Critical Point Calculation with Nonzero Interaction Parameters

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Introduction

Michelsen and Heidemann (1981) formulate the calculation of critical points as an eigenvalue problem. They consider equations of state of the form

$$P = \frac{RT}{v - b} - \frac{a}{(v + \delta_1 b)(v + \delta_2 b)} \tag{1}$$

Their elegant approach has appealing features. When each binary interaction parameter, k_{ij}, is zero they require an eigenvalue of only a 2×2 matrix regardless of the number of components in the mixture. Nonzero interaction parameters, however, require determining an eigenvalue and eigenvector for a matrix having a row and column for each component in the mixture. Actually this is unnecessary; the formulation requiring an eigenvalue of only a 2×2 matrix is extended in the next section to nonzero interaction parameters.

Problem Formulation

Heidemann and Khalil (1980) derived the following criteria for the critical point of a mixture having composition specified by the mole number vector, $\boldsymbol{n}$.

$$Q\Delta \boldsymbol{n} = 0, \quad \Delta \boldsymbol{n}^T \Delta \boldsymbol{n} = 1 \tag{2}$$

and the cubic form

$$C \equiv \sum_i \sum_j \sum_k \Delta n_i \Delta n_j \Delta n_k \left(\frac{\partial^3 A}{\partial n_i \partial n_k \partial n_j}\right)_{T,V} = 0 \tag{3}$$

With Eq. 1 rewritten as $Z = Pv/RT = \kappa F_1 - aF_2/(2bRT)$ the elements, Q_{ij}, of the matrix Q are given by Michelsen and Heidemann (1981) as

$$n_T Q_{ij} \equiv n_T \left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)_{T,V} = n_T RT \left(\frac{\partial \ln f_i}{\partial n_j}\right)_{T,V}$$
$$= RT \left[\frac{\delta_{ij}}{y_i} + (\beta_i + \beta_j) F_1 + \beta_i \beta_j F_1^2\right] - \frac{a_{ij} F_5}{b}$$
$$+ \frac{a}{b}\left[\beta_i \beta_j F_3 + (\beta_i \beta_j - \alpha_i \beta_j - \alpha_j \beta_i) F_6\right] \tag{4}$$

f_i was obtained in the usual way from Eq. 1 (Prausnitz, 1969, pp. 42, 156). The mixing rules and other variables (Michelsen and Heidemann, 1981) are defined in the Notation. Using this notation, Eq. 7 is derived from Eq. 3 by differentiating Eq. 4 with respect to n_k, multiplying by $\Delta n_i \Delta n_j \Delta n_k$ and performing the triple summation. One must be certain to differentiate at constant total volume. Thus, for instance, there is

$$n_T \partial \kappa / \partial n_k = n_T \partial [V/(n_T b)]/\partial n_k = -\kappa \beta_k \tag{5}$$

It is also convenient to employ the partial fraction expansion

$$\frac{\kappa \delta}{(\kappa + \delta)^{n+1}} = \frac{\delta}{(\kappa + \delta)^n} - \frac{\delta^2}{(\kappa + \delta)^{n+1}} \tag{6}$$

when differentiating F_2 and F_3. One finally finds

$$C = RT \left\{ -\sum_i [(\Delta n_i)^3 / y_i^2] + 3\bar{n}(\bar{\beta} F_1)^2 + 2(\bar{\beta} F_1)^3 \right\}$$
$$+ \frac{a}{b}\left[3\bar{\beta}^2(2\bar{\alpha} - \bar{\beta})(F_3 + F_6) - 2\bar{\beta}^3 F_4 - 3\bar{\beta}\bar{a} F_6\right] = 0 \tag{7}$$

Equation 7 corrects a misprint in Eq. 18 of Michelsen and Heidemann (Michelsen, 1984).

From Eq. 2 one has for each component, i,

$$S_i \equiv \sum_j n_T Q_{ij} \Delta n_j = 0 \tag{8}$$

Subsituting from Eq. 4 into Eq. 8 and using $\Sigma_i y_i S_i = 0$ to eliminate $\overline{n}$ yields, as outlined in Appendix A,

$$\begin{aligned} -RT\frac{\Delta n_i}{y_i} + \frac{F_5}{b}\sum_j a_{ij}\Delta n_j \\ = \{RTF_1 + (a/b)[\beta_i(1+F_1)^{-1}F_3 + (\beta_i - \alpha_i)F_6]\}\overline{\beta} \\ + (a/b)(F_1F_5 - F_6)(1+F_1)^{-1}\beta_i\overline{\alpha} \end{aligned} \tag{9}$$

for each i. One assembles Eq. 9 for all components i into a single vector equation, multiplies throughout by b/F_5, and has

$$U\Delta\boldsymbol{n} = \gamma_\beta\overline{\beta} + \gamma_\alpha\overline{\alpha} \tag{10}$$

or

$$\Delta\boldsymbol{n} = U^{-1}\gamma_\beta\overline{\beta} + U^{-1}\gamma_\alpha\overline{\alpha} \tag{11}$$

where γ_α and γ_β are the vectors of coefficients of $\overline{\alpha}$ and $\overline{\beta}$, respectively,

$$\Delta\boldsymbol{n} \equiv (\Delta n_1, \ldots, \Delta n_i, \ldots, \Delta n_I)^T \tag{12}$$

and U is the matrix with elements

$$\begin{aligned} (U)_{ij} &= a_{ij}, \quad i \neq j \\ (U)_{ii} &= a_{ii} - (RT/y_i)(b/F_5) \end{aligned} \tag{13}$$

U is symmetric since $k_{ij} = k_{ji}$. Also since U^{-1} is always postmultiplied by a vector, it is never necessary to compute U^{-1} explicitly. Instead and for instance, one may define product vectors $\boldsymbol{p}_\alpha$ and $\boldsymbol{p}_\beta$, which are column vectors, by $[\boldsymbol{p}_\alpha, \boldsymbol{p}_\beta] \equiv U^{-1}[\gamma_\alpha, \gamma_\beta]$. Then it remains only to solve the linear equations $U[\boldsymbol{p}_\alpha, \boldsymbol{p}_\beta] = [\gamma_\alpha, \gamma_\beta]$ for $\boldsymbol{p}_\alpha$ and $\boldsymbol{p}_\beta$. If

$$\begin{aligned} \boldsymbol{\alpha} &\equiv (\alpha_1, \ldots, \alpha_i, \ldots, \alpha_I)^T \\ \boldsymbol{\beta} &\equiv (\beta_1, \ldots, \beta_i, \ldots, \beta_I)^T \\ \boldsymbol{u} &\equiv (1, 1, \ldots, 1)^T \end{aligned} \tag{14}$$

there is

$$\begin{aligned} \gamma_\alpha &= \left(\frac{a}{F_5}\right)\left(\frac{F_1F_5 - F_6}{1+F_1}\right)\boldsymbol{\beta} \\ \gamma_\beta &= \left(\frac{RTF_1b}{F_5}\right)\boldsymbol{u} + \left(\frac{a}{F_5}\right)\left(\frac{F_3}{1+F_1} + F_6\right)\boldsymbol{\beta} - \left(\frac{aF_6}{F_5}\right)\boldsymbol{\alpha} \end{aligned} \tag{15}$$

When each $k_{ij} = 0$ then $a_{ij} = \alpha_i\alpha_j a$. Michelsen and Heidemann (1981) eliminate the Δn_j by employing $k_{ij} = 0$ to reduce every term containing F_5 in each of $\Sigma_i \alpha_i y_i S_i = 0 = \Sigma_i \beta_i y_i S_i$ and Eq. 9. One eventually obtains their eigenvalue equation, which is quartic in $\sqrt{T}$. Here, the Δn_j are eliminated using Eqs. 11, 12, and 14 to form

$$\begin{aligned} \overline{\alpha} &= \boldsymbol{\alpha}^T\Delta\boldsymbol{n} = \boldsymbol{\alpha}^T U^{-1}\gamma_\beta\overline{\beta} + \boldsymbol{\alpha}^T U^{-1}\gamma_\alpha\overline{\alpha} \\ \overline{\beta} &= \boldsymbol{\beta}^T\Delta\boldsymbol{n} = \boldsymbol{\beta}^T U^{-1}\gamma_\beta\overline{\beta} + \boldsymbol{\beta}^T U^{-1}\gamma_\alpha\overline{\alpha} \end{aligned} \tag{16}$$

The presence of U^{-1} shows the eigenvalue equation is not quartic in $\sqrt{T}$ when the k_{ij} are unrestricted.

Rearranging Eq. 16 produces

$$\begin{bmatrix} D_1 & D_2 \\ D_3 & D_4 \end{bmatrix}\begin{bmatrix} \overline{\beta} \\ \overline{\alpha} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{17}$$

with

$$\begin{aligned} D_1 &\equiv \boldsymbol{\alpha}^T U^{-1}\gamma_\beta = \frac{RTF_1b}{F_5}\boldsymbol{\alpha}^T U^{-1}\boldsymbol{u} \\ &\quad + \left(\frac{a}{F_5}\right)\left(\frac{F_3}{1+F_1} + F_6\right)\boldsymbol{\alpha}^T U^{-1}\boldsymbol{\beta} - \frac{aF_6}{F_5}\boldsymbol{\alpha}^T U^{-1}\boldsymbol{\alpha} \\ D_2 &\equiv \boldsymbol{\alpha}^T U^{-1}\gamma_\alpha - 1 = \left(\frac{a}{F_5}\right)\left(\frac{F_1F_5 - F_6}{1+F_1}\right)\boldsymbol{\alpha}^T U^{-1}\boldsymbol{\beta} - 1 \\ D_3 &\equiv \boldsymbol{\beta}^T U^{-1}\gamma_\beta - 1 = \frac{RTF_1b}{F_5}\boldsymbol{\beta}^T U^{-1}\boldsymbol{u} \\ &\quad + \left(\frac{a}{F_5}\right)\left(\frac{F_3}{1+F_1} + F_6\right)\boldsymbol{\beta}^T U^{-1}\boldsymbol{\beta} - \frac{aF_6}{F_5}\boldsymbol{\beta}^T U^{-1}\boldsymbol{\alpha} - 1 \\ D_4 &\equiv \boldsymbol{\beta}^T U^{-1}\gamma_\alpha = \left(\frac{a}{F_5}\right)\left(\frac{F_1F_5 - F_6}{1+F_1}\right)\boldsymbol{\beta}^T U^{-1}\boldsymbol{\beta} \end{aligned} \tag{18}$$

U is symmetric, and the identity matrix $I = (U^{-1})^T U^T = (U^{-1})^T U$. Thus U^{-1} is symmetric, and $\boldsymbol{\beta}^T U^{-1}\boldsymbol{\alpha} = \boldsymbol{\alpha}^T U^{-1}\boldsymbol{\beta}$ since a scalar clearly equals its transpose.

Equation 17 can have a nontrivial solution only when

$$D_1D_4 - D_2D_3 = 0 \tag{19}$$

A normalization

$$\overline{\alpha} = D_1 \tag{20}$$

is more convenient than $\Delta\boldsymbol{n}^T\Delta\boldsymbol{n} = 1$, given in the second statement of Eq. 2. Equation 20 and the first row of Eq. 17 yield

$$\overline{\beta} = -D_2 \tag{21}$$

The normalization $\overline{\alpha} = 1$ suggested by Michelsen and Heidemann (1981) results in $\overline{\beta} = -D_2/D_1$. This creates difficulty when $D_1 \rightarrow 0$.

One now solves Eqs. 7 and 19 using Eqs. A3, 11, 18, 20, and 21. The critical volume and temperature are the unknowns. If analytic partial derivatives are to be employed, for instance in Newton-Raphson iterations, one may substitute Eq. 11 into the definition of $\overline{a}$ to express it directly in terms of $\overline{\alpha}$ and $\overline{\beta}$.

Numerical Experience

We evaluated critical pressure and temperature for a number of mixtures including the 32 given by Peng and Robinson (1977). For the Peng-Robinson mixtures the average of our absolute values of errors in critical pressures was 2.81% and in critical temperatures was 1.19%. The corresponding values of Peng and Robinson were 2.33% and 1.31%. We attribute the differences between our results and those of Peng and Robinson to differences in binary interaction parameters.

The solution procedure given by Michelsen and Heidemann (1981) is probably suitable for solving Eqs. 7 and 19. Also it might be helpful to replace $n_T Q_{ij}$ by $(T/100) n_T Q_{ij}$ as discussed by Heidemann and Khalil. However, we solved Eqs. 7 and 19 simultaneously using Newton-Raphson iterations. We employed one-sided finite-difference approximations to the partial derivatives required in the Jacobian matrix. Convergence always occurred within three to six iterations. Compared to the Michelsen and Heidemann algorithm for all $k_{ij} = 0$, the algorithm presented here required about 24% more time for a four-component mixture and about 41% more time for a ten-component mixture. This increase in time when $k_{ij} \neq 0$ is largely attributable to forming products such as $\boldsymbol{U}^{-1}\boldsymbol{\alpha}$.

Notation

- A = matrix defined by $(A)_{ij} = a_{ij}$
- A = Helmholtz free energy
- $a \equiv \Sigma_i \Sigma_j y_i y_j a_{ij}$
- $a_{ij} \equiv \sqrt{a_{ii} a_{jj}}\,(1 - k_{ij})$
- $a_{ii} = (\Omega_a R^2 T_{ci}/P_{ci})[1 + (1 - \sqrt{T/T_{ci}}) m_i]^2$
- $\bar{a} \equiv 1/a\, \Sigma_i \Sigma_j \Delta n_i \Delta n_j a_{ij} = \Delta \boldsymbol{n}^T \boldsymbol{A} \Delta \boldsymbol{n}$
- $b \equiv \Sigma_i y_i b_i$
- $b_i \equiv \Omega_b R T_{ci}/P_{ci}$
- C, D = defined by Eqs. 3 and 18, respectively
- $F_1 \equiv 1/(\kappa - 1)$
- $F_2 \equiv 2\{(\delta_1/(\kappa + \delta_1)) - (\delta_2/(\kappa + \delta_2))\}/(\delta_1 - \delta_2)$ $= 2vb/[(v + b\delta_1)(v + b\delta_2)]$
- $F_3 \equiv \{(\delta_1/(\kappa + \delta_1))^2 - (\delta_2/(\kappa + \delta_2))^2\}/(\delta_1 - \delta_2)$
- $F_4 \equiv \{(\delta_1/(\kappa + \delta_1))^3 - (\delta_2/(\kappa + \delta_2))^3\}/(\delta_1 - \delta_2)$
- $F_5 \equiv 2 \ln\{(\kappa + \delta_1)/(\kappa + \delta_2)\}/(\delta_1 - \delta_2)$
- $F_6 \equiv F_2 - F_5$
- f_i = fugacity of component i
- k_{ij} = binary interaction parameter
- m_i = parameter in equation of state, Appendix B
- $\boldsymbol{n}$ = vector of mole numbers; $\boldsymbol{n} \equiv (n_1, \ldots, n_i, \ldots, n_I)^T$
- n_i = number of moles of component i
- n_T = total number of moles in mixture
- $\bar{n}$ = sum of mole increments, Eq. A3; $\bar{n} \equiv \Sigma_i \Delta n_i$
- P = pressure
- Q = matrix of partial derivatives, Eq. 4
- R = gas constant
- S_i = function, Eq. 8
- T = absolute temperature
- U = matrix, Eq. 13
- $\boldsymbol{u}$ = unit vector, Eq. 14
- V = total volume
- v = molar volume
- y_i = mole fraction of component i
- $\equiv$ = " is defined to be"

Greek letters

- $\boldsymbol{\alpha}$ = vector of values of α_i, Eq. 14
- $\alpha_i \equiv 1/a\, \Sigma_j y_j a_{ij}$
- $\bar{\alpha} \equiv \Sigma_i \alpha_i \Delta n_i = \boldsymbol{\alpha}^T \Delta \boldsymbol{n}$
- $\boldsymbol{\beta}$ = vector of values of β_i, Eq. 14
- $\beta_i \equiv b_i/b$
- $\bar{\beta} \equiv \Sigma_i \beta_i \Delta n_i = \boldsymbol{\beta}^T \Delta \boldsymbol{n}$
- $\boldsymbol{\gamma}_\alpha, \boldsymbol{\gamma}_\beta$ = vectors of coefficients of $\bar{\alpha}$ and $\bar{\beta}$, respectively, Eq. 15
- Δ = an increment
- δ_{ij} = Kroneker delta; $\delta_{ij} = 1$ if $i = j$, otherwise $\delta_{ij} = 0$
- δ_1, δ_2 = constants in equation of state, Appendix B
- κ = dimensionless volume; $\kappa \equiv v/b$
- Ω_a, Ω_b = constants in equation of state, Appendix B
- ω = accentric factor

Subscripts

- c = critical property
- i, j, k = component indices
- I = total number of components in the mixture

Superscript

- T = transpose of a vector or matrix

Appendix A

Substituting Eq. 4 into Eq. 8 produces

$$S_i = RT\left[\frac{\Delta n_i}{y_i} + (\beta_i \bar{n} + \bar{\beta})F_1 + \beta_i \bar{\beta} F_1^2\right] + (a/b)\left[\beta_i \bar{\beta} F_3 - (F_5/a)\left(\sum_j a_{ij} \Delta n_j\right) + (\beta_i \bar{\beta} - \alpha_i \bar{\beta} - \bar{\alpha}\beta_i)F_6\right] \quad \text{(A1)}$$

Without placing any restriction upon the k_{ij} one forms

$$\begin{aligned}\sum_i y_i S_i &= RT[\bar{n} + (\bar{n} + \bar{\beta})F_1 + \bar{\beta}F_1^2] + (a/b)\left\{\bar{\beta}F_3 - F_5\left[\sum_j \frac{\Delta n_j}{a} \sum_i y_i a_{ij}\right] + (\bar{\beta} - \bar{\beta} - \bar{\alpha})F_6\right\} \\ &= RT[(1 + F_1)\bar{n} + (F_1 + F_1^2)\bar{\beta}] + (a/b)[\bar{\beta}F_3 - (F_5 + F_6)\bar{\alpha}]\end{aligned} \quad \text{(A2)}$$

Since S_i is zero, one has $\Sigma_i y_i S_i = 0$, and hence

$$\begin{aligned}\bar{n} &= \frac{(F_1 + F_1^2)\bar{\beta}}{1 + F_1} - \frac{(a/b)[\bar{\beta}F_3 - (F_5 + F_6)\bar{\alpha}]}{RT(1 + F_1)} \\ &= -F_1\bar{\beta} - \left(\frac{a}{b}\right)\frac{\bar{\beta}F_3 - (F_5 + F_6)\bar{\alpha}}{RT(1 + F_1)}\end{aligned} \quad \text{(A3)}$$

Next, Eq. A3 is substituted into Eq. A1 and the result equated to zero:

$$\begin{aligned}-RT(\Delta n_i/y_i) + (F_5/b)\Sigma_j a_{ij}\Delta n_j &= RT\bar{\beta}F_1 + RT\beta_i[-F_1\bar{\beta} - (a/b)\{\bar{\beta}F_3 - (F_5 + F_6)\bar{\alpha}\}(RT)^{-1}(1 + F_1)^{-1}]F_1 \\ &\quad + RT\beta_i\bar{\beta}F_1^2 + (a/b)[\beta_i\bar{\beta}F_3 + (\beta_i\bar{\beta} - \alpha_i\bar{\beta} - \bar{\alpha}\beta_i)F_6] \\ &= RT\bar{\beta}F_1 + (a/b)\{\beta_i\bar{\beta}F_3[1 - (1 + F_1)^{-1}F_1] + (F_5 + F_6)(1 + F_1)^{-1}F_1\beta_i\bar{\alpha} + (\beta_i\bar{\beta} - \alpha_i\bar{\beta} - \bar{\alpha}\beta_i)F_6\} \\ &= RT\bar{\beta}F_1 + (a/b)\{\beta_i\bar{\beta}F_3(1 + F_1)^{-1} + (\beta_i - \alpha_i)\bar{\beta}F_6 + [(F_5 + F_6) \cdot (1 + F_1)^{-1}F_1 - F_6]\beta_i\bar{\alpha}\}\end{aligned} \quad \text{(A4)}$$

A final rearrangement produces Eq. 9.

Appendix B

The SRK (Soave Redlich-Kwong) equation requires

$$\delta_1 = 1, \quad \delta_2 = 0$$

$$\Omega_a = 0.45724, \quad \Omega_b = 0.08664$$

$$m_i = 0.4870 + 1.574\omega_i - 0.176\omega_i^2$$

The Peng-Robinson equation requires

$$\delta_1 = 1 + \sqrt{2}, \quad \delta_2 = 1 - \sqrt{2},$$

$$\Omega_a = 0.45724, \quad \Omega_b = 0.07780$$

$$m_i = 0.37464 + 1.5422\omega_i - 0.26992\omega_i^2$$

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Manuscript received May 28, 1985, and revision received Oct. 29, 1985.