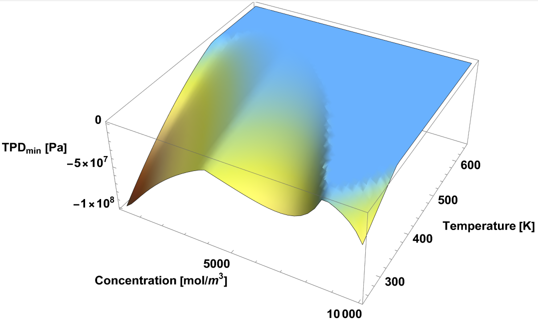
$$P^{EOS}(T, \mathbf{c}^*) \geq \max_{\mathbf{c}\in\mathbf{S}_e} P^{EOS}_{plane}(T, \mathbf{c})$$

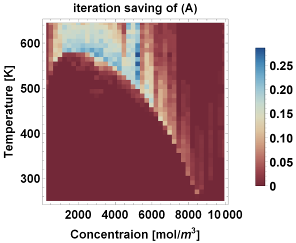
- Likewise with chemical potentials.

$$\mu(\mathbf{c}^*) \geq \max_{\mathbf{c}\in\mathbf{S}_e} \mu_i^{upper}(\mathbf{c})$$

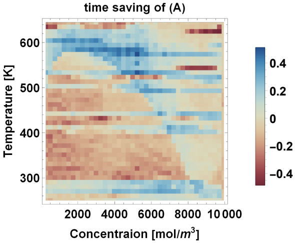
$$\mu(\mathbf{c}^*) \leq \min_{\mathbf{c}\in\mathbf{S}_e} \mu_i^{lower}(\mathbf{c})$$

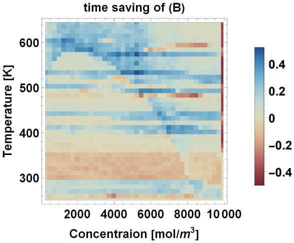
Example - methan-penthan mixture iteration saving





Example - methan-penthan mixture mixture time saving





Conclusion

- If we want to prove the instability of the mixture, computational time is small. Usually in the first few iterations of the algorithm the local minima with negative sign is found and the instability proven.
- The real challenge of this problem is the proof of stability.
- Alternative bounding based on tangent hyperplane of the simplex lead to improvement in computation time and in number of iterations particularly in the proximity of the phase envelope.

Thank you for your attention!

- Mikyška, J.; Firoozabadi A. , Investigation of Mixture Stability at Given Volume, temperature and number of moles.
- Smejkal T.; Mikyška J., VTN-phase stability testing using the Branch and Bound strategy and the convex-concave splitting of Helmhotz free energy density.
- Jüngel, A., Mikyška, J., and Zamponi, N., Existence analysis of a single phase flow mixture with van der Waals pressure.

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