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Supporting Information

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

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In this work, the critical point calculations using the crossover *CPA* EoS were done by applying Michelsen's[1] modification of Heideman and Khalil's algorithm.[2] The method is used to solve the stability and criticality conditions given by:

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

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

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:

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

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:

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

and if a non-zero vector Δn is found, the criticality condition has to be considered. Michelsen[1] proposed the following condition to replace eq 2:

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

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*.

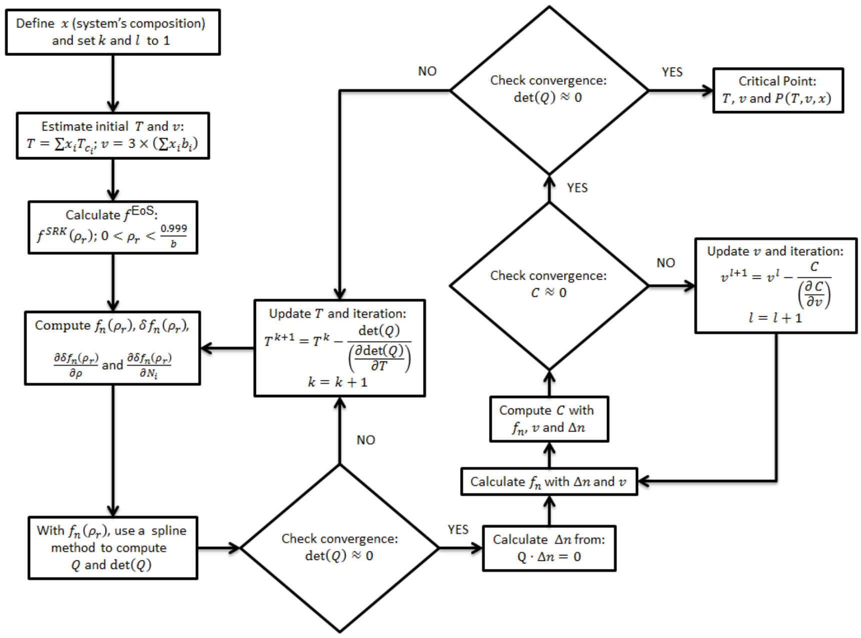

Figure S1: Flowchart for calculating the critical point of a system using a crossover *EoS*.

References

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(2) Heidemann, R. A.; Khalil, A. M. The Calculation of Critical Poins. *AIChE Journal*, **1980**, 26, 769-779