



Modeling the Critical and Phase Equilibrium Properties of Pure Fluids and Mixtures with the Crossover Cubic-Plus-Association Equation of State

Vinhal, Andre P. C. M.; Yan, Wei; Kontogeorgis, Georgios M.

Published in:
Journal of Chemical and Engineering Data

Link to article, DOI:
[10.1021/acs.jced.9b00492](https://doi.org/10.1021/acs.jced.9b00492)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Vinhal, A. P. C. M., Yan, W., & Kontogeorgis, G. M. (2020). Modeling the Critical and Phase Equilibrium Properties of Pure Fluids and Mixtures with the Crossover Cubic-Plus-Association Equation of State. *Journal of Chemical and Engineering Data*, 65(3), 1095-1107. <https://doi.org/10.1021/acs.jced.9b00492>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Supporting Information

Modelling the Critical and Phase Equilibrium Properties of Pure Fluids and Mixtures with the Crossover Cubic-Plus-Association Equation of State

Andre P. C. M. Vinhal¹, Wei Yan², Georgios M. Kontogeorgis^{1,*}

¹Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

²Center for Energy Resources Engineering (CERE), Department of Chemistry, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

*Corresponding author. E-mail: gk@kt.dtu.dk

In this work, the critical point calculations using the crossover CPA EoS were done by applying Michelsen's¹ modification of Heideman and Khalil's algorithm.² The method is used to solve the stability and criticality conditions given by:

$$\left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)_{T,V,n_{i \neq j}} = 0 \quad (1)$$

$$\left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k}\right)_{T,V,n_{i \neq j,k}} = 0 \quad (2)$$

The algorithm is schematically represented by Figure S1. The efficient computation of the stability condition is based on the approach that, for a point to lie on the limit of stability, the matrix Q with elements $\left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)$ should have a zero determinant:

$$\det(Q) = 0 \quad (3)$$

If this condition is not respected, the temperature is changed until convergence is reached. Besides, with the change of T it

is required to re-evaluate f_n , the free energy density. If the previous condition holds, there should be a vector Δn that satisfy the expression:

$$Q \cdot \Delta n = 0 \quad (4)$$

and if a non-zero vector Δn is found, the criticality condition has to be considered. Michelsen¹ proposed the following condition to replace eq 2:

$$C = \Delta n \cdot \left[\frac{\partial q_{ij}(n+s\Delta n)}{\partial s}\right] \cdot \Delta n = 0 \quad (5)$$

where $\frac{\partial q_{ij}(n+s\Delta n)}{\partial s}$ is the derivative of q_{ij} with respect to the directional increment s . Consequently, if eq 5 is greater than a predetermined tolerance, the volume of the system is changed and the free energy density (f_n) needs to be re-evaluated. The critical point is reached at a certain T and v when both $\det(Q)$ and C are close to zero. The critical pressure is calculated using the crossover CPA EoS.

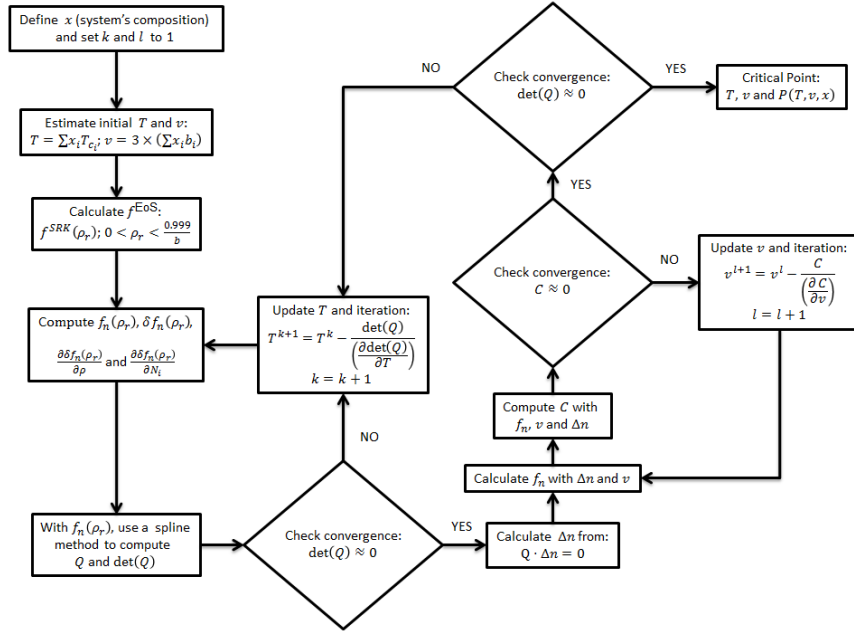


Figure S1: Flowchart for calculating the critical point of a system using a crossover EoS.

References

- (1) Michlsen, M. L. Calculation of Phase Envelopes and Critical Points for Multicomponent Mixtures. *Fluid Phase Equilib.*, **1980**, 4, 1-10
- (2) Heidemann, R. A.; Khalil, A. M. The Calculation of Critical Points. *AIChE Journal*, **1980**, 26, 769-779