

Efficient calculation of fluid phase equilibria with equations of state

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The task

given:

- a fluid consisting of N components
- with known composition $\vec{x}' \equiv (x'_1, x'_2, \dots, x'_N)$ [mole fractions]
- at temperature T

requested:

- composition of equilibrium phase $\vec{x}'' \equiv (x''_1, x''_2, \dots, x''_N)$
- equilibrium pressure p

Note: The unknown properties have different dimensions. → The path of the computations depends on the units used.

E.g., during the iteration a deviation vector may appear, $(\Delta x''_1, \Delta p)$ — Can we say that the length of this vector is $\sqrt{(\Delta x''_1)^2 + (\Delta p)^2}$?

Many computer programs use \vec{x}'' and V'_m, V''_m internally, but the problem of having different dimensions remains.

Phase equilibrium criteria

2-phase equilibrium (here: fluid phases)

temperature criterion:

$$T' = T''$$

pressure criterion:

$$p' = p''$$

chemical potential criterion

$$\mu'_i = \mu''_i \quad i = 1, \dots, N$$

Stability criteria

for pure fluids:

$$\left(\frac{\partial^2 A}{\partial V^2} \right)_T \geq 0$$

for binary mixtures:

$$\left(\frac{\partial^2 G_m}{\partial x_1^2} \right)_{p,T} \geq 0$$

Why do we need two different criteria for the same phenomenon?

Isochoric formulation: definitions

... the esthetic approach to fluid phase equilibria!

get rid of mole fractions x_i !

treat the total volume V as a constant, use only amounts of substance (“mole numbers”) n_i as variables

alternative view:

express compositions by means of particle densities (concentrations):

$$\rho_i = \frac{n_i}{V} = \frac{x_i}{V_m}$$
$$\rho = \sum_i \rho_i = \frac{1}{V_m}$$
$$x_i = \frac{\rho_i}{\rho}$$

Isochoric formulation: equilibrium criteria

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{V, T, n_{j \neq i}} = \frac{1}{V} \left(\frac{\partial A}{\partial \rho_i} \right)_{\rho_{j \neq i}}$$

$$\mu'_i = \mu''_i \quad \Rightarrow \quad \left(\frac{\partial A'}{\partial \rho_i} \right) = \left(\frac{\partial A''}{\partial \rho_i} \right) \quad \text{with} \quad i = 1, \dots, N$$

derivation of the pressure:

$$pV = G - A \quad G = \sum_i^N \mu_i n_i = V \sum_i^N \mu_i \rho_i$$

$$p = -\frac{1}{V} \left(A + \sum_i^N \left(\frac{\partial A}{\partial \rho_i} \right) \rho_i \right)$$

at this stage, switch to the Helmholtz energy *density*: $\Psi = A/V$ (Sengers & Levelt Sengers):

$$p = -\Psi + \sum_i^N \left(\frac{\partial \Psi}{\partial \rho_i} \right) \rho_i$$

$$p' = p'' \quad \Rightarrow \quad \sum_i^N \left(\frac{\partial \Psi''}{\partial \rho_i} \right) \rho_i'' - \sum_i^N \left(\frac{\partial \Psi'}{\partial \rho_i} \right) \rho_i' = \Psi'' - \Psi'$$

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the μ equilibrium criterion written in terms of Ψ :

$$\mu_i' = \mu_i'' \Rightarrow \left(\frac{\partial \Psi'}{\partial \rho_i} \right) = \left(\frac{\partial \Psi''}{\partial \rho_i} \right) \quad \text{with } i = 1, \dots, N$$

insertion into the pressure criterion:

$$\sum_i^N \left(\frac{\partial \Psi}{\partial \rho_i} \right) (\rho_i'' - \rho_i') = \Delta \Psi$$

phase equilibrium criteria with vector notation:

$$\begin{aligned} \vec{\mu}' = \vec{\mu}'' &\Rightarrow \nabla_{\rho} \Psi'' = \nabla_{\rho} \Psi' \\ p' = p'' &\Rightarrow \nabla_{\rho} \Psi \cdot \Delta \vec{\rho} = \Delta \Psi \\ &\text{with } \Delta \vec{\rho} = \vec{\rho}'' - \vec{\rho}' \end{aligned}$$

Algorithm 1: finding initial values

total differential of Ψ :

$$d\Psi = -\frac{S_m}{V_m} dT + \sum_{i=1}^N \left(\frac{\partial \Psi}{\partial \rho_i} \right) d\rho = -\frac{S_m}{V_m} dT + \nabla \Psi \cdot d\vec{\rho}$$

integration of $d\Psi$ along an isothermal path between $\vec{\rho}'$ and $\vec{\rho}''$

- in the limit $\vec{\rho}'' \rightarrow \vec{\rho}'$:

$$\int_{\vec{\rho}'}^{\vec{\rho}''} \nabla \Psi d\vec{\rho} = \nabla \Psi \cdot \Delta \vec{\rho} = \Delta \Psi$$

(= the pressure criterion)

- for longer distances, up to 2nd order:

$$\int_{\vec{\rho}'}^{\vec{\rho}''} \nabla \Psi d\vec{\rho} = \nabla \Psi \cdot \Delta \vec{\rho} + \frac{\lambda}{2} (\Delta \vec{\rho})^2 = \Delta \Psi$$

calculate the gradient:

$$\nabla_{\rho} \cdot \nabla_{\rho} \Psi \cdot \Delta \vec{\rho} + \nabla_{\rho} \Psi + \lambda \Delta \vec{\rho} = \nabla_{\rho}(\Delta \Psi)$$

left-hand side: Hessian of the Helmholtz energy density:

$$\Psi \equiv \nabla_{\rho} \cdot \nabla_{\rho} \Psi = \begin{pmatrix} \Psi_{11} & \Psi_{12} & \dots & \Psi_{1N} \\ \Psi_{21} & \Psi_{22} & \dots & \Psi_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_{N1} & \Psi_{N2} & \dots & \Psi_{NN} \end{pmatrix} \quad \text{with } \Psi_{ij} = \left(\frac{\partial^2 \Psi}{\partial \rho_i \partial \rho_j} \right)$$

right-hand side:

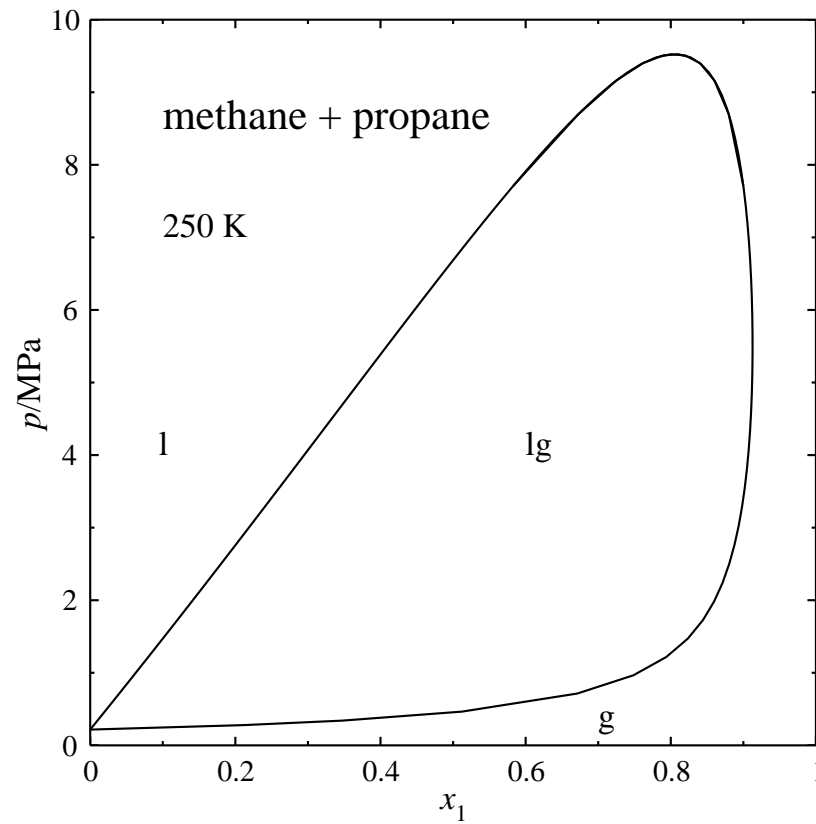
$$\nabla_{\rho}(\Delta \Psi) = \nabla_{\rho'} \Psi' - \underbrace{\nabla_{\rho'} \Psi''}_{=0} = \nabla_{\rho'} \Psi'$$

after insertion of these two equations:

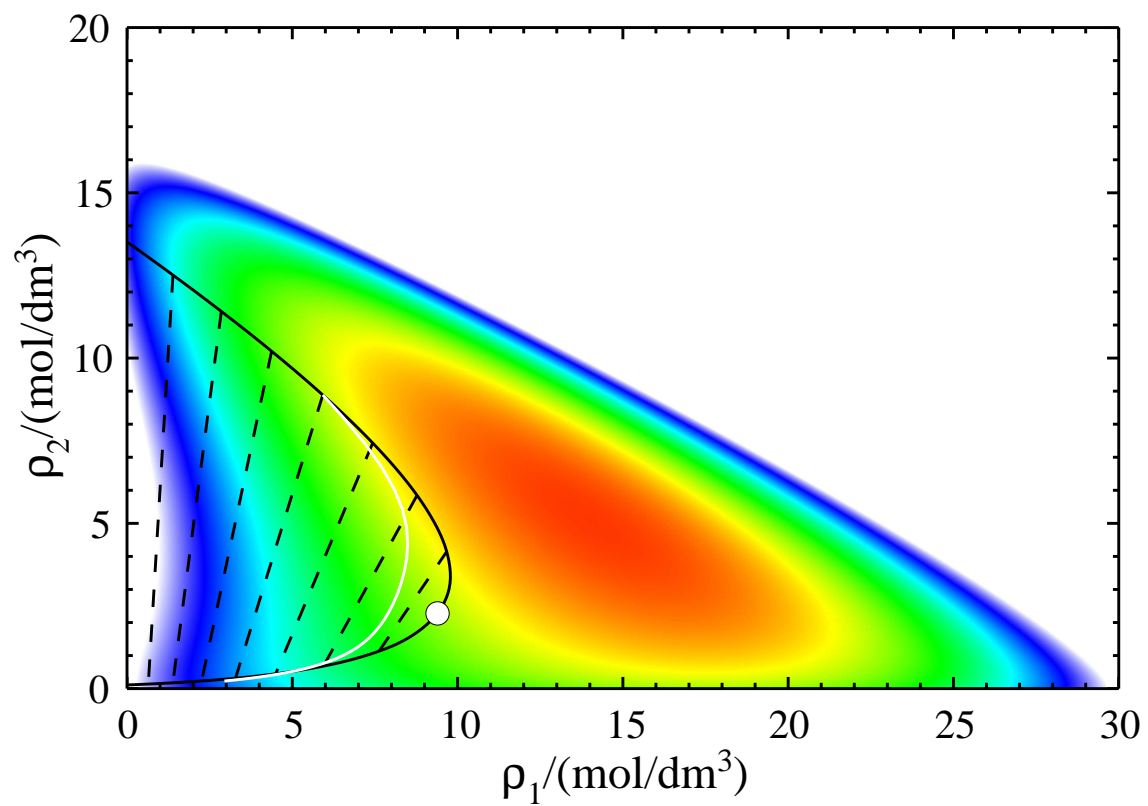
$$\Psi \Delta \vec{\rho} + \lambda \Delta \vec{\rho} = 0$$

Note: This is an eigenvalue problem.

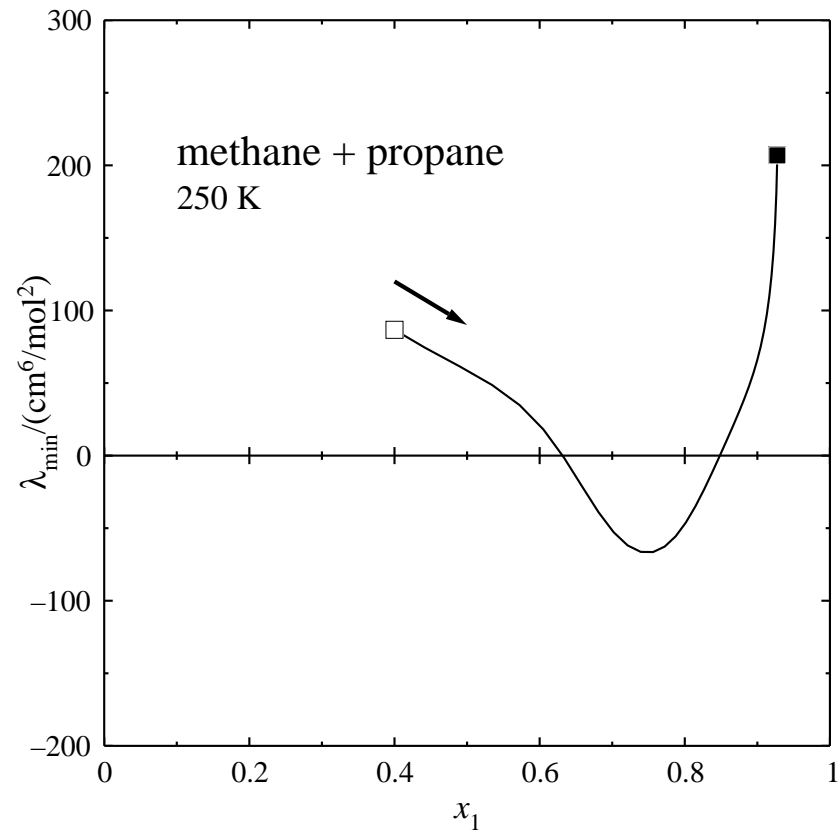
- If the start phase ($\vec{\rho}'$) is stable, all eigenvalues are positive.
- If $\Delta \vec{\rho}$ is small, one of the eigenvectors (most likely the one belonging to the lowermost eigenvalue) points to the equilibrium phase.
- If $\Delta \vec{\rho}$ is not small, the path from the start phase to the equilibrium phase is curved, with the local eigenvector defining its direction.



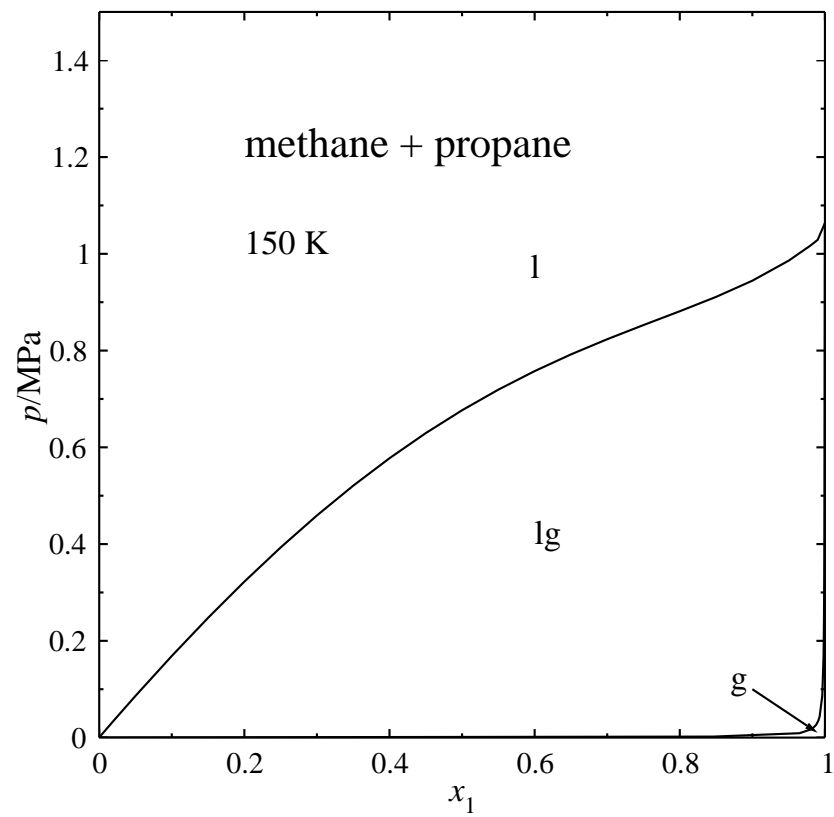
Supercritical example: px_1 diagram of $\{\text{CH}_4 + \text{C}_3\text{H}_8\}$ at 250 K. Calculation method: PR+1FS (Peng–Robinson EOS with Soave’s 1-fluid mixing rules). No interpolation is required at the critical point.



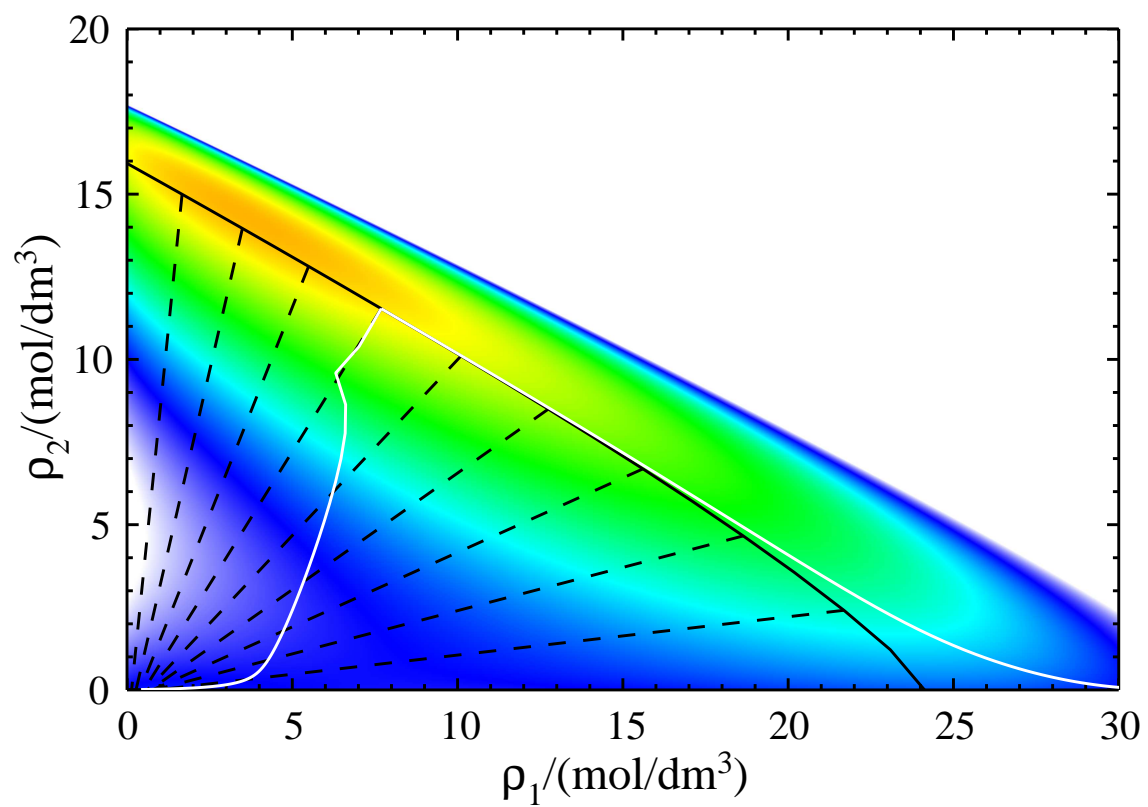
$\Psi(\rho_1, \rho_2)$ diagram of $\{\text{CH}_4 + \text{C}_3\text{H}_8\}$ at 250 K. —: phase envelope, - - -: conodes, white: eigenvector path. Colour code: “rainbow” (red = low, violet = high, white = very high or forbidden).



Behaviour of the lowermost eigenvalue (= principal curvature of the Ψ surface) along the search path.
Note that there must be a concave region between the two coexisting phases.



Subcritical example: px_1 diagram of $\{\text{CH}_4 + \text{C}_3\text{H}_8\}$ at 150 K.



$\Psi(\rho_1, \rho_2)$ diagram of $\{\text{CH}_4 + \text{C}_3\text{H}_8\}$ at 150 K. —: phase envelope, - - -: connodes, white: eigenvector path.

Algorithm 2: solving the equilibrium conditions

the conditions:

$$\begin{aligned}\nabla_{\rho}\Psi'' &= \nabla_{\rho}\Psi' \\ \nabla_{\rho}\Psi \cdot \Delta\vec{\rho} &= \Delta\Psi \quad \text{with } \Delta\vec{\rho} = \vec{\rho}'' - \vec{\rho}'\end{aligned}$$

This is a system of $N + 1$ nonlinear equations for ρ' and $\vec{\rho}''$. It can be solved with common methods, e.g. the Marquardt–Levenberg method.

Note: The orthobaric molar volumes do not appear in these equations, except as sums of the ρ_i . It is not necessary to calculate the molar volumes from the pressure at each iteration step.

CPU time [s] for the computation of 1 isotherm (40 states):

model	G_m -based	Ψ -based
PR + 1FS	0.09	0.10
XD + 1FPKP	2.45	0.55
PCSAFT + 1FGS	10.50	0.36

PR + 1FS: Peng–Robinson EOS, 1-fluid theory after Soave (cubic)

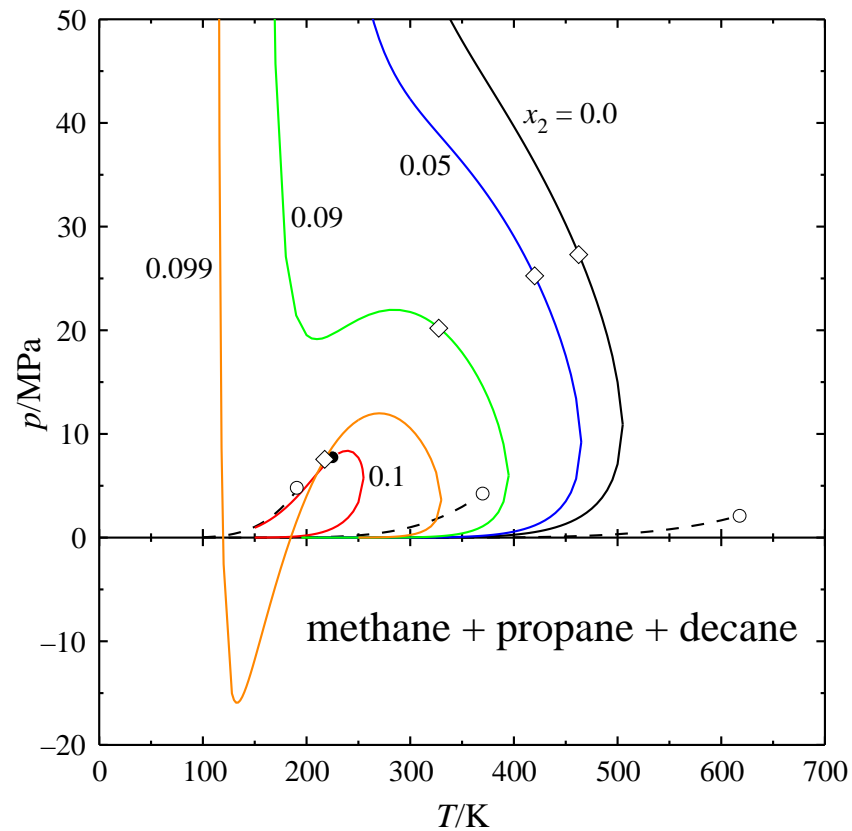
XD + 1FPKP: Xiang–Deiters EOS, Plöcker–Knapp–Prausnitz mixing rules (corresponding states, noncubic)

PCSAFT + 1FGS: PC-SAFT EOS, mixing rules of Groß & Sadowski (noncubic)

software: *ThermoC*, <http://thermoc.uni-koeln.de/index.html>

As the molar volumes do not have to be computed from the pressure, the calculation can follow isopleths into the negative-pressure regime.

(useful for work with metastable states, but also a way to locate liquid–liquid phase splitting)



Isopleths of $\{x_1 \text{CH}_4 + x_2 \text{C}_3\text{H}_8 + x_3 \text{C}_{10}\text{H}_{22}\}$ with $x_1 = 0.9$; parameter: x_2 .

Incidentally ...

The phase stability criterion (spinodal criterion) in isochoric thermodynamics is that Ψ , the Hessian of $\Psi(\vec{\rho})$ must be positive definite.

Consequently,

$$\det \Psi > 0$$

must be fulfilled (necessary condition, but neither sufficient nor efficient!).

For a pure fluid, this translates into

$$\left(\frac{\partial^2 \Psi}{\partial \rho^2} \right)_T > 0 ,$$

for a binary mixture, into

$$\begin{vmatrix} \Psi_{11} & \Psi_{12} \\ \Psi_{12} & \Psi_{22} \end{vmatrix} > 0 \quad \text{with} \quad \Psi_{ij} = \left(\frac{\partial^2 \Psi}{\partial \rho_i \partial \rho_j} \right)_T .$$

Conclusion

The isochoric approach leads to a symmetric and esthetically satisfying formulation of the phase equilibrium problem.

The search for initial values (Algorithm 1)

- is 1-dimensional even for multicomponent mixtures,
- is especially efficient if the coexisting phases have similar density vectors (VLE near to critical points, LLE).

The calculation of the phase compositions (Algorithm 2)

- shows robust convergence in the vicinity of critical points,
- is not affected by azeotropy,
- can be done for negative pressures, if required,
- saves CPU time in connexion with noncubic equations of state.

Acknowledgments

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Thank you for your attention!