A REDUCTION METHOD FOR PHASE EQUILIBRIUM CALCULATIONS WITH CUBIC EQUATIONS OF STATE

D. V. Nichita
Programa de Yacimientos Naturalmente Fracturados, Instituto Mexicano del Petroleo,
Eje Central Lázaro Cárdenas 152, 07730 México D.F., México
*Current address: UMR 5150 CNRS, Laboratoire des Fluides Complexes,
Phone: +(33) (5) 5940 7685, Fax: +(33) (5) 5940 7725,
Université de Pau et des pays de l’Adour, BP 1155, 64013 Pau Cedex, France.
E-mail: dnichita@univ-pau.fr

(Received: December 12, 2005 ; Accepted: May 4, 2006)

Abstract - In this work we propose a new reduction method for phase equilibrium calculations using a general form of cubic equations of state (CEOS). The energy term in the CEOS is a quadratic form, which is diagonalized by applying a linear transformation. The number of the reduction parameters is related to the rank of the matrix $\mathbf{C}$ with elements $(1-C_{ij})$, where $C_{ij}$ denotes the binary interaction parameters (BIPs). The dimensionality of the problem depends only on the number of reduction parameters, and is independent of the number of components in the mixture.

Keywords: Equation of state; Binary interaction parameters; Reduction method; Linear transformation.

INTRODUCTION

For two-phase flash calculations, the algorithms used to ensure the convergence toward the solution iterates on $nc$ (number of components in the mixture) independent variables (which can be mole fractions, number of moles or logarithms of equilibrium constants). In many petroleum and chemical engineering applications, which may require a considerable number of flash calculations, it is practically impossible to have an extended description of mixtures composition, because this imply solving large dimension problems. Usually, individual components are lumped into pseudocomponents to reduce the problem dimensionality. An alternative way of reducing the dimensionality of the problem is the use of the so-called reduction methods.

In any reduction method, a quadratic form is replaced by the sum of a small number of scalar products. This leads to a system of a reduced number of equations, usually much less than $nc$. The number of independent variables is not dependent on the number of components in the mixture.

The first reduced flash model was presented by Michelsen (1986). Michelsen showed that the phase equilibrium problem can be solved using only three independent variables if all BIPs in the CEOS are zero. Michelsen’s three-equation flash is extremely efficient, but the restriction on BIPs may be unacceptable for many actual problems. Jensen and Fredenslund (1987) extended the Michelsen method, for nonzero BIPs of only one component in the mixture, by solving a system of only five equations. The reduction theorem introduced by Hendriks (1988) establish the conditions under which a reduced number of equations can be solved for flash calculations and phase stability. A set of independent variables for reduced flash using the spectral
decomposition (SD) was given by Hendriks and van Bergen (1992). If the matrix $\mathbf{C}$ has only $m$ nonzero eigenvalues, then the number of independent variables is $m+2$. A different reduction method, requiring $2c+3$ (where $c$ is the number of components with nonzero BIPs) independent variables was presented by Nichita and Minescu (1998, 2004). For an exact solution, the $2c+3$ method needs the same number of independent variables as SD. However, SD provides good approximation of the solution if terms corresponding to small nonzero eigenvalues are neglected. Care must be taken when some nonzero eigenvalues are removed, because the one-diagonal condition is no more fulfilled, and proper scaling is required. More recently, the hypersphere decomposition of $\mathbf{C}$ has been used to reduce dimensionality, even for full-ranked $\mathbf{C}$ matrices (Nichita, 2004b).

For any reduction method, the reduction parameters are defined as (Hendriks, 1988)

$$Q_\alpha = \sum_{i=1}^{nc} q_{i\alpha}x_i; \alpha = 1, m$$

and

$$Q_M = B = \sum_{i=1}^{nc} B_ix_i$$

where $M=m+1$, and $q_{i\alpha}; \alpha = 1, m; i = 1, nc$ are the elements of the reduction matrix (that depend on the reduction method used), with $q_{Mi} = B_i$.

The vector of the $M$ reduction parameters is

$$\mathbf{Q} = (Q_1, Q_2, ..., Q_m, B)^T$$

The key factor that allow to solve a system of equations of a reduced dimensionality for the flash problem is that the fugacity coefficient depends at given pressure and temperature only on the reduction parameters, and not on composition, $\phi_i = \phi_i(p, T, \mathbf{Q})$.

The reduction method proved to be a useful tool for phase equilibrium calculation. We have solved different kinds of phase equilibrium problems: two-phase flash calculations (Nichita and Minescu, 1998, 2004, Nichita et al., 2003), phase stability analysis (Nichita et al., 2002), multiphase equilibrium calculations (Nichita et al., 2004), critical point calculation (Nichita, 2005, 2006), and phase envelope construction for mixtures with many components (Nichita, 2004a).

This paper presents a new reduction method and illustrates the diversity of approaches suitable for reducing the dimensionality of the phase equilibrium problems. The proposed method is based on the procedure suggested by Tisza (1977) for quadratic forms diagonalization by using linear transformations.

THE CUBIC EQUATION OF STATE

In this work, a general form of two-parameter CEOS is used. It incorporates the Soave-Redlich-Kwong (SRK, Soave, 1972) and Peng-Robinson (PR, Peng and Robinson, 1976) CEOS. However, it is worth noting that any EOS that observes the restrictions of the reduction theorem can be used.

$$p = \frac{RT}{v-b} - \frac{a}{(v+\delta_1b)(v+\delta_2b)}$$

For the SRK CEOS $\delta_1=0$ and $\delta_2=1$, and for the PR CEOS $\delta_1=1+\sqrt{2}; \delta_2=1-\sqrt{2}$.

With, $A = \frac{a}{RT}$, $B = \frac{b}{RT}$, and $Z = \frac{v}{RT}$, the implicit form of the CEOS is obtained

$$Z^3 + \left[ (\delta_1 + \delta_2 -1)B - 1 \right] Z^2 + \left[ A + \delta_1\delta_2B^2 - (\delta_1 + \delta_2)B(B+1) \right] Z - \left[ AB + \delta_1\delta_2B^2(B+1) \right] = 0$$

The van der Waals mixing rules are used for the energy, $A$, and for the volume, $B$, coefficients of the CEOS

$$A = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j A_{ij}$$

$$B = \sum_{j=1}^{nc} x_j B_j$$

where:

$$A_{ij} = A_{ji} = (1-C_{ij})\sqrt{A_iA_j}; i, j = 1, nc$$

$$A_i = \frac{\Omega_i p_i}{T_i^2} \left[ 1 + m_i \left( 1 - \sqrt{T_i} \right) \right]^2; i = 1, nc$$
In Eq. (9) and (10), \( \Omega_a, \Omega_b, \) and \( m_i(\omega) \) are EOS dependent. Their particular values for the SRK and the PR CEOS can be found for example in Michelsen (1986).

The fugacity coefficients are given by
\[
\ln \varphi_i = (Z-1) \frac{B_i}{B} - \ln(Z-B) - \frac{A}{\Delta B} \left( \frac{2 \psi_i - B_i}{A - B} \right) \ln \left( \frac{Z + \delta_1 B}{Z + \delta_2 B} \right) ; \ i = 1, nc \tag{11}
\]
with:
\[
\psi_i = \sum_{j=1}^{nc} A_{ij} x_j ; \ i = 1, nc \tag{12}
\]
and \( \Delta = \delta_1 - \delta_2 \).

THE PROPOSED REDUCTION METHOD

The energy term in the CEOS given by the van der Waals mixing rules is a quadratic form
\[
A = \sum_{i=1}^{nc} \sum_{j=1}^{nc} (1 - C_{ij}) \alpha_i \alpha_j x_i x_j \tag{13}
\]
which can be written as
\[
A = \sum_{i=1}^{nc} \sum_{j=1}^{nc} u_{ij} \xi_i \xi_j \tag{14}
\]
where \( \alpha_i = \sqrt{A_i} \).

\[
\xi_i = \alpha_i x_i \tag{15}
\]
and
\[
u_{ij} = (1 - C_{ji}) \tag{16}
\]
Obviously, \( u_{ij} = u_{ji} \).

The key of the reduction method is to express the CEOS energy parameter \( A \) as
\[
A = \sum_{i=1}^{nc} \lambda_i Q_i^2 \tag{17}
\]
that is, to diagonalize the quadratic form (14).

Usually, the diagonalization is performed by spectral decomposition of the matrix \( U \equiv \Bar{C} \) (Hendriks and van Bergen, 1992). In this work we propose a different approach for diagonalization, by using a linear transformation (Tisza, 1977).

The transformation connecting mole fractions (via \( \xi_i \)) to \( Q_i \) is of the “triangular” form
\[
\begin{align*}
Q_1 &= \xi_i + a_{12} \xi_2 + a_{13} \xi_3 + \ldots + a_{1nc} \xi_{nc} \\
Q_2 &= \xi_2 + a_{23} \xi_3 + \ldots + a_{2nc} \xi_{nc} \\
&\vdots \\
Q_i &= \xi_i + \ldots + a_{in} \xi_{nc} \\
&\vdots \\
Q_{nc} &= \xi_{nc}
\end{align*}
\tag{18}
\]
where
\[
a_{ij} = \frac{u_{ij}}{u_{ii}} ; i, j = 1, nc \tag{19}
\]
and represents a linear transformation of the form
\[
Q = \mathcal{R} \xi \tag{21}
\]
that connects the reduction parameters to mole fractions via $\xi$. The elements of the matrix $T$ are

$$t_{ij} = \begin{cases} 0 & j < i \\ 1 & j = i \\ a_{ij} & j > i \end{cases}$$  \hspace{1cm} (22)

The matrix $U$ is singular in many cases, i.e., its rank $r < n_c$. If the rank of $U$ is $r = n_c - s$, the last $s$ diagonal elements in Eq. (17) are vanishing, $\lambda_{r+1} = \ldots = \lambda_{n_c} = 0$, therefore we have

$$\lambda_i \begin{cases} \neq 0; i = 1, m \\ = 0; i = m + 1, n_c \end{cases}$$  \hspace{1cm} (23)

The coefficients $\lambda_i$ can be calculated by a step-by-step construction of the linear transformation in a straightforward manner. However, a simple procedure suggested by Tisza (1977) can be used, starting from the observation that the linear transformation (18) is unimodular, hence the determinant of $U$ is invariant

$$\lambda_1 \lambda_2 \ldots \lambda_{n_c} = D_{n_c}$$  \hspace{1cm} (24)

with

$$D_{n_c} = \text{det}(U)$$  \hspace{1cm} (25)

Eq. (24) also holds for the principal minors $D_k$ of $D_{n_c}$

$$\lambda_1 \lambda_2 \ldots \lambda_k = D_k; k < n_c$$  \hspace{1cm} (26)

where

$$D_k = \begin{vmatrix} u_{11} & u_{12} & \ldots & u_{1k} \\ u_{21} & u_{22} & \ldots & u_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ u_{k1} & u_{k2} & \ldots & u_{kk} \end{vmatrix}$$  \hspace{1cm} (27)

If the matrix $U$ is not full-ranked, $r < n_c$, then $D_k \neq 0$ for $k \leq r$, and $D_k = 0$ for $k = r + 1, n_c$.

From Eq. (26), we have

$$\lambda_k = \frac{D_k}{D_{k-1}}; k \leq r$$  \hspace{1cm} (28)

The first $m$ reduction parameters are

$$Q_\alpha = \sum_{j=1}^{n_c} t_{aj} \xi_j; \alpha = 1, m$$  \hspace{1cm} (29)

where $m = r$, and the last reduction parameter $Q_M$, for $M = m + 1$ is given by Eq. (2).

The elements of the matrix $U$ can be written as

$$u_{ij} = \sum_{\alpha=1}^{m} \lambda_\alpha t_{a\alpha} t_{ij}$$  \hspace{1cm} (30)

The coefficient $\psi_i$ in the CEOS is

$$\psi_i = \sum_{j=1}^{n_c} (1 - C_{ij}) \alpha_i \lambda_i = \alpha_i \sum_{j=1}^{n_c} u_{ij} \xi_j$$  \hspace{1cm} (31)

and combining Eq. (30) with Eq. (31), we obtain

$$\psi_i = \alpha_i \sum_{\alpha=1}^{m} \lambda_\alpha t_{a\alpha} Q_\alpha$$  \hspace{1cm} (32)

Because $\lambda_\alpha = 0$ for $\alpha = r + 1, \ldots, n_c$, the summation in Eq. (17) is only up to $m = r$, and the CEOS coefficient $A$ is given by

$$A = \sum_{\alpha=1}^{m} \lambda_\alpha Q_\alpha^2$$  \hspace{1cm} (17')

Finally, at given pressure and temperature, the fugacity coefficients are function of the reduction parameters, and independent on composition

$$\ln \varphi_i(Q) = (Z(Q) - 1) \frac{t_{Mi}}{Q_M} - \ln(Z(Q) - Q_M) - \frac{1}{\Delta Q_M} \left( 2 \sum_{\alpha=1}^{m} \lambda_\alpha t_{a\alpha} Q_\alpha - \frac{t_{Mi}}{Q_M} \sum_{\alpha=1}^{m} \lambda_\alpha Q_\alpha^2 \right)$$  \hspace{1cm} (33)

where the compressibility factor depends at given $p$ and $T$ only on the reduced variables, $Z = Z(Q)$, if $A$ from Eq. (6) is replaced in Eq. (5). The expression of the fugacity coefficients is exactly the same as used
by Nichita et al. (2003, 2004); here $\lambda_\alpha$ are those obtained from Eq. (28) instead of eigenvalues of $U$, and $t_{ij}$ are replacing the corresponding eigenvectors. Note that for all BIPs zero, the Michelsen’s three-equation flash is obtained, by putting $\lambda_1 = nc$, and $t_{ij} = 1/\sqrt{nc}; i = 1, nc$.

The calculations proceed as follows: the minors $D_k$ are calculated for increasing $k$, starting with $D_1 = u_{11} = 1$ (for convenience $D_0 = 1$), and $\lambda_k$ are calculated with Eq. (28); $k$ is increased until $D_k = 0$ (more precisely $D_k < \varepsilon$). The last $k$ giving a non-zero determinant is equal to the rank of $U$. Components must be properly ordered, the first $c$ components being those with non-zero BIPs. If the BIPs between a component and two other consecutive components are equal ($C_{ij} = C_{i,j+1}$), and this leads to $D_k = 0$ for some $k < r$, one of these BIPs is altered by a small perturbation (say 1%); this does not affect phase equilibrium results, but prevents computational problems.

The structure of the matrix $U$ is doubly bordered, the rank depending on the number of components having non-zero BIPs. For hydrocarbon mixtures this matrix is generally rank-deficient, i.e. singular. The proposed method requires usually only the calculation of low order determinants, up to $r$. For systems with many components, this avoids matrix operations for large dimensions (calculation of eigenvalues and eigenvectors).

Implementation of the proposed reduction method requires only minor changes in the existing codes based on SD. The subroutine for eigenvalues and eigenvectors calculation is replaced with the subroutine based on the proposed method. None of the phase equilibrium routine needs any modification. Only different formal parameters are transferred to these routines, $\lambda_k$ instead of eigenvalues, and $t_{ij}$ from Eq. (29) instead of eigenvectors.

## APPLICATIONS

A variety of phase equilibrium problem we have studied before has been addressed using the proposed reduction method. Applications for mixtures with $nc$ ranging from 6 to 52, described in previous papers on two-phase flash (Nichita et al., 2003, Nichita and Minescu, 2004), phase stability testing (Nichita et al., 2002), three-phase vapor-liquid-liquid flash (Nichita et al., 2004), critical point calculation (Nichita, 2005, 2006), phase diagram construction (Nichita, 2004a), were reworked.

For all situations, the results are reproduced using the proposed reduction method. Phase equilibrium calculations using the proposed reduction method and the SD reduction method requires approximately the same number of iterations, and thus the same computational effort.

### The MY10 Mixture

The first exemplification is given here for the MY10 mixture, taken from Metcalfe and Yarborough (1979). The MY10 synthetic mixture contains 10 normal-alkanes, with composition and BIPs of methane (taken from Firoozabadi and Pan, 2002) with the remaining components given in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition</th>
<th>$C_{C_{ij}}$</th>
<th>$C_{CO_2j}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.35(*)</td>
<td>0</td>
<td>0.093</td>
</tr>
<tr>
<td>C2</td>
<td>0.03</td>
<td>0</td>
<td>0.128</td>
</tr>
<tr>
<td>C3</td>
<td>0.04</td>
<td>0</td>
<td>0.123</td>
</tr>
<tr>
<td>nC4</td>
<td>0.06</td>
<td>0.020</td>
<td>0.136</td>
</tr>
<tr>
<td>nC5</td>
<td>0.04</td>
<td>0.020</td>
<td>0.125</td>
</tr>
<tr>
<td>nC6</td>
<td>0.03</td>
<td>0.025</td>
<td>0.131</td>
</tr>
<tr>
<td>nC7</td>
<td>0.05</td>
<td>0.025</td>
<td>0.120</td>
</tr>
<tr>
<td>nC8</td>
<td>0.05</td>
<td>0.035</td>
<td>0.120</td>
</tr>
<tr>
<td>nC10</td>
<td>0.30</td>
<td>0.045</td>
<td>0.120</td>
</tr>
<tr>
<td>nC14</td>
<td>0.05</td>
<td>0.045</td>
<td>0.120</td>
</tr>
<tr>
<td>CO2</td>
<td>(0…0.99)(*)</td>
<td>0.093</td>
<td>-</td>
</tr>
</tbody>
</table>

(*) components with non-zero BIPs

| Table 1: Composition and BIPs for MY10 mixture |
Table 2: Reduction for the MY10 mixture

<table>
<thead>
<tr>
<th>Non-zero λ</th>
<th>Spectral decomposition</th>
<th>Proposed reduction method</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ₁</td>
<td>9.957329</td>
<td>1</td>
</tr>
<tr>
<td>λ₂</td>
<td>0.070664</td>
<td>0.0396</td>
</tr>
<tr>
<td>λ₃</td>
<td>-0.027993</td>
<td>-2.50e-7</td>
</tr>
</tbody>
</table>

Table 3: Reduction for the MY10/CO₂ mixture

<table>
<thead>
<tr>
<th>Non-zero λ</th>
<th>CO₂ BIPs from Table 1</th>
<th>All CO₂ BIPs equal to 0.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ₁</td>
<td>10.748714</td>
<td>10.751442</td>
</tr>
<tr>
<td>λ₂</td>
<td>0.220662</td>
<td>0.177351</td>
</tr>
<tr>
<td>λ₃</td>
<td>0.064257</td>
<td>0.036115</td>
</tr>
<tr>
<td>λ₄</td>
<td>-0.032768</td>
<td>-0.000769</td>
</tr>
<tr>
<td>λ₅</td>
<td>-0.000864</td>
<td>0</td>
</tr>
</tbody>
</table>

As can be seen from Tables 2 and 3, the number of non-zero λₖ in our reduction method is equal to the number of eigenvalues in the SD method. Therefore the number of reduction parameters (M=r+1) and of independent variables for phase equilibrium calculations (for example M+=r+2 for a two-phase flash) is the same for the two approaches.

For case a, calculations are detailed below step-by-step. The component ordering is: CO₂, C₁, nC₄ to nC₁₄, C₂, C₃.

The determinant D for k=6 is

\[ D_6 = \begin{vmatrix} 1.000 & 0.907 & 0.864 & 0.875 & 0.869 & 0.880 \\ 0.907 & 1.000 & 0.980 & 0.978 & 0.975 & 0.975 \\ 0.864 & 0.980 & 1.000 & 1.000 & 1.000 & 1.000 \\ 0.875 & 0.979 & 1.000 & 1.000 & 1.000 & 1.000 \\ 0.869 & 0.975 & 1.000 & 1.000 & 1.000 & 1.000 \\ 0.880 & 0.975 & 1.000 & 1.000 & 1.000 & 1.000 \end{vmatrix} \]

We start with D₁=1 (D₀ is set to 1 for convenience) and λ₁=1. For k=2, D₂=0.177351 and λ₂=D₂/D₁=0.177351; for k=3, D₃=6.405e-3 and λ₃=D₃/D₂=0.036115; for k=4, D₄=-4.927e-6, giving λ₄=D₄/D₃=-0.000769, then D₅=2.97e-9 for k=5 and λ₅=D₅/D₄=-0.000603. For k=6 the determinant is zero, D₆=0, and all other determinants Dₖ, k>6 are also zero, thus λₖ=0 for k=6, ..., 11, and we keep for λ only the first five nonzero values listed in Table 3; The elements of the transformation matrix T are given by Eq. (22). This detailed calculation show clearly how easy to implement the proposed method is.

A 52 Component Mixture

The next example is for a natural occurring hydrocarbon mixture with many components. Sample C from Pedersen et al. (1985) is a heavy gas-condensate for which a detailed description of the C₇+ fraction is available, including the paraffin-naphthene-aromatic distribution. The mixture has 52 components, critical properties and acentric factors being calculated as described in Nichita (2005). The BIPs of methane with other hydrocarbon components are assigned according to Katz and Firoozabadi (1978), and BIPs of carbon dioxide and nitrogen with the hydrocarbon components are CO₂ jC₀ = 0.12 and N₂ jC₀ = 0.1.

The rank of matrix U is r=5. The five nonzero eigenvalues and nonzero values of λₖ obtained by the reduction method are given in Table 4. Note that only determinants up to order five are computed to complete the reduction for this 52 component mixture.
CONCLUSIONS

A reduction method is proposed, based on diagonalization of quadratic forms by means of linear transformations. The number of reduction parameters is the same as for reduction method based on spectral decomposition.

The codes for phase equilibrium calculation with the spectral decomposition reduction method can be used for the proposed reduction method without any modification of the phase equilibrium routines. Some previously addressed problems were reworked for the new reduction method. Results are identical and the number of iterations required for phase equilibrium calculation, and thus the computational effort is almost the same as for the spectral decomposition method.

The proposed method requires usually only the calculation of low order determinants. For systems with many components, this avoids matrix operations for large dimensions (calculation of eigenvalues and eigenvectors).

ACKNOWLEDGEMENT

I gratefully acknowledge the support from Instituto Mexicano del Petroleo, Programa de Yacimientos Naturalmente Fracturados, under project no. D00084.

NOMENCLATURE

Symbols

A  attractive parameter in the CEOS
A_i  component parameter in CEOS
A_ij  CEOS cross parameter
a  attractive parameter in the CEOS
a_ij  component CEOS coefficient
B  volume parameter in the CEOS
B_i  component CEOS coefficient
B Covolume in the CEOS
C  matrix with elements 1-Cij
C_{ij}  binary interaction coefficients between components i and j
D_{nc}  determinant of the matrix U
D_k  principal minors of D_{nc}
M  number of reduction parameters
m  number of nonzero eigenvalues
nc  number of components
p  pressure
Q  vector of reduction parameters
Q_{ux}  reduction parameters
q_{ei}  elements of the eigenvectors
R  universal gas constant
r  rank of matrix C
T  temperature
T  transformation matrix
t_{ij}  elements of T
U  identic with C
u_{ij}  elements of U
v  molar volume
x_i  mole fraction, component i
Z  compressibility factor

Greek Letters

δ_{1, δ_2}  constants in CEOS
Δ  δ_1-δ_2
φ_i  fugacity coefficients
λ  eigenvalues
ψ_i  component CEOS coefficient
ξ_{ij}  given by Eq. (15)
Ω_a, Ω_b  coefficients in the CEOS
ω  acentric factor

Subscripts

c  critical
i,j,k  component index
r  reduced
α  reduction parameter index
REFERENCES