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Phase Envelope Construction for Mixtures with Many Components

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A reduction method for constructing vapor–liquid equilibrium phase envelopes with cubic equations of state is presented. The paper describes the calculation procedures for saturation (dewpoint/bubblepoint) pressures and temperatures, quality lines (for given mole fraction or volume fraction of one of the equilibrium phases), cricondentherm and cricondenbar points, the critical point, and the spinodal. The phase envelope construction is fully automatic. The saturation points are calculated throughout the critical region by stepping around the phase envelope in pressure or temperature increments. An extrapolation procedure taking advantage of the Jacobian matrix available from a previous step is used. Problem formulation in terms of reduced variables leads to simpler partial derivatives with respect to pressure and temperature. The proposed method is successfully tested for several representative hydrocarbon mixtures with various phase envelope shapes.

1. Introduction

The construction of mixture phase envelopes is an important problem in phase equilibrium calculations, with many applications in chemical thermodynamics and hydrocarbon reservoir thermodynamics. It is very useful for process simulation and reactor design and for the study of hydrocarbon reservoir fluids. The most popular approaches for phase envelope construction are those of Michelsen,^{1,2} Li and Nghiem,³ and Ziervogel and Poling.⁴ The main difficulties in constructing phase envelopes are pointed out in the literature.^{1–3,5,6} Saturation points calculation is one of the basic phase equilibrium calculation problems. The number of solutions for a given specification is not known in advance; there may be multiple solutions or no solution at all. The fact that the solution is not unique imposes the use of carefully chosen initial estimates; otherwise, incorrect trivial or nontrivial solutions are found. Moreover, in the near critical region, it is not clear whether the saturation points are dewpoints (DP) or bubblepoints (BP).

Complete phase envelope construction of multicomponent mixtures requires the resolution of nonlinear systems of equations of the order $n_c + 1$ (n_c is the number of components) for saturation pressures/temperatures and quality lines and evaluation of determinants of order n_c for critical point and spinodal calculation. The computer time spent for linear algebra operations involved in these calculations is proportional at least to n_c^2 .

For hydrocarbon mixtures, one may often need a detailed description of heavy fractions composition (including the paraffin–naphthene–aromatic distribution),^{7,8} leading to mixtures with many components. It is a common practice to lump several components into a pseudocomponent to reduce the overall number of components. However, if at some conditions, the detailed composition is again required, a delumping (or inverse lumping) procedure^{9,10} is used to recover it. Lumped and delumped phase envelopes differ (in some cases to a high extent) from the original phase envelope.

This work is based on a different way of reducing the dimensionality of phase equilibrium calculations, namely the reduction method.^{11,12} The idea behind the application of any reduction method is to find a different formulation of the problem, based on a different set of independent variables, whose number is smaller, or preferably much smaller, than for the original set of variables. Several reduction procedures have been proposed in the literature.^{11–16} In terms of phase equilibrium calculation, this consists in replacing the traditional variables (mole numbers, mole fractions, partition coefficients) with some linear combinations of them. Consequently, the solution is no more sought in the compositional hyperspace (defined by mole fractions), but in the reduced hyperspace (defined by the new introduced variables). If for the reduction method the dimen-

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sionalities of the problem (number of independent variables) is much smaller than for the classical methods, one can expect important decreases of computational effort. Besides, it seems that hypersurfaces in the reduction methods are smoother than those in conventional ones, and thus, robustness may be improved.

Previously, we have successfully applied different reduction methods to solve various kinds of phase equilibrium problems: two-phase flash,^{15,17} phase stability analysis,^{18,19} multiphase flash,¹⁹ extrapolations,^{15,17} and critical points.^{20,21} In this work, we use for phase diagrams construction a reduction method applied for the general form of two-parameter cubic equations of state (EoS), including the Soave–Redlich–Kwong (SRK)²² EoS and the Peng–Robinson (PR)²³ EoS. The reduction is effectively achieved by spectral decomposition of the matrix $\bar{\mathbf{C}}$ 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, $M = m + 1$ (where m is the number of nonzero or non-negligible eigenvalues of the matrix $\bar{\mathbf{C}}$) and is independent of the number of components n_c . The reduction method is extremely efficient for mixtures with many components and relatively few nonzero BIPs; this is the case for most practical applications involving hydrocarbon mixtures and classical contaminants (CO_2 , N_2 , H_2S , H_2O).

We present a reduction procedure to calculate phase boundaries and key points on the phase envelope such as the critical point, cricondentherm (CMT), and cricondenbar (CMP). A recently developed reduction method is used for critical point calculation (and optional for spinodal construction). Here, we detail calculation of BP and DP pressures and temperatures, quality lines, CMT, and CMP, all calculation being based on the reduction method.

The phase envelope construction is fully automatic; most features are adopted from previous algorithms,^{1,4} but in this work, *all* calculations are performed using reduction methods. The bubblepoints and dewpoints are calculated throughout the critical region by stepping around the phase envelope in pressure or temperature increments. An extrapolation procedure taking advantage of the Jacobian matrix available from a previous step is used. Specification of the independent variables is also done automatically. The proposed method is tested for several hydrocarbon mixtures having various phase envelope shapes, for n_c values ranging from 6 to 52 and M ranging from 2 to 10.

2. Reduced Variables for Cubic EoS

The general form of the two-parameter cubic EoS^{11,24} is used in this work

$$p = \frac{RT}{v_m - b} - \frac{a}{(v_m + \delta_1 b)(v_m + \delta_2 b)} \quad (1)$$

The SRK EoS and PR EoS are particular cases of eq 1. For the PR EoS, $\delta_{1,2} = 1 + \sqrt{2}$ and for the SRK EoS, $\delta_1 = 0$ and

$\delta_2 = 1$. These two equations are currently the most widely used EoSs in chemical and petroleum industry simulations, due to their relatively simple form; high accuracy can be obtained by tuning the EoS parameters to available experimental data.

The implicit form (in the compressibility factor, $Z = pv_m/RT$) of the two-parameter cubic EoS is

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

is obtained using the classical notation $A = ap/(RT)^2$ and $B = bp/RT$.

The van der Waals mixing rules are used for the energy, A , and for the volume, B , parameters:

$$A = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} y_i y_j A_{ij}; \quad B = \sum_{j=1}^{n_c} y_j B_j; \\ A_{ij} = A_{ji} = (A_i A_j)^{0.5} (1 - C_{ij}); \quad i, j = 1, n_c \quad (3)$$

where

$$A_j = \frac{\Omega_a p_{vj}}{T_{vj}^2} \alpha_j(T); \quad B_j = \frac{\Omega_b p_{vj}}{T_{vj}}; \\ \alpha_j(T) = [1 + m(\omega_j)(1 - T_{vj}^{0.5})]^2 \quad (4)$$

and the specific values of Ω_a and Ω_b and the expression of m as a function of the acentric factor ω for each EoS can be found in the literature.^{22,23}

The fugacity coefficient of component i is given by the relation

$$\ln \varphi_i = (Z - 1) \frac{B_i}{B} - \ln(Z - B) - \frac{A}{\Delta B} \left(2 \frac{\psi_i}{A} - \frac{B_i}{B} \right) \ln \left(\frac{Z + \delta_1 B}{Z + \delta_2 B} \right) \quad (5)$$

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

$$\psi_i = \sum_{j=1}^{n_c} A_{ij} y_j \quad (6)$$

The key of the reduced phase equilibrium approach is to express EoS parameters (A and B) and ψ_i (eq 6) in terms of a small number of scalar products, i.e., Q_α , called “reduction parameters” (see the work of Hendriks¹²). In other words, all quantities involved in fugacity coefficient expressions must be linear forms or decomposable to linear forms. This can be done by using the spectral decomposition of the symmetric matrix $\bar{\mathbf{C}}$ with elements $(1 - C_{ij})$, $i, j = 1, n_c$, which is

$$\bar{\mathbf{C}} = \mathbf{S} \mathbf{\Lambda} \mathbf{S}^T \quad (7)$$

where $\mathbf{\Lambda} = \text{diag}(\lambda_i); i = 1, n_c$ is the set of eigenvalues associated to the right-hand-side eigensystem \mathbf{S} of $\bar{\mathbf{C}}$. If $r = \text{rank } \bar{\mathbf{C}} < n_c$, the matrix is singular and has only $m = r$ nonzero eigenvalues. In this case, the diagonal matrix $\mathbf{\Lambda} = \text{diag}(\lambda_i); i = 1, r$ contains only the nonzero eigenvalues, $\mathbf{S} \in \mathbf{R}^{(n_c \times r)}$, and eq 2 reads

$$1 - C_{ij} = \sum_{\alpha=1}^m \lambda_\alpha q_{\alpha i} q_{\alpha j} \quad (8)$$

or, by multiplying eq 2 by $(A_i A_j)^{1/2}$

$$A_{ij} = \sum_{\alpha=1}^m \lambda_\alpha q_{\alpha i} q_{\alpha j} \quad (9)$$

where $q_{\alpha i} = q_{\alpha i}' \sqrt{A_i}$.

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Let the reduction parameters be defined as

$$Q_\alpha = \sum_{i=1}^{n_c} q_{\alpha i} y_i; \quad \alpha = 1, m \quad (10a)$$

and

$$Q_M \equiv B = \sum_{i=1}^{n_c} B_i y_i \quad (10b)$$

where $M = m + 1$, then the vector of reduction parameters is $\mathbf{Q} = (Q_1, Q_2, \dots, Q_m, B)^T$.

The EoS coefficients A and ψ_i can be written as

$$A(\mathbf{Q}) = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} y_i y_j \left(\sum_{\alpha=1}^m \lambda_\alpha q_{\alpha i} q_{\alpha j} \right) = \sum_{\alpha=1}^m \lambda_\alpha \left(\sum_{i=1}^{n_c} \sum_{j=1}^{n_c} q_{\alpha i} q_{\alpha j} y_i y_j \right) = \sum_{\alpha=1}^m \lambda_\alpha \left(\sum_{i=1}^{n_c} q_{\alpha i} y_i \right)^2 = \sum_{\alpha=1}^m \lambda_\alpha Q_\alpha^2 \quad (11)$$

and

$$\psi_i(\mathbf{Q}) = \sum_{j=1}^{n_c} y_j \sum_{\alpha=1}^m \lambda_\alpha q_{\alpha i} q_{\alpha j} = \sum_{\alpha=1}^m \lambda_\alpha q_{\alpha i} \sum_{j=1}^{n_c} q_{\alpha j} y_j = \sum_{\alpha=1}^m \lambda_\alpha q_{\alpha i} Q_\alpha; \quad i = 1, n_c \quad (12)$$

Because A and ψ_i are functions only of the reduction parameters (and not on compositions), B is a reduction parameter itself, and the compressibility factor depends at given p and T only on the reduction parameters, $Z = Z[A(\mathbf{Q}), B(\mathbf{Q})] = Z(\mathbf{Q})$, the fugacity coefficient (eq 5) can be expressed as a function only of \mathbf{Q} :

$$\ln \varphi_i(\mathbf{Q}) = (Z(\mathbf{Q}) - 1) \frac{q_{Mi}}{Q_M} - \ln(Z(\mathbf{Q}) - Q_M) - \frac{1}{\Delta Q_M} \times \left(2 \sum_{\alpha=1}^m \lambda_\alpha q_{\alpha i} Q_\alpha - \frac{q_{Mi}}{Q_M} \sum_{\alpha=1}^m \lambda_\alpha Q_\alpha^2 \right) \ln \left(\frac{Z(\mathbf{Q}) + \delta_1 Q_M}{Z(\mathbf{Q}) + \delta_2 Q_M} \right) \quad (13)$$

Furthermore, the fugacity coefficients can be more conveniently written in the form

$$\ln \varphi_i(\mathbf{Q}) = h_0(\mathbf{Q}) + h_B(\mathbf{Q}) \cdot B_i + \sum_{\alpha=1}^m q_{\alpha i} h_\alpha(\mathbf{Q}); \quad i = 1, n_c \quad (14)$$

where

$$h_0 = -\ln(Z - B) \quad (15a)$$

$$h_B = \frac{Z-1}{B} + \frac{A}{\Delta B^2} \ln \left(\frac{Z + \delta_1 B}{Z + \delta_2 B} \right) \quad (15b)$$

$$h_{q\alpha} = -\frac{2\lambda_\alpha Q_\alpha}{\Delta B} \ln \left(\frac{Z + \delta_1 B}{Z + \delta_2 B} \right); \quad \alpha = 1, M \quad (15c)$$

The partial derivatives of the component fugacity coefficients with respect to the reduction parameters Q_β can be calculated analytically from

$$\left(\frac{\partial \ln \varphi_i}{\partial Q_\beta} \right)_{p,T,Q_{\gamma \neq \beta}} = \frac{\partial h_0}{\partial Q_\beta} + \frac{\partial h_B}{\partial Q_\beta} B_i + \sum_{\alpha=1}^m \frac{\partial h_{q\alpha}}{\partial Q_\beta} q_{\alpha i} \quad (16)$$

and their expressions can be found in the work of Nichita et al.¹⁹

One can use any EoS model for the fugacity coefficient, provided it can be expressed only as a function of the reduced

variables. It is worth mentioning that eq 14 holds for any alternative reduction method.^{15,16} For hydrocarbon mixtures containing the classical contaminants (carbon dioxide, nitrogen, hydrogen sulfide, water, etc.), usually the BIPs matrix has many zero entries, only a few components having nonzero BIPs with the remaining ones, that is $m = r < n_c$. What we are effectively achieving is the reduction of the number of independent variables in any type of calculation, since the fugacity coefficient is depending on $m + 1$ reduced variables rather than on n_c compositional variables.

If some of the nonzero eigenvalues are small, a further reduction is possible if $m < r$, but the results are only approximative. If some nonzero eigenvalues are neglected, care must be taken to rescale the eigenvectors to preserve all diagonal elements of $\bar{\mathbf{C}}$ equal to unity, as we have previously suggested.²⁰ In this work we use only $m = r$, thus the results are “exact” (i.e., identical to the results obtained by classical methods, provided the same—very strict—tolerances are used in convergence criteria).

It should be noted that application of the reduction methods is restricted by the mixing rules in the EoS; the method is not applicable for Huron–Vidal like mixing rules and for the association approach, as in the cubic plus association equation of state (CPA EoS).

3. Phase Envelope Construction. *3.1. Saturation Points Calculation.* Classical methods for saturation points (DP/BP pressure/temperature) calculation involve the resolution of $n_c + 1$ equations (n_c equalities of fugacities and an additional equation, which is a particular form of the Rachford–Rice equation). The independent variables are mole fractions or natural logarithms of equilibrium constants and either pressure or temperature. Nghiem et al.⁶ presented and compared saturation pressure calculations for different choices of independent variables in the conventional approach.

As seen next, if reduced variables are used, it is possible to calculate saturation points by solving a reduced set of only $M + 1$ equations.

The error equations for saturation points calculation are

$$e_\alpha \equiv \sum_{i=1}^{n_c} q_{\alpha i} w_i - Q_\alpha w = 0; \quad \alpha = 1, M \quad (17a)$$

and

$$e_{M+1} \equiv \sum_{i=1}^{n_c} w_i - 1 = 0 \quad (17b)$$

where w_i are mole fractions of an incipient phase (denoted by the index W).

The n_c equilibrium equations (equality of fugacities) have been replaced by only M (eqs 17). There are $M + 1$ equations with $M + 1$ unknowns in the nonlinear system, namely the M reduced variables for the incipient phase, \mathbf{Q}_w , and v (that can be either pressure or temperature, the remaining one being the specification, s), thus the vector of independent variables is $\xi = (Q_{1w}, \dots, Q_{Mw}, v)^T$. Different iteration types are defined for saturation points calculations (see Table 1). Selection of the suitable calculation type prevents ill-conditioning of nonlinear systems. Specific values of all involved quantities for different calculation types are given in Table 1. The elements of the Jacobian matrix for the Newton–Raphson (NR) method are

$$\frac{\partial e_\alpha}{\partial Q_{\beta w}} = \sum_{i=1}^{n_c} q_{\alpha i} \frac{\partial w_i}{\partial Q_{\beta w}} - \delta_{\alpha\beta}; \quad \alpha, \beta = 1, M \quad (18a)$$

Table 1. Different Iteration Types for Saturation Points Calculation

saturation point	spec	independent variables	W	F	w_i	c_i (eq19)	A (eqs20,21)	B (eq29)	d_i (eq25)	iteration type
DP pressure	T	Q_{1L}, \dots, Q_{ML}, p	L	V	x_i	$-1/K_i^2$	0	0	2	PQL
BP pressure	T	Q_{1V}, \dots, Q_{MV}, p	V	L	y_i	1	1	0	2	PQV
DP temperature	p	Q_{1L}, \dots, Q_{ML}, T	L	V	x_i	$-1/K_i^2$	0	1	θ_i	TQL
BP temperature	p	Q_{1V}, \dots, Q_{MV}, T	V	L	y_i	1	1	1	θ_i	TQV

$$\frac{\partial e_\alpha}{\partial v} = \sum_{i=1}^{n_c} \frac{\partial q_{\alpha i}}{\partial v} w_i + \sum_{i=1}^{n_c} q_{\alpha i} \frac{\partial w_i}{\partial v}; \quad \alpha = 1, M \quad (18b)$$

$$\frac{\partial e_{M+1}}{\partial Q_{\beta W}} = \sum_{i=1}^{n_c} \frac{\partial w_i}{\partial Q_{\beta W}}; \quad \beta = 1, M \quad (18c)$$

$$\frac{\partial e_{M+1}}{\partial v} = \sum_{i=1}^{n_c} \frac{\partial w_i}{\partial v} \quad (18d)$$

Partial derivatives of the incipient phase mole fractions are

$$\frac{\partial w_i}{\partial \xi_\beta} = z_i c_i \frac{\partial K_i}{\partial \xi_\beta}; \quad i = 1, n_c; \beta = 1, M \quad (19)$$

where $K_i = y_i/x_i$, $i = 1, n_c$, are the equilibrium constants and c_i depends on calculation type (see Table 1).

The derivatives of K -values are

$$\frac{\partial K_i}{\partial Q_{\beta W}} = (-1)^A K_i \frac{\partial \ln \varphi_{iW}}{\partial Q_{\beta W}}; \quad i = 1, n_c; \beta = 1, M \quad (20)$$

and

$$\frac{\partial K_i}{\partial v} = (-1)^A K_i \left(\frac{\partial \ln \varphi_{iW}}{\partial v} - \frac{\partial \ln \varphi_{iF}}{\partial v} \right); \quad i = 1, n_c \quad (21)$$

where A is either even or odd, depending on calculation type (it is taken as 0 for DP and 1 for BP calculations).

In deriving fugacity coefficients, one must take into account that at given feed composition $\varphi_{iF} = \varphi_{iF}(Q_F(p, T), p, T)$, $i = 1, n_c$, where

$$Q_{\alpha F} = \sum_{i=1}^{n_c} q_{\alpha i} z_i; \quad \alpha = 1, m; \quad Q_{MF} \equiv B_F = \sum_{i=1}^{n_c} B_i z_i \quad (22)$$

while at given phase composition $\varphi_i = \varphi_i(Q, p, T)$, $i = 1, n_c$, and Q does not depend on p and T since it is an independent variable, as well as p or T . Therefore, the partial derivatives of fugacity coefficients are given by

$$\frac{\partial \ln \varphi_{iF}}{\partial v} = \left(\frac{\partial \ln \varphi_{iF}}{\partial v} \right)_{Q_F} + \sum_{\alpha=1}^M \left(\frac{\partial \ln \varphi_{iF}}{\partial Q_{\alpha F}} \right) \frac{\partial Q_{\alpha F}}{\partial v}; \quad i = 1, n_c \quad (23)$$

and

$$\frac{\partial \ln \varphi_{ik}}{\partial v} = \sum_{\alpha=1}^M h_{\alpha k} \frac{\partial q_{\alpha i}}{\partial v} = \sum_{\alpha=1}^m h_{\alpha k} \frac{\partial q_{\alpha i}}{\partial v} + h_{Bk} \frac{\partial B_i}{\partial v}; \quad i = 1, n_c; k = W, F \quad (24)$$

which can be further written by

$$\left(\frac{\partial \ln \varphi_{ik}}{\partial v} \right)_Q = \frac{1}{v} [h_{\psi k} \psi_{ik} d_i + (-1)^B h_{Bk} B_i]; \quad i = 1, n_c \quad (25)$$

where

$$h_{\psi k} = -\frac{2}{\Delta B_k} \ln \left(\frac{Z_k + \delta_1 B_k}{Z_k + \delta_2 B_k} \right) \quad (26)$$

In eq 25, for saturation temperature calculations, $B = 0$ and $d_i \equiv \theta_i(T)$, given by

$$\theta_i = 1 + \frac{m(\omega_i) \sqrt{T_{ri}}}{2[1 + m(\omega_i)(1 - \sqrt{T_{ri}})]} \quad (27)$$

while for saturation pressure calculations, $B = 1$ and $d_i = 2$.

It is very important to note here that the partial derivatives with respect to pressure $(\partial \ln \varphi_i / \partial v)_{Q,s}$ are much simpler than those used in the conventional approach, $(\partial \ln \varphi_i / \partial v)_{x,s}$, because the functions h are dependent on v through the compressibility factor Z , and thus, when the implicit form of the cubic EoS is derived with respect to v , we have

$$\left(\frac{\partial Z}{\partial v} \right)_{Q,s} = \sum_{\alpha=1}^M \left(\frac{\partial Z}{\partial Q_{\alpha}} \right)_{v,s, Q_{\beta \neq \alpha}} \left(\frac{\partial Q_{\alpha}}{\partial v} \right)_s = 0 \quad (28)$$

because $(\partial Q_{\alpha} / \partial v)_s = 0$, Q and v being both independent variables.

The remaining derivatives required in the expressions of the Jacobian matrix are

$$\frac{\partial q_{\alpha i}}{\partial v} = \begin{cases} (-1)^B \frac{q_{\alpha i}}{v} d_i^{(-1)^{B-1}}; & \alpha = 1, m \\ (-1)^B \frac{B_i}{v}; & \alpha = M \end{cases} \quad (29)$$

Initial estimates for DP or BP calculations are generated using the Wilson²⁵ empirical relationship for K values only for the first point. As shown later, during the automatic phase envelope construction, an extrapolation procedure is used to initialize saturation points calculations.

3.2. Quality Lines. For quality lines calculation, one can keep constant either the phase mole fraction or the phase volume fraction.

(a) For liquid mole fraction L fixed, $M + 1$ error equations are required. Depending on whether the specification is T or p , the vectors of independent variables are $\xi = (Q_{1L}, \dots, Q_{ML}, p)^T$ or $\xi = (Q_{1L}, \dots, Q_{ML}, T)^T$, respectively. The first M error equations are the same as for saturation points calculation, and last error equation is the Rachford–Rice equation

$$e_{M+1} \equiv \sum_{i=1}^{n_c} (y_i - x_i) = \sum_{i=1}^{n_c} \frac{z_i (K_i - 1)}{L + V K_i} = 0 \quad (30)$$

The above formulation is used if $L < V$; if $V < L$, the vector of independent variables is $\xi = (Q_{1V}, \dots, Q_{MV}, v)^T$.

(b) For liquid volume fraction S_L (or $S_V = 1 - S_L$) fixed. The liquid saturation (volume “liquid to feed” ratio) is

$$S_L = \frac{V_L}{V_L + V_V} = \frac{L Z_L}{L Z_L + V Z_V} \quad (31)$$

and an additional error equation is added to the system

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$$e_{M+2} \equiv L - \frac{S_L Z_V}{S_L Z_V + (1 - S_L) Z_L} = 0 \quad (32)$$

In this case, the vector of independent variables is $\xi = (Q_{1L}, \dots, Q_{ML}, v, L)^T$ or $\xi = (Q_{1V}, \dots, Q_{MV}, v, L)^T$.

3.3. Extrapolation. Suppose we have calculated a saturation point at a reference specification s^* , and we need now the saturation pressure at $s = s^* + \Delta s$, with Δs being reasonably small. We can then proceed in a similar manner as described in our earlier work on direct reduced flash calculations.^{15,17} By differentiating the error equations (written at reference conditions) with respect to the primary variables, we obtain a linear system of equations in $\xi = (Q_{1W}, \dots, Q_{MW}, v)^T$, for which the coefficients matrix is already available (Jacobian matrix \mathbf{J}^* at reference conditions), and only the elements of the right-hand-side (RHS) vector of simple expressions $(-\partial e_\alpha / \partial s)^*$; $\alpha = 1, M$ are required; see eqs 18b and 18d.

The extrapolated results can be further refined by using a third degree polynomial based on information from the last two points, as described by Michelsen.¹ Defining a similar extrapolation procedure for quality lines construction is straightforward. This ensures rapid convergence of the Newton–Raphson iterations; the number of iterations depends on the specification (p/T) step and on how close the critical point is.

3.4. Cricondentherm and Cricondenbar. It is important to determine the exact location of some key points on the phase envelope, such as the maximum pressure ($\partial p / \partial T = 0$), and maximum temperature ($\partial T / \partial p = 0$) points on the phase diagram. The location of CPT and CPM can be estimated during the phase envelope construction, within pressure or temperature intervals where derivatives $\partial T / \partial p$ or $\partial p / \partial T$ are changing sign, and then can be refined by interpolation. Here, we give the equations required for an exact calculation of CPT and CPM. The basis of their calculation is to express the following derivatives:

$$\left(\frac{\partial p}{\partial T} \right)_Q = - \left(\frac{\partial e_{M+1}}{\partial T} \right)_{p,Q} \left/ \left(\frac{\partial e_{M+1}}{\partial p} \right)_{T,Q} \right. \quad (33a)$$

or

$$\left(\frac{\partial T}{\partial p} \right)_Q = - \left(\frac{\partial e_{M+1}}{\partial p} \right)_{T,Q} \left/ \left(\frac{\partial e_{M+1}}{\partial T} \right)_{p,Q} \right. \quad (33b)$$

The CMT equation is

$$e_{M+2} \equiv \left(\frac{\partial T}{\partial p} \right)_Q = \frac{\partial e_{M+1}}{\partial p} = 0 \quad (34a)$$

and the CMP equation is

$$e_{M+2} \equiv \left(\frac{\partial p}{\partial T} \right)_Q = \frac{\partial e_{M+1}}{\partial T} = 0 \quad (34b)$$

For CMT and CMP calculations, there are $M + 2$ independent variables, with the vector of independent variables $\xi = (Q_{1W}, \dots, Q_{MW}, p, T)^T$. One of either eq 34a or eq 34b is added to the $M + 1$ equations of the saturation points calculation. The following second-order partial derivatives of the fugacity coefficient are required:

$$\frac{\partial^2 \ln \varphi_i}{\partial T^2} = - \frac{1}{T^2} \left[-\psi_i h_{\psi_i} (1 - \theta_i) + 2T \frac{\partial \ln \varphi_i}{\partial T} \right]; \quad i = 1, n_c \quad (35a)$$

$$\frac{\partial^2 \ln \varphi_i}{\partial p^2} = \frac{1}{p^2} \frac{\psi_i h_{\psi_i}}{2}; \quad i = 1, n_c \quad (35b)$$

$$\frac{\partial^2 \ln \varphi_i}{\partial T \partial p} = \frac{1}{Tp} \left[-\psi_i h_{\psi_i} \theta_i + T \frac{\partial \ln \varphi_i}{\partial T} \right]; \quad i = 1, n_c \quad (35c)$$

$$\frac{\partial^2 \ln \varphi_i}{\partial Q_\alpha \partial p} = \frac{1}{p} \left(2 \frac{\partial h_{\psi_i}}{\partial Q_\alpha} \psi_i + h_{\psi_i} \frac{\partial \psi_i}{\partial Q_\alpha} + \frac{\partial h_B}{\partial Q_\alpha} B_i \right); \quad i = 1, n_c; \alpha = 1, M \quad (35d)$$

$$\frac{\partial^2 \ln \varphi_i}{\partial Q_\alpha \partial T} = - \frac{1}{T} \left(- \frac{\partial h_{\psi_i}}{\partial Q_\alpha} \psi_i \theta_i + h_{\psi_i} \frac{\partial \psi_i}{\partial Q_\alpha} + \frac{\partial h_B}{\partial Q_\alpha} B_i \right); \quad i = 1, n_c; \alpha = 1, M \quad (35e)$$

where

$$\frac{\partial \psi_i}{\partial Q_\alpha} = \sum_{\gamma=1}^m \lambda_{\gamma} q_{\gamma i}; \quad i = 1, n_c; \alpha = 1, M \quad (36)$$

Note again the very simple expressions of second-order partial derivatives. For the classical approach, these derivatives are far more complicated; they are evaluated numerically by Michelsen.⁵ High quality initial guesses are available using interpolation from the neighboring points; this provides excellent initial estimates, only few (usually one) Newton iterations being required for convergence.

3.5. Spinodal and Critical Points. We have recently shown^{20,21} that for a cubic EoS one can reduce the dimensionality of the critical point calculation problem, using the Heidemann and Khalil criticality criteria.²⁶ The first criticality condition is the equation of the intrinsic limit of thermodynamic stability (the spinodal, which represents the underlying property of a phase diagram and separates intrinsically unstable states from metastable states); the dimensionality of the problem is reduced from n_c to M . The second criticality condition, which locates the critical point(s) on the spinodal, can also be expressed only in terms of reduced parameters.^{20,21} The critical point calculation method used here is applicable to nonzero BIPs in the EoS, and it is a generalization of Michelsen and Heidemann²⁷ method for all BIPs zero.

3.6. Phase Envelope Construction Strategy. One can not say that the phase envelope construction strategy is new; most of the features are treated following Michelsen,¹ and some elements from Ziervogel and Poling⁴ are adopted. The novelty of what is proposed here consists in using the reduction methods for *all* calculations involved in phase envelope construction. Spectral decomposition of the matrix $\bar{\mathbf{C}}$ is done once for all and used in all calculations; the computer time spent for decomposition is negligible if a large number of phase equilibrium calculations are performed.

The most important factor in tracing saturation points on the phase envelope is a proper selection of the correct iteration type at given conditions. Phase envelope construction can be started either from the BP or DP side; however, for hydrocarbon systems, the BP curve often trends upward at a low temperature, while the DP curve behaves normally. Thus, calculations are started with TQL iterations (DP temperature) at a low pressure, as suggested by Michelsen; initial estimates are generated by using Wilson's empirical relationship for K values.²⁵ The extrapolation is then used to get improved initial estimates for subsequent calculations.

The dimensionless slope of the phase envelope is defined as⁴

$$\beta = \frac{d(\ln p)}{d(\ln T)} \quad (37)$$

and is available at any calculation stage.

Let us define the points $I+$ on the phase envelope with temperature $T_{I+} = T|_{\beta=1}$ and pressure $p_{I+} = p|_{\beta=1}$, and the

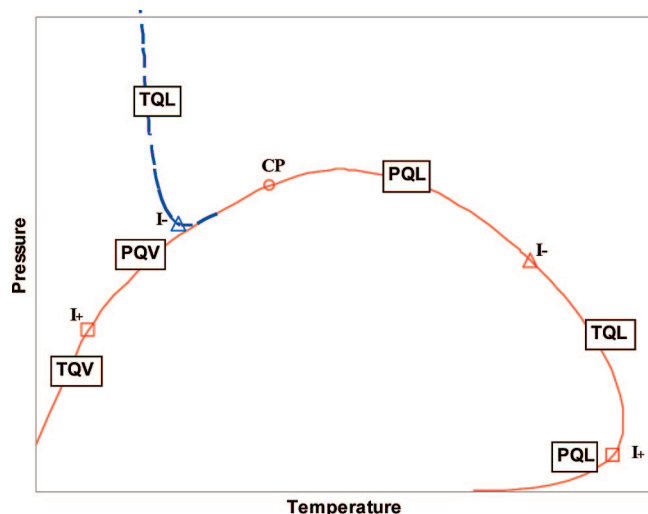


Figure 1. Iteration type for saturation points calculation along the phase envelope.

points I_- with temperature $T_{I_-} = T|_{\beta=-1}$ and pressure $p_{I_-} = p|_{\beta=-1}$, as sketched in Figure 1.

At any of these points, a switch between different saturation points calculation methods is performed. The sequence of iteration types depends on the relative position of the characteristic points of the phase envelope (CP, I_- , I_+).

For closed phase envelopes (i.e., BP pressure tends to zero at a low temperature), some iteration sequences are as follows (see Figure 1):

(a) for $T_{CP} < T_{I_+}$, the sequence is TQL, PQL, TQL, and TQV;

(b) for $T_{I_+} < T_{CP} < T_{I_-}$, the sequence is TQL, PQL, PQV, and TQV;

(c) for $T_{I_-} < T_{CP}$, the sequence is TQL, TQV, PQV, and TQV.

PQL iterations are then used to complete the envelope (the remaining portion of the lower DP curve) for low pressures at high temperatures.

For open shape phase envelopes (i.e., BP or DP pressures tends to very high values at a certain low temperature), one can have the following sequence:

(a) if there is one CP, TQL, PQL, PQV, TQV; TQL, PQL, TQL, TQV; or TQL, TQV, PQV, TQV, depending on the relative position of the CP and the two I_- points;

(b) if there is no CP, TQL, PQL, TQL.

For transition between these two cases (the phase boundary exhibits a minimum in pressure), additional switches between iteration types are required. In all cases, the sequence of iteration types is selected automatically as calculations are advancing.

The bubblepoints and dewpoints are calculated throughout the critical region by stepping around the phase envelope in pressure or temperature increments. The specification (pressure or temperature) steps are selected by targeting the desired number of NR iterations,^{1,3} usually from three to five. If convergence is obtained in less than three iterations, the step is increased (a maximum allowed step is specified); if more than five iterations are required for convergence, then the step is decreased. Steps are larger far from CP and become smaller as the CP is approached. The algorithm is robust with no convergence problems (such as convergence to the trivial solution) in the near-critical region. Note that, in Michelsen's classical approach, the automatically chosen step variable is

Table 2. Relevant Data for Selected Mixtures

mixture	n_c	no. of nonzero BIPs	comp with nonzero BIPs	no. of nonzero eigenvalues	$m + 2$
sample A	34	3	C ₁ , CO ₂ , N ₂	5	7
sample B	24	3	C ₁ , CO ₂ , N ₂	5	7
sample C	52	3	C ₁ , CO ₂ , N ₂	5	7
NS	27	4	C ₁ , C ₂ , CO ₂ , N ₂	7	9

normally the K factor of either the least volatile or the most volatile component. However, K factors are specific to the compositional space and it is not feasible to specify one of the K factors in a reduction method; thus, we have chosen as specifications T and p .

As pointed out by Michelsen,¹ the algorithm as developed here is not suitable for mixtures with multiple critical points, VLL equilibrium boundaries, etc. but can be in some cases adapted to a specific problem.

For the quality lines, the procedure is similar to that used for phase boundary construction, using automatic selection of iteration type and an appropriate extrapolation procedure. For example, at given V , the second specification is either p or T , the other variable being calculated; a switch between iteration types is performed at any $(\partial V/\partial v)_s = \pm 1$. Exact T and p conditions of CTM and CPM are calculated using criteria defined by eqs 34a and 34b, using initial guesses obtained by interpolation. If required, the spinodal curve is traced by solving the reduced spinodal equation²⁰ for temperature at increasing molar volumes starting from a molar volume $v_m = b + \varepsilon$; the process is discontinued when a predetermined (low) temperature is reached on the lower branch of the spinodal.

4. Results and Discussion

The proposed method was first tested for several synthetic hydrocarbon mixtures, which mimics reservoir oil and gas-condensate systems. Then, the method is applied to four natural occurring hydrocarbon mixtures, having various phase envelope shapes, and thus requiring different iteration type sequences. Component critical properties and acentric factors, as well as nonzero BIPs are presented in the Supporting Information. Other relevant data for all mixtures are given in Table 2, and nonzero eigenvalues of the matrix \bar{C} are given in Table 3.

Compositions for samples A (gas condensate, $n_c = 34$), B (heavy oil, $n_c = 24$), and C (heavy gas condensate, $n_c = 52$, with a detailed PNA distribution) are taken from the work of Pedersen et al.⁸ Nonzero BIPs are for methane (C_{C1-j} are calculated according to the work of Katz and Firoozabadi²⁸), carbon dioxide ($C_{CO2-j} = 0.12$), and nitrogen ($C_{N2-j} = 0.1$), leading for all three mixtures to only five nonzero eigenvalues (given in Table 3). The properties of heavy components (critical temperature, critical pressure, and acentric factor) are assigned using Riazi and Al-Sahhaf^{29,30} correlations. No attempts were made to fit experimental data for these mixtures.

Figure 2 (sample A), Figure 3 (sample B), and Figure 4 (sample C) depict phase boundaries, spinodal curves (including for negative pressures and LL instability), critical points, and quality lines. Key points on the phase envelopes are reported in Table 4.

The sequence of iteration types for tracing phase boundaries for the three mixtures is as follows: TQL, PQL, TQL, TQV,

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(26) Heidemann, R. A.; Khalil, A. M. *AIChE J.* **1980**, *26*, 769–779.

(27) Michelsen, M. L.; Heidemann, R. A. *AIChE J.* **1981**, *27*, 521–523.

Table 3. Nonzero Eigenvalues for Selected Mixtures

mixture	nonzero eigenvalues						
	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7
sample A	33.539798	0.305535	0.133428	−0.076868	0.098106		
sample B	23.566354	0.295319	−0.039818	0.098447	0.079697		
sample C	51.544429	0.309907	0.104009	0.097397	−0.055743		
NS	26.508802	0.336384	0.146109	0.064051	−0.055050	0.013755	−0.014051

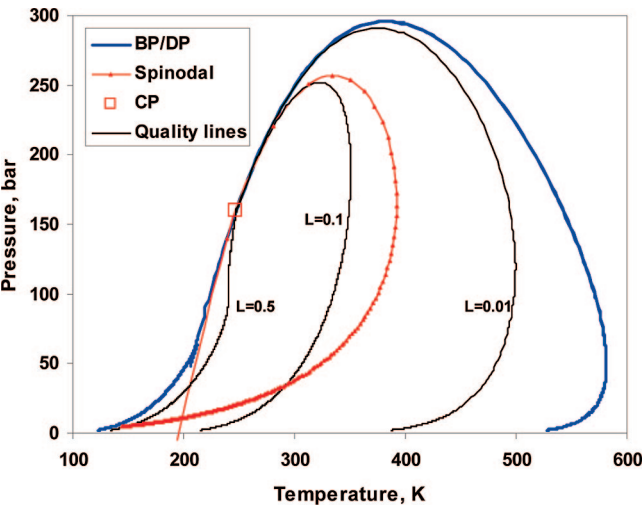


Figure 2. Phase envelope of sample A.

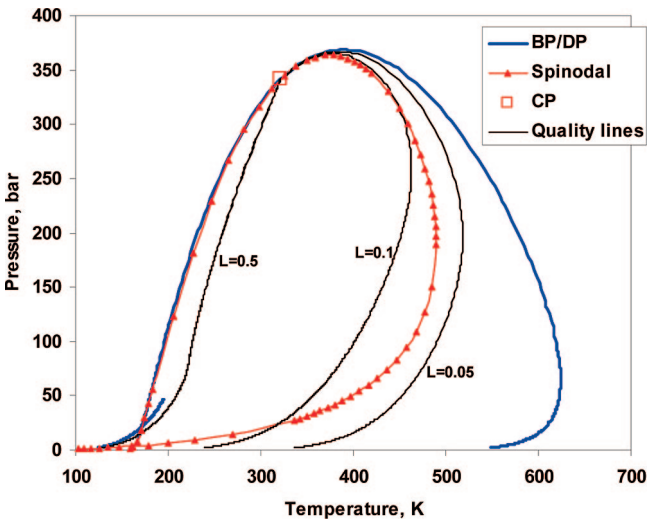


Figure 4. Phase envelope of sample C.

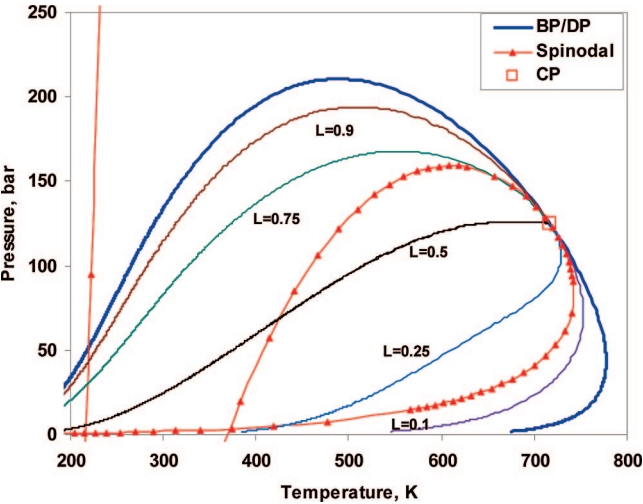


Figure 3. Phase envelope of sample B.

Table 4. Key Points on the Phase Envelopes of Selected Mixtures

mixture	CP		CTM		CPM	
	T_c (K)	p_c (bar)	T (K)	p (bar)	T (K)	p (bar)
sample A	247.27	160.12	581.61	49.19	382.71	295.79
sample B	716.12	125.27	777.42	43.43	488.86	210.65
sample C	321.50	341.42	624.05	64.02	389.53	368.46
NS			619.78	82.25		

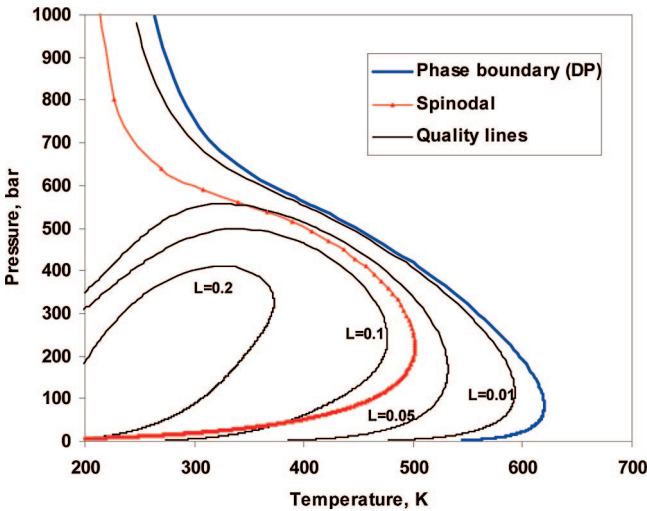


Figure 5. Phase envelope of NS gas condensate.

PQV (sample A); TQL, TQV, PQV, TQV (sample B); and TQL, PQL, PQV, TQV, PQV (sample C). PQL iterations complete phase diagram with the remaining portion of the lower dewpoint locus.

The last system studied is a North Sea (Lille Frigg reservoir) gas condensate (denoted here as NS) described by 27 components. Feed composition, all component properties, and nonzero BIPs can be found tabulated in the work of Nichita et al.³¹ (see also the Supporting Information). Only C₁, C₂, CO₂, and N₂ have nonzero BIPs, leading to seven nonzero eigenvalues. The phase envelope (plotted in Figure 5) is open-shaped, with only dewpoints and with no critical point; the cubic form in the second criticality condition $C < 0$ ($\forall v, T$) satisfies the spinodal equation. For this mixture, the iteration sequence for saturation points calculation is as follows: TQL, PQL, TQL.

For all the test examples considered, the dimensionality of the problem is reduced (see Table 2); however, this reduction is spectacular for mixtures with many components and relatively few nonzero BIPs, such as hydrocarbon reservoir fluids. The larger the number of components, the more efficient the proposed method is.

We advocate the proposed method because:

(i) It requires lower computation time than similar classical approaches.

(31) Nichita, D. V.; Broseta, D.; Leibovici, C. F. *J. Pet. Sci. Eng.* **2007**, 59 (1–2), 59–72.

Table 5. Number of Independent Variables for Various Calculation Types

calculation type	no. of independent variables	
	classical	reduction
flash	n_c	$M + 1$
saturation pressure/temperature	$n_c + 1$	$M + 1$
cricondentherm and cricondenbar	$n_c + 2$	$M + 2$
critical point and spinodal	n_c^a	M^a
quality lines, molar	$n_c + 1$	$M + 1$
quality lines, volume	$n_c + 2$	$M + 2$

^a Dimensions for quadratic and cubic forms; independent variables are κ and T .

(ii) It is simple.

(iii) It has high robustness.

(iv) By significantly reducing problem dimensionality, it avoids high-order linear algebra operations.

Saturation points calculations are somewhat similar in nature with phase stability testing; the tangent plane distance (TPD) surface is smoother in the hyperspace defined by reduced variables than in the compositional space.^{32,18} Quality lines calculation are similar in nature with flash calculations; again, these calculations are more robust and efficient if the reduction method is used (less iterations and less time per iteration are required for convergence).^{14,15,17,19} Significant simplifications are obtained for partial derivatives with respect to pressure and temperature.

Note that alternative sets of reduction parameters may be used;^{15,16} in the formalism presented here $\sqrt{\lambda_\alpha} q_{\alpha i}$ should be replaced by the appropriate expressions of reduction matrix elements.

For the proposed method, all features related to phase envelope construction are treated in the reduced hyperspace instead of the compositional hyperspace as in all previous methods; to our knowledge, this is the first time that saturation points, cricondentherm, cricondenbar, and quality lines are calculated using the results of the reduction theorem. The method is simple to implement provided a reduced flash code is available. In this work, a code for reduced flash¹⁷ was readily adapted.

We believe that the proposed calculation method may be an attractive candidate to be incorporated in chemical process design and simulation software.

5. Conclusions

All calculations required for phase envelope construction have been formulated in terms of the reduced variables. The proposed procedure is fast, accurate, and robust, it avoids round-off errors associated with large matrices manipulation, and the reduction of problem dimensionality is very attractive for mixtures with many components. For our approach, first- and second-order partial derivatives of fugacity coefficients with respect to pressure and temperature have much simpler expressions than the same derivatives for the classical Michelsen approach. The method is the more efficient if the number of components in the mixture is larger and the number of nonzero binary parameters is smaller, i.e. $m \ll n_c$. It is recommended for hydrocarbon mixtures with many components, and its application ranges from process design and simulation to petroleum

reservoir engineering problems. Finally, Table 5 shows the problem dimensionality for different kinds of calculations for both classical and reduction approaches.

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Nomenclature

A = EoS parameter
 a = attractive parameter in the EoS
 A_i = component parameter in EoS
 B = EoS parameter
 b = covolume in the EoS
 B_i = component EoS coefficient
 \bar{C} = matrix with elements $1 - C_{ij}$
 C_{ij} = binary interaction parameters between components i and j
 f_i = fugacity of component i
 K_i = equilibrium constant of component i
 M = number of reduction parameters
 m = number of nonzero eigenvalues
 n_c = number of components
 p = pressure
 Q_α = reduction parameters
 $q_{\alpha i}'$ = elements of the eigenvectors of matrix \bar{C}
 R = universal gas constant
 r = rank of matrix \bar{C}
 s = specification (can be p or T)
 S = saturation
 T = temperature
 V = vapor mole fraction
 v = iteration variable (can be p or T)
 w_i = mole fraction of incipient phase, component i
 Z = compressibility factor
 z_i = feed composition

Greek Symbols

$\delta_{\alpha\beta}$ = Kronecker delta
 δ_1, δ_2 = constants in EoS
 $\Delta = \delta - \delta_2$
 λ_α = eigenvalues of matrix \bar{C}
 Ω_a, Ω_b = constants in the EoS
 ω_i = acentric factor
 ξ = vector of independent variables
 φ_i = fugacity coefficient

Superscripts

T = transposed
 * = reference conditions

Subscripts

c = critical
 ij = component index
 k = phase index
 F = feed
 r = reduced
 W = incipient phase
 α, β = reduction parameter index

Supporting Information Available: Composition, component properties, and methane nonzero BIPs for all numerical examples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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