A New Method for Critical Points Calculation from Cubic EOS

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Development of accurate and efficient methods for direct calculation of critical points is valuable for phase equilibrium calculations in chemical and petroleum engineering. A new method for critical points calculation is developed. For critical point calculation methods, the spinodal equation is given by setting to zero a determinant of nc (number of components) or nc-1 order, containing second-order derivatives of thermodynamic potentials. In this approach, this determinant has a lower order, which does not depend on the number of components in the mixture, but on the number of reduction parameters, with no restrictions on the binary interaction parameters (BIPs). The new method has been tested for several mixtures having various phase diagram shapes, and proved its reliability. The computation effort for each step for correcting temperature and molar volume can be significantly reduced. The proposed method is particularly efficient for mixtures with many components and few nonzero BIPs. Cubic two-parameter EOS are used; however, the proposed method can be applied for any EOS that observes the restrictions of the Reduction Theorem. © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 1220–1227, 2006
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Introduction

Criticality criteria for multicomponent systems may be expressed in many different ways. The most widely used mathematical formulation of the criticality criteria is that presented by Heidemann and Khalil[1] in 1980. The first criticality condition is the equation for the intrinsic limit of thermodynamic stability (spinodal)

$$\det(\boldsymbol{D}) = 0 \tag{1}$$

with

$$D_{ij} = \left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)_{T,V,n_{k\neq i,j}}; \quad i, j = 1, nc \tag{2}$$

or, equivalently

$$\boldsymbol{D} \cdot \Delta \boldsymbol{n} = 0 \tag{3}$$

together with the normalization condition

$$\Delta \boldsymbol{n}^T \Delta \boldsymbol{n} = 1 \tag{4}$$

where

$$\Delta \boldsymbol{n} = (\Delta n_1, \Delta n_2, \ldots, \Delta n_{nc})^T \tag{5}$$

The second criticality conditions locates the critical point(s) on the spinodal

$$C = \sum_{k=1}^{nc} \sum_{j=1}^{nc} \sum_{i=1}^{nc} \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k}\right)_{T,V,n_{l\neq i,j,k}} \Delta n_i \Delta n_j \Delta n_k = 0 \tag{6}$$

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The method of Heidemann and Khalil consists in nested iterations; in the outer loop Eq. 6 is solved for volume, and in the inner loop Eq. 1 is solved for temperature. It is obvious that the most costly part of the calculation is solving Eq. 1.

In this work we are using the reduction method to reduce the order of the determinant in the spinodal equation, and information from spinodal calculation is used to evaluate the cubic form C. The results of the reduction theorem (Hendriks[2]) are used to reduce the dimensionality of the problem. For many actual mixtures, such as hydrocarbon reservoir fluids and petrochemical mixtures, covering a variety of petroleum and chemical engineering problems, spectacular computer time savings can be obtained for critical point calculations.

A very important application of critical point calculations is in enhanced oil recovery using miscible gas (carbon dioxide or in some cases nitrogen) injection. The multicomponent reservoir oil – injection gas mixtures are always very close to the mixtures critical point at reservoir conditions, and it is important to know the location of the critical point to properly manage a reservoir. Since dynamic simulation is used (usually to represent a 20+ year time span), and the reservoir composition is changing during the simulation, phase equilibrium and critical point calculations are done repeatedly, and also represents the most time-consuming part of the calculation. Some of the mixtures selected in the applications section arise from such calculations.

Cubic EOS

In this work we use a general form of two-parameter EOS, including the PR EOS (Peng and Robinson[3]) and the SRK EOS (Soave[4])

$$p(\boldsymbol{n}, V, T) = \frac{nRT}{V - bn} - \frac{an^2}{(V + \delta_1 bn)(V + \delta_2 bn)} \tag{7}$$

with

$$\boldsymbol{n} = (n_1, n_2, \ldots, n_{nc})^T \tag{8}$$

The van der Waals mixing rules are used for the energy, a and for the volume, b parameters of the EOS

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} y_i y_j a_{ij} \tag{9}$$

$$b = \sum_{j=1}^{nc} y_j b_j \tag{10}$$

where

$$a_{ij} = a_{ji} = (a_i a_j)^{0.5}(1 - k_{ij}); \quad i, j = 1, nc \tag{11}$$

$$a_i = \Omega_a \frac{R^2 T_{ci}^2}{p_{ci}} [1 + m(\omega_i)(1 - T_{ri}^{0.5})]^2 \tag{12}$$

$$b_i = \Omega_b \frac{RT_{ci}}{p_{ci}} \tag{13}$$

in which $T_{rj}=T/T_{cj}$ and $p_{rj}=p/p_{cj}$ are the reduced temperature and pressure of component j (with critical temperature T_{cj} and pressure p_{cj}), and the k_{ij} is the BIP between components i and j. The values of δ_1, δ_2, Ω_a and Ω_b and the expression of m as a function of the acentric factor ω for the PR and SRK EOS are given in Appendix A.

The general expression for the Helmholtz free energy is

$$A = \int_V^\infty \left(p - \frac{nRT}{V}\right) dV - RT \sum_{i=1}^{nc} n_i \ln\left(\frac{V}{n_i RT}\right) + \sum_{i=1}^{nc} n_i (u_i^0 - Ts_i^0) \tag{14}$$

The Helmholtz free energy A is relative to a reference state of pure ideal gas at system temperature and unit pressure. For the general form of two-parameter EOS (Eq. 7), the Helmholtz free energy is given by

$$A(\boldsymbol{n}, V, T) = -nRT \ln\left(\frac{V - bn}{nRT}\right) - \frac{an}{\Delta b} \ln\left(\frac{V + \delta_1 bn}{V + \delta_2 bn}\right) + RT \sum_{i=1}^{nc} n_i \ln y_i - nRT \tag{15}$$

with $\Delta = \delta_1 - \delta_2$.

Reduction Parameters

As suggested by Hendriks and van Bergen,[5] we consider the truncated spectral expansion of the EOS parameter

$$a_{ij} \cong \sum_{\alpha=1}^{m} \lambda_\alpha q_{\alpha i} q_{\alpha j}; \quad i, j = 1, nc \tag{16}$$

where m is the number of nonzero or non-negligible eigenvalues λ_α, of the matrix with elements a_{ij}, and $q_{\alpha i}$ are the elements of the corresponding eigenvectors $\boldsymbol{q}_\alpha = (q_{\alpha 1}, q_{\alpha 2}, \ldots, q_{\alpha nc})^T$. It is more convenient to calculate once for all the eigenvalues and eigenvectors $\mathbf{q}'_\alpha$ of the matrix $\mathbf{K}$ with elements (1-k_{ij}), then to calculate

$$q_{\alpha i} = q'_{\alpha i} \sqrt{a_i}; \quad \alpha = 1, m; \quad i = 1, nc \tag{17}$$

The *reduction parameters* are defined as

$$Q_\alpha = \sum_{i=1}^{nc} q_{\alpha i} y_i; \quad \alpha = 1, M \tag{18}$$

where $q_{\alpha i}$ are the elements of the *“reduction matrix”*.[2]

Combining Eqs. 9 and 16, the energy term of the EOS can be written as

$$a = \sum_{\alpha=1}^{m} \lambda_\alpha Q_\alpha^2 \tag{19}$$

The last reduction parameter is b

$$Q_M \equiv b = \sum_{i=1}^{nc} b_i y_i \tag{20}$$

and the corresponding elements of the reduction matrix are $q_{Mi} \equiv b_i$, $i = 1, nc$.

Finally, the set of $M+1$ reduction parameters is

$$\boldsymbol{Q} = (Q_1, Q_2, \ldots, Q_m, b)^T = (Q_1, Q_2, \ldots, Q_m, Q_M)^T \tag{21}$$

Usually, for many actual mixtures, many of the BIPs are zero. The BIP matrix is sparse, the matrix **K** is often rank-deficient, and $m \ll nc$. The matrix **K** has the rank one if all BIPs are zero. Each component having nonzero BIPs introduces two nonzero eigenvalues, unless the BIPs with the remaining components are equal. In the latter case, only one nonzero eigenvalue is introduced by such a component (since the number of linearly independent rows or columns is reduced by one). Therefore, the rank of **K** is $r = m = 2n_B + 1 - n_E$, where n_B is the number of components with nonzero BIPs, and n_E is the number of components having equal nonzero BIPs with the remaining components. Application of the reduction method for phase equilibrium calculation is particularly efficient for mixtures with many components and few nonzero BIPs.

The Helmholtz free energy can be expressed as

$$A = nRT\left[\sum_{i=1}^{nc} y_i \ln y_i + h\boldsymbol{Q}, v, T)\right] \tag{22}$$

with the function h

$$h(\boldsymbol{Q}, v, T) = \ln\left(\frac{v - Q_M}{RT}\right) - \frac{\sum_{\alpha=1}^{m} \lambda_\alpha Q_\alpha^2}{\Delta RTQ_M} \ln\left(\frac{v + \delta_1 Q_M}{v + \delta_2 Q_M}\right) - 1 \tag{23}$$

depending only on reduction parameters, molar volume, and temperature.

In this work cubic two-parameter EOS are used; however, the proposed method can be applied for any EOS that observes the restrictions of the Hendriks' Reduction Theorem.[2]

Intrinsic limit of stability

The elements of the matrix **D** required for calculating the stability limit are given by (Michelsen and Heidemann[6])

$$\begin{aligned} nD_{ij} \equiv n\left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)_{T,V,n_{k\neq i,j}} &= nRT\left(\frac{\partial \ln f_i}{\partial n_j}\right)_{T,V,n_{j\neq i}} \\ &= RT\left[\frac{\delta_{ij}}{y_i} + (\beta_i + \beta_j)F_1 + \beta_i\beta_j F_1^2\right] - \frac{a_{ij}}{b}F_5 \\ &+ \frac{a}{b}[\beta_i\beta_j F_3 + (\beta_i\beta_j - \alpha_i\beta_j - \alpha_j\beta_i)F_6]; \quad i, j = 1, nc \end{aligned} \tag{24}$$

where

$$\alpha_i = 1/a \sum_{j=1}^{n} y_j a_{ij} \tag{25}$$

$$\beta_i = \frac{b_i}{b} \tag{26}$$

and F_k are functions of the molar volume only (see Notation).

The matrix **D** containing second-order partial derivatives of thermodynamic potentials with respect to mole numbers has a special form; its elements can be expressed as

$$D_{ij} = \frac{\delta_{ij}}{y_i} + \sum_{\alpha=1}^{M+1} \sum_{\beta=1}^{M+1} H_{\alpha\beta} q_{\alpha i} q_{\beta j}; \quad i, j = 1, nc \tag{27}$$

The matrix **H** contains second-order partial derivatives of thermodynamic potentials with respect to the reduction parameters. Derivatives of Gibbs free energy were given by Hendriks and van Bergen.[5] Here we will use derivatives of Helmholtz free energy to express **D**; in this case, the matrix **H** contains additionally partial derivatives of the compressibility factor.

The reduction theorem[2] states that the *nc*x*nc* matrix **D** is positive definite (for a thermodynamic stable system), or singular (for systems on the limit of thermodynamic stability) for the same conditions where the $(M+1)\times(M+1)$ matrix **S** is positive definite or singular, respectively, where **S** is given by

$$\mathbf{S} \equiv \mathbf{I} + \boldsymbol{\Psi}^T \boldsymbol{\Psi} \mathbf{H} \tag{28}$$

or

$$S_{\alpha\beta} = \delta_{\alpha\beta} + \sum_{i=1}^{nc} \psi_{i\alpha} \sum_{\gamma=1}^{M+1} \psi_{i\gamma} H_{\gamma\beta}; \quad \alpha, \beta = 1, M + 1 \tag{29}$$

where

$$\Psi_{i\alpha} = \sqrt{y_i}\, q_{\alpha i}; \quad i = 1, nc; \quad \alpha = 1, M + 1 \tag{30}$$

and

$$q_{M+1,i} = 1; \quad i = 1, nc \tag{31}$$

If we define

$$Y_{\alpha\beta} = \sum_{i=1}^{nc} \psi_{i\alpha}\psi_{i\beta} \tag{32}$$

then

$$S_{\alpha\beta} = \delta_{\alpha\beta} + \sum_{\gamma=1}^{M+1} H_{\gamma\beta}Y_{\alpha\gamma}; \quad \alpha,\ \beta = 1,\ M+1 \tag{33}$$

or in matrix form

$$\mathbf{S} = \mathbf{I} + \mathbf{Y}^T\mathbf{H} \tag{34}$$

The equation of the spinodal is

$$\det(\boldsymbol{S}) = 0 \tag{35}$$

Once we have obtained the elements of **H** matrix, we are able to locate the spinodal by evaluating determinants det ($\boldsymbol{S}$) of order $M+1$ ($m+2$), instead of nc order determinants as required by the Heidemann and Khalil[1] intrinsic stability criterion. This leads to significant reduction of computer time if $M \ll nc$.

To obtain the elements of **H** matrix, we derive twice the Helmholtz free energy with respect to mole numbers. First derivation gives the chemical potentials

$$\frac{\mu_i(\boldsymbol{Q})}{RT} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \ln y_i + h(\boldsymbol{Q}) + \sum_{\alpha=1}^{M} (q_{\alpha i} - Q_\alpha)\frac{\partial h(\boldsymbol{Q})}{\partial Q_\alpha} + (Z(\boldsymbol{Q}) - 1); \quad i = 1, nc \tag{36}$$

viewed as functions of the reduction parameters at given temperature, molar volume, and composition.

The compressibility factor Z is obtained by rearrangement of Eq. 7

$$Z(T,\ \kappa,\ \mathbf{Q}) = \kappa F_1 - \frac{\sum_{\alpha=1}^{m} \lambda_\alpha Q_\alpha^2}{Q_M RT}\frac{F_2}{2} \tag{37}$$

where κ is the dimensionless volume

$$\kappa = \frac{v}{b} \tag{38}$$

The relationship

$$\left(\frac{\partial Q_\alpha}{\partial n_j}\right)_{n_{k\neq j}} = \frac{1}{n}(q_{\alpha j} - Q_\alpha); \quad \alpha = 1,\ M; \quad j = 1,\ nc \tag{39}$$

has been used for obtaining Eq. 36.

Second derivation gives after some rearrangement

$$\frac{n}{RT}\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,V,n_{k\neq j}} = \frac{\delta_{ij}}{y_i} - 1 + \sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}(q_{\alpha i} - Q_\alpha)(q_{\beta_j} - Q_\beta) \times \frac{\partial^2 h}{\partial Q_\alpha \partial Q_\beta} + \phi_{ij}(T,\ \kappa,\ \boldsymbol{Q}) \tag{40}$$

where

$$\phi_{ij}(T,\ \kappa,\ \boldsymbol{Q}) = \sum_{\alpha=1}^{M}(q_{\alpha i} - Q_\alpha)\frac{\partial Z}{\partial Q_\alpha} + \sum_{\beta=1}^{M}(q_{\beta_j} - Q_\beta)\frac{\partial Z}{\partial Q_\beta} + (Z-1) + a\frac{\partial Z}{\partial a} + b\frac{\partial Z}{\partial b} \tag{41}$$

and

$$\left(\frac{\partial Z}{\partial Q_\alpha}\right)_{T,V,Q_{\beta\neq\alpha,\alpha=1,M}} = -\frac{\lambda_\alpha Q_\alpha}{bRT}F_2; \quad \alpha = 1, m \tag{42}$$

$$\left(\frac{\partial Z}{\partial Q_M}\right)_{T,V,Q_\alpha,\alpha=1,m} \equiv \frac{\partial Z}{\partial b} = \frac{1}{b}\left(\kappa F_1^2 + \frac{a}{bRT}F_3\right) \tag{43}$$

$$\left(\frac{\partial Z}{\partial a}\right)_{T,V,b} = -\frac{F_2}{2bRT} \tag{44}$$

The derivatives of the compressibility factor with respect to mole numbers required by the derivation are

$$n\left(\frac{\partial Z}{\partial n_j}\right)_{T,V,n_{k\neq j}} = \sum_{\alpha=1}^{M}(q_{\alpha j} - Q_\alpha)\frac{\partial Z}{\partial Q_\alpha}; \quad \alpha = 1,\ M; \quad j = 1,\ nc \tag{45}$$

Finally we get

$$\frac{n}{RT}\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,V,n_{k\neq j}} = \frac{\delta_{ij}}{y_i} + \sum_{\alpha=1}^{M+1}\sum_{\beta=1}^{M+1} q_{\alpha i}q_{\beta j}H_{\alpha\beta}; \quad i,j = 1, nc \tag{46}$$

with

$$H_{\alpha\beta} = H_{\beta\alpha} = \left(\frac{\partial^2 h}{\partial Q_\alpha \partial Q_\beta}\right)_{Q_{\gamma\neq\alpha,\beta}}; \quad \alpha,\ \beta = 1,\ M \tag{47}$$

$$H_{\alpha,M+1} = H_{M+1,\alpha} = \frac{\partial Z}{\partial Q_\alpha} - \sum_{\beta=1}^{M} Q_\beta h_{\alpha\beta}; \quad \alpha = 1,\ M \tag{48}$$

$$H_{M+1,M+1} = -1 + \sum_{\alpha=1}^{M}\sum_{\beta=1}^{M} Q_\alpha Q_\beta h_{\alpha\beta} - 2\sum_{\alpha=1}^{M} Q_\alpha \frac{\partial Z}{\partial Q_\alpha} + (Z-1) + a\frac{\partial Z}{\partial a} + b\frac{\partial Z}{\partial b} \tag{49}$$

The partial derivatives of h with respect to the reduction parameters are given in Appendix B. Elements of the matrix **S** are calculated from Eq. 33, and scaled as suggested by Heidemann and Khalil.[1]

Second Criticality Condition

The cubic form from Eq. 6 can be expressed in a closed form (Michelsen and Heidemann[6])

$$n^2C \equiv RT\left\{-\sum_{i=1}^{nc}\left[\frac{(\Delta n_i)^3}{y_i^2}\right] + 3\bar{n}(\bar{\beta}F_1)^2 + 2(\bar{\beta}F_1)^3 + \frac{a}{b}[3\bar{\beta}^2 \times (2\bar{\alpha} - \bar{\beta})(F_3 + F_6) - 2\bar{\beta}^3F_4 - 3\overline{\beta a}F_6]\right\} = 0 \quad (50)$$

where

$$\bar{\alpha} \equiv \sum_{i=1}^{nc} \alpha_i \Delta n_i = \boldsymbol{a}^T \boldsymbol{\Delta n} \quad (51)$$

$$\bar{\beta} \equiv \sum_{i=1}^{nc} \beta_i \Delta n_i = \beta^T \boldsymbol{\Delta n} \quad (52)$$

$$\bar{a} \equiv \frac{1}{a}\sum_{i=1}^{nc}\sum_{j=1}^{nc} \Delta n_i \Delta n_j a_{ij} \quad (53)$$

$$\bar{n} = \sum_{i=1}^{nc} \Delta n_i \quad (54)$$

The key in our approach is to express Δn_i, and all other quantities from Eq. 50, that is, $\bar{\alpha}$, $\bar{\beta}$, $\bar{a}$, and $\bar{n}$ in terms of some quantities available from the spinodal calculation.

Let us consider the product of matrix **S** with the vector **ΔQ**

$$\boldsymbol{S}\Delta\boldsymbol{Q} = 0 \quad (55)$$

where the vector **ΔQ** is

$$\Delta\boldsymbol{Q} = (\Delta Q_1, \ldots, \Delta Q_M, \Delta Q_{M+1})^T \quad (56)$$

having the elements

$$\Delta Q_\alpha = \sum_{i=1}^{nc} q_{\alpha i}\Delta n_i'; \quad \alpha = 1, M \quad (57)$$

and

$$\Delta Q_{M+1} = \sum_{i=1}^{nc} \Delta n_i' = \frac{\sum_{i=1}^{nc} \Delta n_i}{\bar{n}} = 1 \quad (58)$$

with $\Delta n_i'$ defined as

$$\Delta n_i' = \frac{\Delta n_i}{\bar{n}}; \quad i = 1, nc \quad (59)$$

It can be easily proved that **ΔQ** computed from Eq. 55 and $\boldsymbol{\Delta n}$ which satisfies Eq. 3 are related by Eq. 57–59. The vector **ΔQ** is found by back substitution using the upper triangular form of the **S** matrix available from resolution of Eq. 35. The vector **ΔQ** is normalized by

$$\Delta\boldsymbol{Q}^T\Delta\boldsymbol{Q} = 1 \quad (60)$$

The restriction

$$(\Delta\boldsymbol{Q}^{(\nu)})^T\Delta\boldsymbol{Q}^{(0)} > 0 \quad (61)$$

is used to avoid discret jumps due to sign changes in **ΔQ**, ν being the iteration level.

The quantities $\bar{\alpha}$,$\bar{\beta}$, and $\bar{a}$, are related to $\bar{n}$ through

$$\bar{\alpha} = \frac{1}{a}\left[\sum_{i=1}^{nc}\left(\sum_{j=1}^{nc} y_j a_{ij}\right)\Delta n_i\right]\bar{n} \quad (62)$$

$$\bar{\beta} = \frac{\Delta b}{b}\bar{n} \quad (63)$$

$$\bar{a} = \frac{\Delta a}{a}\bar{n}^2 \quad (64)$$

Let us define

$$\overline{\alpha'}(\mathbf{Q}, \Delta\mathbf{Q}) = \frac{\bar{\alpha}}{\bar{n}} = \frac{1}{a}\sum_{\alpha=1}^{M}\lambda_\alpha Q_\alpha \Delta Q_\alpha \quad (65)$$

$$\overline{\beta'}(\mathbf{Q}, \Delta\mathbf{Q}) = \frac{\bar{\beta}}{\bar{n}} = \frac{\Delta b}{b} = \frac{\Delta Q_M}{Q_M} \quad (66)$$

$$\overline{a'}(\Delta\mathbf{Q}) = \frac{\bar{a}}{\bar{n}^2} = \frac{1}{a}\sum_{\alpha=1}^{M}\lambda_\alpha \Delta Q_\alpha^2 \quad (67)$$

and express $\boldsymbol{\Delta n'}$ as

$$RT\frac{\Delta n_i'}{y_i} = \frac{F_5}{b}\sum_{j=1}^{nc} a_{ij}\Delta n_j - \left\{\left[RTF_1 + \frac{a}{b}[F_8\beta_i + F_6(\beta_i - \alpha_i)]\right]\overline{\beta'} + \left[\frac{a}{b}(F_5 + F_7)\beta_i\right]\overline{\alpha'}\right\} \quad (68)$$

Equation 68 is obtained by rearrangement of Eq. 9 from Billingsley and Lam.[7] Considering Eq. 16, one obtains

Table 1. Critical Point Calculation for Selected Mixtures

Mixture	nc and Order of HK Determinant	No. of Non-Zero BIPs	Comp. with Non-Zero BIPs	No. of Non-Zero Eigenvalues	Order of RED Determinant	Number of Iterations on κ in the Outer Loop
Y8	6	0	—	1	3	4
M7	7	1	N_2	2	4	4
NCG9	8	3	C_1, C_2, C_3	6	8	4
MY10	10	1	C_1	3	5	3
MY10/CO_2	11	2	C_1, CO_2	5	7	(3 . . . 5)*
Sample A	34	3	C_1, CO_2, N_2	5	7	4
Sample B	24	3	C_1, CO_2, N_2	5	7	3
Sample C	24	3	C_1, CO_2, N_2	5	7	4

*Depending on CO_2 participation in the mixture.

$$\Delta n_i' = \frac{y_i}{RT}\left[\frac{F_5}{b}u_i + \frac{a}{b}F_6\overline{\beta'}\alpha_i - \frac{a}{b}E\beta_i - RTF_1\overline{\beta'}\right] \quad (69)$$

with the notations

$$u_i = \sum_{\alpha=1}^{M} \lambda_\alpha q_{\alpha i}\Delta Q_\alpha \quad (70)$$

and

$$E = (F_6 + F_8)\overline{\beta'} + (F_5 + F_7)\overline{\alpha'} \quad (71)$$

Finally, the cubic form is

$$\frac{n^2}{\bar{n}^3}C \equiv RT\left\{-\sum_{i=1}^{nc}\left[\frac{(\Delta n_i')^3}{y_i^2}\right] + 3(\overline{\beta'}F_1)^2 + 2(\overline{\beta'}F_1)^3 + \frac{a}{b}[3\overline{\beta'^2}(2\overline{\alpha'} - \overline{\beta'})(F_3 + F_6) - 2\overline{\beta'^3}F_4 - 3\overline{\beta'a'}F_6]\right\} = 0 \quad (72)$$

Because, $\overline{\alpha'}$, $\overline{\beta'}$, and $\overline{a'}$ are functions of $\boldsymbol{Q}$ and $\Delta\boldsymbol{Q}$, see Eqs. 65–67, and $\Delta\mathbf{n}'$ can be expressed as a function of $\overline{\alpha'}$, $\overline{\beta'}$, and $\Delta\boldsymbol{Q}$, the cubic form C can be viewed as a function of only $\boldsymbol{Q}$ and $\Delta\boldsymbol{Q}$ at given temperature and molar volume

$$C = C(T, \kappa, \boldsymbol{Q}, \Delta\boldsymbol{Q}) \quad (73)$$

This means that information obtained in the spinodal calculation with Eqs. 35 and 55 by evaluating lower order determinants, that is, $\Delta\boldsymbol{Q}$ at given T and κ, is sufficient for evaluating the cubic form. The cubic form is scaled with $(\kappa - 1)^2$ as recommended by Heidemann and Khalil.[1]

Calculation procedure

Nested iterations are performed to calculate the critical point, similarly with Heidemann and Khalil.[1] In the outer loop we iterate on the dimensionless volume for solving Eq. 72, while in the inner loop iterations are performed on temperature to solve Eq. 35. We use Newton-Raphson (NR) iterations with numerical derivatives.

Starting from $\kappa^{(0)} = 3.5$, Eq. 35 is solved for temperature with the NR method with $T^{(0)} = 1.5T_{pc}$ (higher initial values for temperature may be required for heavy oils; $T_{pc} = \Sigma_{i=1}^{nc} y_iT_{ci}$ is the mixture pseudocritical temperature), then $\Delta\mathbf{Q}$ is obtained by back substitution. Values of $\overline{\alpha'}$, $\overline{\beta'}$, and $\overline{a'}$ are calculated, then $\Delta n_i'$ is recovered from Eq. 69, and the cubic form is evaluated. The dimensionless volume is corrected with the NR method, until the convergence criterion is met.

Applications

The proposed method has been tested for a large number of mixtures, having various phase diagram shapes, and proved its reliability. Usually 4–7 iterations are required in the inner loop calculations, and convergence in the outer loop is achieved in 3–6 iterations.

Table 1 gives a comparison of determinants order between the Heidemann and Khalil[1] (HK) method and the proposed method (RED), for various selected mixtures.

The Y8 mixture (Yarborough[8]), and the MY10 mixture (Metcalfe and Yarborough[9]), are synthetic mixtures of normal alkanes. For Y8 all BIPs are zero, thus, there is only one nonzero eigenvalue that equals nc. For MY10, there are10 components and nonzero methane BIPs, giving three nonzero eigenvalues. When carbon dioxide is added in various amounts to the MY10 mixture, there are five nonzero eigenvalues. A 7 component mixture containing normal alkanes and nitrogen, denoted M7, is taken from Michelsen.[10] The only nonzero BIPs (equal to 0.1) are between nitrogen and hydrocarbon components, giving only two nonzero eigenvalues. Mixture NCG9 from Nagarajan et al.[11] exhibits open shaped phase envelope and spinodal (Nichita et al.[12]).

Samples A (gas condensate with 34 components), B (heavy oil with 24 components), and C (heavy gas condensate with 24 components) are from Pedersen et al.[13] Nonzero BIPs are for methane, carbon dioxide, and nitrogen, leading for all three mixtures to 5 nonzero eigenvalues.

For the mixtures in Table 1, components having nonzero BIPs with the remaining components are specified; the number of nonzero eigenvalues of the matrix $\mathbf{K}$ is also given. For all situations, the dimensionality of the problem is reduced; however, this reduction becomes spectacular for mixtures with many components. Reducing the dimensionality of the problem is important because the most expensive part of the calculation algorithm is the evaluation of a determinant (which is known to be an nc^3 process). The larger the number of components, the more efficient the proposed method is.

Note that for all examples considered, convergence is obtained in the same number of iterations (given in Table 1) with the HK and the proposed method. We have used the same initial guesses, the same stopping conditions for the iterative process (giving the same accuracy), and the same scaling factors for quadratic and cubic forms. The convergence path in the κ-T plane is almost the same for both methods, but lower order determinants are calculated in our method.

Finally, it is worth noting that the formalism presented in this work can be used for any set of reduction parameters; the spectral decomposition of the matrix **K** is not necessary if different reduction parameters[14] are used.

Conclusions

An efficient procedure has been developed for critical points calculation using the Heidemann and Khalil criticality criteria. The proposed method is based on the reduction theorem and it requires low-order determinants evaluation in the spinodal equation. The cubic form can be evaluated using the information from spinodal calculation.

For the computationally most expensive part of the algorithm, the dimensionality can be significantly reduced using the proposed method. The method is particularly efficient for mixtures with many components and few nonzero BIPs, such as naturally occurring hydrocarbon mixtures. The computer time savings can be spectacular for such calculations.

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Notation

A = Helmholtz free energy
a = attractive parameter in the EOS
a_i = component parameter in EOS
a_{ij} = component EOS coefficient
$\bar{a}$ = given by Eq. 53
$\bar{a}'$ = given by Eq. 67
b_i = component EOS coefficient
b = covolume in the EOS
C = cubic form
$\boldsymbol{D}$ = matrix of partial derivatives
D_{ij} = elements of matrix $\mathbf{D}$
E = given by Eq. 71
$F_1 = 1/(\kappa-1)$
$F_2 = 2[\delta_1/(\kappa + \delta_1) - \delta_2/(\kappa + \delta_2)]/\Delta$
$F_3 = \{[\delta_1/(\kappa + \delta_1)]^2 - [\delta_2/(\kappa + \delta_2)]^2\}/\Delta$
$F_4 = \{[\delta_1/(\kappa + \delta_1)]^3 - [\delta_2/(\kappa + \delta_2)]^3\}/\Delta$
$F_5 = 2 \ln[(\kappa + \delta_1)/(\kappa + \delta_2)]/\Delta$
$F_6 = F_2 - F_5$
$F_7 = -F_2/(1 + F_1)$
$F_8 = F_3/(1 + F_1)$
f_i = fugacity, component i
$\mathbf{H}$ = matrix of partial derivatives
$H_{\alpha\beta}$ = elements of $\mathbf{H}$ matrix
h = function of $\mathbf{Q}$, v, and T
$h_{\alpha\beta}$ = second-order derivatives of h
$\boldsymbol{K}$ = matrix with elements, $1-k_{ij}$
k_{ij} = binary interaction parameters between components i and j
M = number of reduction parameters
m = number of nonzero eigenvalues
n = total number of moles
n_i = mole number of component i
nc = number of components
p = pressure
$\boldsymbol{Q}$ = vector of reduction parameters
Q_α = reduction parameters
$\boldsymbol{q}_\alpha$ = eigenvectors
$q_{\alpha i}$ = elements of the eigenvectors
R = universal gas constant
$\boldsymbol{S}$ = matrix in spinodal equation
$S_{\alpha\beta}$ = elements of $\mathbf{S}$ matrix
T = temperature
u_i = given by Eq. 70
V = total volume
v = molar volume
y_{i} = mole fraction, component i
$\boldsymbol{Y}$ = matrix given by Eq. 32
$Y_{\alpha\beta}$ = elements of matrix $\mathbf{Y}$
Z = compressibility factor

Greek letters

α_i = given by Eq. 25
β_i = given by Eq. 26
$\bar{\alpha}$ = given by Eq. 51
$\bar{\beta}$ = given by Eq. 52
$\bar{\alpha}'$ = given by Eq. 65
$\bar{\beta}'$ = given by Eq. 66
δ_{ij} = Kroneker delta
δ_1, δ_2 = constants in EOS
$\Delta = \delta_1 - \delta_2$
$\Delta\boldsymbol{Q}$ = vector defined by Eq. 56
ϕ_{ij} = given by Eq. 41
κ = dimensionless volume
λ = eigenvalues
$\boldsymbol{\psi}$ = matrix defined by Eq. 30
$\psi_{\alpha i}$ = elements of matrix $\boldsymbol{\psi}$
Ω_a, Ω_b = coefficients in the EOS
ω = acentric factor

Subscripts

c = critical
i,j = component index
r = reduced
pc = pseudocritical
α = reduction parameter index
β = reduction parameter index

Superscripts

T = transposed
ν = iteration level
0 = initial

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Appendix A

The EOS parameters are as follows

$$m(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2; \quad \text{for} \quad \omega < 0.5$$
$$m(\omega) = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016667\omega^3; \quad \text{for} \quad \omega \geq 0.5 \qquad \text{(A1)}$$

$$m(\omega) = 0.48508 + 1.55171\omega - 0.15613\omega^2 \qquad \text{(A2)}$$

Appendix B

First and second-order derivatives of h with respect to the reduction parameters are:

$$\left(\frac{\partial h}{\partial Q_\alpha}\right)_{Q_{\beta \neq \alpha}} = -\frac{\lambda_\alpha Q_\alpha}{bRT} F_5; \quad \alpha = 1, m \qquad \text{(B1)}$$

$$\left(\frac{\partial h}{\partial b}\right)_{Q_\alpha} = \frac{1}{b}\left[Z - 1 + \frac{a}{2bRT} F_5\right] \qquad \text{(B2)}$$

$$h_{\alpha\beta} = \left(\frac{\partial^2 h}{\partial Q_\alpha \partial Q_\beta}\right)_{Q_{\gamma \neq \alpha,\beta}} = -\frac{\lambda_\alpha \delta_{\alpha\beta}}{bRT} F_5; \quad \alpha, \beta = 1, m \qquad \text{(B3)}$$

$$h_{\alpha M} = \left(\frac{\partial^2 h}{\partial Q_\alpha \partial b}\right)_{Q_{\beta \neq \alpha}} = -\frac{\lambda_\alpha Q_\alpha}{b^2 RT} F_6; \quad \alpha = 1, m \qquad \text{(B4)}$$

$$h_{MM} = \left(\frac{\partial^2 h}{\partial b^2}\right)_{Q_\alpha} = \frac{1}{b^2}\left[F_1^2 + \frac{a}{bRT}(F_3 + F_6)\right] \qquad \text{(B5)}$$

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