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# A simple approximate density-based phase envelope construction method

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## Abstract

A new simple density-based method is proposed for approximate phase envelope construction of constant composition multicomponent mixtures. The phase envelope is traced in the molar density-temperature plane (with a unique saturation temperature at given mixture molar density) and the pressure is calculated explicitly from the equation of state (EoS). The computational procedure is very easy to implement and a reduced system of only three equations must be solved for three variables (molar densities of feed and incipient phases and temperature), irrespective of the number of components in the mixture. The EoS must not be solved for volume and the elements of the Jacobian matrix have simple forms; the partial derivatives of fugacity coefficients with respect to compositions are not required. A simple and computationally inexpensive correction procedure highly improves results by updating the reference conditions at each point on the phase envelope. Simple equations for calculation of maximum temperature and pressure points are presented. The proposed method was tested for a variety of mixtures, ranging from natural gases to heavy oils, using a general form of two-parameter cubic EoS. For usual (closed) phase envelopes, the entire phase boundary is remarkably well reproduced. Certain unusual (open-shaped, with a bubble point branch extending to infinity) phase envelopes are also entirely traced up to very high pressures, while in certain cases the method fails at low temperatures (where the approximation of equilibrium constants becomes inadequate), but provides an excellent approximation for a wide temperature range. The proposed method is not dependent of the thermodynamic model (any pressure-explicit EoS can be used), it is recommended for mixtures with many components and it may be particularly attractive for complex EoS.

**Keywords:** phase envelope, tangent plane distance, density-based method, molar density, equilibrium constants, Newton method

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## 1. Introduction

Calculation of saturation points is an important type of basic phase equilibrium calculations. The phase envelope is a fingerprint of a mixture of given composition. From a computational point of view, it is more difficult than phase splitting [1]. The number of solutions is not known in advance; the problem can have multiple solutions (i.e., several saturation temperatures at given pressure) or no solution (i.e. no saturation pressure for temperatures above the cricondentherm). Moreover, it is a priori unknown whether a saturation point is a dew or a bubble point and algorithms may encounter convergence problems around critical points if the initialization is poor, or convergence to the trivial solution (corresponding to spinodal conditions) may occur.

Many stand-alone saturation points calculation methods were proposed (Baker and Luks [2], Michelsen [3], Nghiem et al. [4], Varotsis [5] and recently Nikolaidis et al. [6]). However, the only entirely safe procedure is the automated construction of the phase envelope using continuation methods (Michelsen [7], Asselineau et al. [8]); calculations start at an “easy” point where an unproblematic convergence is expected, then an extrapolation procedure provides good initial guess for Newton iterations. Various implementations were proposed by Li and Nghiem [9], Ziervogel and Poling [10], Nichita [11], Venkatarathnam [12], Nikolaidis et al. [13].

Saturation point calculations are closely related to the phase stability problem, which consists in the minimization of the tangent plane distance (TPD) function [14] to find all stationary points. In all saturation points calculation methods, the system of equations contains the zero TPD condition. In the conventional PT-based approach, the Gibbs free energy is the central thermodynamic potential; volume is a dependent variable and is calculated from the EoS at given pressure, temperature and composition.

In recent years, volume-based methods [15] have received increased attention in the literature for solving a variety of phase equilibrium problems at different specifications. In volume-based phase equilibrium calculation methods, the Helmholtz free energy is the central thermodynamic potential and volume is a primary variable. The EoS is not solved for volume and simpler partial derivatives (no implicit functions) are required to assemble Hessian and Jacobian matrices, thus volume-based methods are attractive for complex EoS. The pressure is calculated explicitly from the EoS and negative pressures are allowed [16-19].

For phase stability testing, the first TPD function in terms of component molar densities was proposed by Nagarajan et al. [20]. Michelsen [14] expressed the TPD function in mole fractions and

molar volume and later Mikyška and Firoozabadi [16] and Castier [21] derived the TPD function in terms of mole numbers and volume. Several volume-based phase stability testing methods were proposed, at PT or VTN specifications, using global [22,23] and local (modified Newton) [16,17,20,21,24] optimization methods.

In phase envelope construction, a volume-based method was proposed by Kunz et al. [25] and very recently a density-based method was presented by Nichita [18]. Molar densities were used in various phase envelope construction procedures by Quinones-Cisneros and Deiters [26], Deiters [27] and Bell and Deiters [28]. Phase envelopes in the molar density-temperature plane were indirectly constructed from phase stability [16,17] or flash calculations [29]. Volume-based methods were recently shown (Sandoval et al. [19] and Nichita [30,31]) to be particularly attractive for phase envelope construction including capillary pressure, due to the explicit in volume nature of interfacial tension models.

Michelsen [32] proposed a simple approximate method for phase boundary calculations, in which a reduced nonlinear system of only two equations with two variables (pressure and temperature) is solved. The partial derivatives of the fugacity coefficient with respect to compositions are not required. An effective refinement procedure and a very simple correction procedure are proposed to improve the accuracy of the approximate method. It is remarkable how good approximations of exact phase envelopes are obtained using the simplified method (in Michelsen's examples, as well as in other applications of his method to various hydrocarbon mixtures (Pokki [33], Gu et al [34]), using a very simple scaling law for equilibrium constants. Some limitations of the approximate method are mentioned, such as mixtures with several critical points, mixtures with no critical point and some complex mixtures for which the approximation of equilibrium constants is inadequate.

In this work, a simple approximate density-based phase envelope construction method is proposed, which can be seen as the density-based counterpart of Michelsen's conventional simplified approximate method. A nonlinear system with only three equations and three unknowns (molar densities of feed and incipient phase and temperature) must be solved. The EoS must not be solved for volume and the elements of the Jacobian matrix are simpler than in the conventional approach.

This paper is structured as follows. First, Michelsen's approximate phase envelope construction procedure is briefly presented, then the proposed density-based method is introduced (including the correction step and equations of temperature and pressure extrema) and tested for several mixtures with various usual (closed) and unusual (open-shaped) phase envelopes, before concluding.

## 2. Michelsen's PT approximate method

Michelsen [32] proposed a simple approximate phase envelope construction method, briefly presented below, in which a nonlinear system of only two equations is solved for temperature and pressure.

First, let us recall that in conventional PT-based phase stability testing, the TPD function (Michelsen [14]) is

$$D = \sum_{i=1}^{nc} x_i h_i \quad (1)$$

where

$$h_i = \ln f_i(P, T, \mathbf{x}) - \ln f_{iz}(P, T, \mathbf{z}) \quad (2)$$

The idea behind Michelsen's approximate procedure is to relate approximate equilibrium constants,  $K_i$  (thus compositions), at any point on the phase boundary, to exact equilibrium constants ( $K_i^*$ ), calculated at some reference conditions. This is done via the very simple equation

$$K_i = (K_i^*)^\alpha \quad (3)$$

or

$$\ln K_i = \alpha \ln K_i^* \quad (4)$$

The scaling exponent is  $\alpha = 1$  at the reference conditions and  $\alpha = 0$  at the critical point. The equilibrium constants are

$$K_i = Y_i / z_i \quad (5)$$

From Eqs. (4) and (5), the (formal) mole numbers are

$$\ln Y_i = \ln z_i + \alpha \ln K_i^* \quad (6)$$

and the mole fractions in the trial phase are obtained by normalization

$$x_i = \frac{Y_i}{\sum_{i=1}^{nc} Y_i} \quad (7)$$

From Eq. (6) and (7), mole fractions depend only on  $\alpha$ ,  $\mathbf{x} = \mathbf{x}(\alpha)$  and further from Eq. (2),  $h_i = h_i(P, T, \alpha)$ . Thus, a single variable (the scaling exponent) replaces the  $nc$  compositions used in exact methods.

Two functions of  $T$ ,  $P$  and  $\alpha$  were defined [32]

$$f_1(T, P, \alpha) = \sum_{i=1}^{nc} x_i h_i = 0 \quad (8)$$

and

$$f_2(T, P, \alpha) = \sum_{i=1}^{nc} z_i h_i = 0 \quad (9)$$

The function  $f_1$  is exactly the TPD function [14] in Eq. (1), which must be zero at saturation points. The independent variables are  $\boldsymbol{\xi} = (\ln P, \ln T)^T$  and  $\alpha$  is the specification.

The nonlinear system  $\mathbf{f} = \mathbf{0}$  is solved by the Newton method

$$\mathbf{J} \Delta \boldsymbol{\xi} = -\mathbf{f} \quad (10)$$

where the Jacobian matrix  $\mathbf{J}$  is a  $[2 \times 2]$  matrix and the residual vector is  $\mathbf{f} = (f_1, f_2)^T$ .

The required partial derivatives are  $\partial \ln \varphi_i / \partial T$  and  $\partial \ln \varphi_i / \partial P$ , the partial derivatives of the fugacity coefficient with respect to mole numbers need not be calculated, and the partial derivatives with respect to  $\alpha$  required in the extrapolation procedure are evaluated numerically.

Calculations start at  $\alpha=1$  at the reference conditions, with a low pressure dew point or bubble point temperature and  $\alpha$  is decreased towards  $\alpha=0$  at the ‘‘critical point’’ and beyond at negative values. Two correction procedures are proposed to update the results if deviations become too large.

All points on the approximate phase boundary are located inside the two-phase region and the phase boundary calculated with the simplified method is exact for a binary mixture, because in this case the equality of fugacities for both components is satisfied at the solution of the system [32].

The simplified procedure is not generally applicable. It may not reproduce accurately bubble points at low pressures starting with equilibrium constants from a lower dew point. For certain mixtures, calculations cannot be continued at lower temperatures neither without nor with correction, since the simple scaling approach is inadequate at these temperature and pressure conditions. An example is given for a mixture with liquid demixing at low temperatures, exhibiting a swallowtail

pattern. Other limitations are for mixtures with no critical point or mixtures with multiple critical points.

### 3. Density-based approximate method

Michelsen's conventional (PT-based) simplified approximate approach [31] is formulated in a density-based framework, following the recent exact density-based phase envelope construction method of Nichita [18].

#### 3.1. Phase stability testing at temperature, volume and moles specifications

As mentioned before and discussed in detail in Ref. [18], saturation point calculations are closely related to phase stability testing and the system of equations in any saturation point calculation method must contain the zero-TPD function condition.

The TPD function in terms of molar densities is (Nagarajan et al. [20])

$$D(\mathbf{d}, T) = \sum_{i=1}^{nc} d_i [\ln f_i(\mathbf{d}, T) - \ln f_{iz}(\mathbf{d}_z, T)] - \frac{P(\mathbf{d}, T) - P_z(\mathbf{d}_z, T)}{RT} \quad (11)$$

where  $\mathbf{d}$  is the vector of component molar densities in the trial phase,  $\mathbf{d} = (d_1, \dots, d_{nc})^T$ , with

$$d_i = \frac{n_i}{V} = \frac{x_i}{v} = x_i d; i = 1, nc \quad (12)$$

and  $\mathbf{d}_z = (d_{1z}, \dots, d_{nc,z})^T$  is the vector of component molar densities of the feed (the phase investigated),

$$d_{iz} = \frac{n_{iz}}{V_z} = \frac{z_i}{v_z} = z_i d_z; i = 1, nc \quad (13)$$

with  $n_{iz} = Fz_i$ .

The TPD function in Eq. (11) can be used for both VTN (at volume, temperature and moles) [16,17,21,23] and volume-based PT phase stability testing [20,22,24]. The volume-based phase stability problem is a bound- and linear inequality-constrained minimization of the TPD function usually solved by local minimization (using modifications of the Newton method) [16,17,20,21,24],

constrained optimization (by formulation of phase stability as a dual optimization problem) [35,36] or global optimization methods [22,23]. In phase envelope construction, this TPD function is used in Refs. [18,31].

In density-based saturation point calculations [18], the system of equations includes the equality of fugacities and pressures, which ensures the zero TPD condition. In the temperature-pressure (or molar density-temperature) plane, the saturation points are the only points where the solution of the equation  $TPD=0$  is nontrivial (giving the composition of the incipient phase), corresponding to a global minimum of the TPD function. All other stationary points with  $TPD=0$  (saddle points and maxima) correspond to a trivial solution. A detailed discussion can be found in Ref. [18]; see also Refs. [37,38] for the behavior of the TPD surface around saturation points.

### 3.2. Saturation point equations

The equilibrium constants at some reference conditions are

$$K_i^* = \frac{x_i^*}{z_i}; i = 1, nc \quad (14)$$

At the solution of exact saturation point calculations, thus at reference conditions,  $x_i^* = Y_i^*$  since  $\sum_{i=1}^{nc} Y_i^* = 1$ . This last relation is not satisfied on the approximate phase boundary (except at the "critical point", where all equilibrium constants equal unity at  $\alpha=0$ ). The equilibrium constants at any point on the phase boundary are related to those at reference conditions ( $K_i^*$ ) by Eq. (4).

From  $x_i = d_i / d$ , component molar densities can be related to  $\ln K_i^*$  by

$$\ln d_i = \ln d + \ln z_i + \alpha \ln K_i^* + \theta(\alpha) \quad (15)$$

where the mixture molar density of the incipient phase is  $d = 1/v$ . The parameter  $\theta$  corresponds to the normalization in Eq. (7) and is given by

$$\theta(\alpha) = s \ln \left[ \sum_{i=1}^{nc} z_i (K_i^*)^{-s\alpha} \right] \quad (16)$$

where  $s = +1$  if calculations are started on the dew point side and  $s = -1$  on the bubble point side.



Equation (15) is the key equation in the density-based simplified approach. This means that  $d_i = d_i(d, \alpha)$ , thus the fugacity and pressure of the incipient phase are functions of  $d$ ,  $T$  and  $\alpha$ . In the approximate method,  $nc$  variables in the exact density-based method (molar densities) are replaced by only two variables,  $\alpha$  and  $d$ . Since  $d_{iz} = d_z z_i$ , the fugacity and pressure of the reference phase are functions of  $d_z$  and  $T$ .

Three functions of molar densities ( $d$  and  $d_z$ ), temperature and  $\alpha$  are defined as

$$\Phi_1(d_z, d, T, \alpha) = \sum_{i=1}^{nc} d_i(d, \alpha) [\ln f_i(d, T, \alpha) - \ln f_{iz}(d_z, T)] = 0 \quad (17)$$

$$\Phi_2(d_z, d, T, \alpha) = \sum_{i=1}^{nc} d_{iz}(d_z) [\ln f_i(d, T, \alpha) - \ln f_{iz}(d_z, T)] = 0 \quad (18)$$

and

$$\Phi_3(d_z, d, T, \alpha) = \frac{P(d, T, \alpha) - P_z(d_z, T)}{RT} = 0 \quad (19)$$

The first two functions correspond to the two functions in the conventional method, Eqs. (8) and (9), multiplied by the molar densities  $d$  and  $d_z$ , respectively. The third function is used in the pressure equality equation, which closes the system of equations.

The nonlinear system of three equations is

$$\Phi(\xi) = 0 \quad (20)$$

where  $\Phi = (\Phi_1, \Phi_2, \Phi_3)^T$ .

From Eqs. (11), (17) and (19), the TPD function can be written as

$$D = \Phi_1 - \Phi_3 \quad (21)$$

Thus, at the solution of the system of equations, the TPD function  $D=0$ . The second equation ( $\Phi_2=0$ ) ensures the continuity of the approximate phase boundary at its critical point (as in the conventional method [32]), because  $d_i \rightarrow d_{iz}$  when  $\alpha \rightarrow 0$ .

It is evident that for a binary mixture, Eqs. (17) and (18) ensure the equality of fugacities (as in the conventional method [18]) and Eq. (19) ensures the equality of pressures, that is, the simplified method is exact in this case.

The results of the density-based method are identical to Michelsen's ones [32], since in both conventional and density-based methods, the compositions of the incipient phase depend solely on the same approximation of equilibrium constants given by Eq. (4). When Eqs. (17) to (19) are satisfied at  $T$  and  $d_z$ , Eqs. (8) and (9) are satisfied at  $T$  and  $P = P_z(d_z, T)$ .

### 3.3. Resolution of the non-linear system

The linear system in the Newton method is

$$\mathbf{J}\Delta\xi = -\Phi \quad (22)$$

The vector containing the three independent variables is  $\xi = (\ln d_z, \ln d, \ln T)^T$  and  $\alpha$  is always the specification.

The elements of the  $[3 \times 3]$  Jacobian matrix are

$$J_{11} = \frac{\partial\Phi_1}{\partial \ln d_z} = -\frac{1}{RT} \sum_{i=1}^{nc} d_i \frac{\partial P_z}{\partial d_{iz}} \quad (23a)$$

$$J_{12} = \frac{\partial\Phi_1}{\partial \ln d} = \Phi_1 + \frac{d}{RT} \frac{\partial P}{\partial d} \quad (23b)$$

$$J_{13} = \frac{\partial\Phi_1}{\partial \ln T} = T \sum_{i=1}^{nc} d_i \left( \frac{\partial \ln f_i}{\partial T} - \frac{\partial \ln f_{iz}}{\partial T} \right) \quad (23c)$$

$$J_{21} = \frac{\partial\Phi_2}{\partial \ln d_z} = \Phi_2 - \frac{d_z}{RT} \frac{\partial P_z}{\partial d_z} \quad (23d)$$

$$J_{22} = \frac{\partial\Phi_2}{\partial \ln d} = \frac{1}{RT} \sum_{i=1}^{nc} d_{iz} \frac{\partial P}{\partial d_i} \quad (23e)$$

$$J_{23} = \frac{\partial\Phi_2}{\partial \ln T} = T \sum_{i=1}^{nc} d_{iz} \left( \frac{\partial \ln f_i}{\partial T} - \frac{\partial \ln f_{iz}}{\partial T} \right) \quad (23f)$$

$$J_{31} = \frac{\partial\Phi_3}{\partial \ln d_z} = -\frac{d_z}{RT} \frac{\partial P_z}{\partial d_z} \quad (23g)$$

$$J_{32} = \frac{\partial\Phi_3}{\partial \ln d} = \frac{d}{RT} \frac{\partial P}{\partial d} \quad (23h)$$

$$J_{33} = \frac{\partial \Phi_3}{\partial \ln T} = \frac{1}{R} \left[ \frac{\partial P}{\partial T} - \frac{\partial P_z}{\partial T} - \frac{P - P_z}{T} \right] \quad (23i)$$

The equations used in the differentiation process are

$$\frac{\partial d_i}{\partial \ln d} = d_i \quad (24)$$

(from Eq. 15), the symmetry of second order derivatives of the Helmholtz free energy with respect to mole numbers and volume written as

$$\frac{\partial \ln f_i}{\partial d} = \frac{1}{dRT} \frac{\partial P}{\partial d_i}; i = 1, nc \quad (25)$$

and from Euler theorem on homogeneous functions (the chemical potential and pressure are homogeneous function of first order, see Ref. [18])

$$\sum_{i=1}^{nc} d_i \frac{\partial \ln f_i}{\partial d_j} - \frac{1}{RT} \frac{\partial P}{\partial d_j} = 0; j = 1, nc \quad (26)$$

and

$$\sum_{i=1}^{nc} d_i \frac{\partial P}{\partial d_i} - d \frac{\partial P}{\partial d} = 0 \quad (27)$$

The above equations are valid for any EoS; the required partial derivatives are  $\partial \ln f_i / \partial T$ ,  $\partial P / \partial T$ ,  $\partial P / \partial d$  and  $\partial P / \partial d_i$ ; note that the partial derivatives of fugacities with respect to molar densities,  $\partial \ln f_i / \partial d_j$ , are not required. For a general form of two-parameter cubic EoS used in this work, containing the Soave-Redlich-Kwong (SRK) EoS [39] and the Peng-Robinson (PR) EoS [40,41], these partial derivatives (having quite simple forms) can be found in Ref. [18]. The partial derivatives in the density-based method are much simpler than those in the conventional (pressure-based) approach for any EoS (since no implicit functions are involved in the differentiation).

The thermodynamic functions (fugacity and pressure) and their partial derivatives are usually expressed (and coded in phase equilibrium packages and simulators) as functions of mole numbers, volume and temperature, which are the natural variables for a pressure-explicit equation of state. In the density-based method, the functions and derivatives are in terms of component molar densities and temperature. However, due to homogeneity properties, as shown in Nichita [17,18], there is no need to recast the EoS in terms of molar densities, and existing routines can be used to calculate the required functions and partial derivatives. The relations to pass from partial derivatives of pressure

with respect to mole numbers and volume to those with respect to  $d_i$  and  $d$ , respectively, using the homogeneity properties of pressure, are given in Ref. [18].

Concerning the summations in Eqs. (23a) and (23e), at least for cubic EoS, they can be replaced by a mixed partial derivative formally similar to  $\partial P / \partial d$  (in a sense similar to "mixed volumes" [42]). Also the sums in Eqs. (23e) and (23f) can be replaced by quantities with a simpler expression than that of  $\partial \ln f_i / \partial T$ .

### 3.4. Phase envelope construction

The phase envelope construction procedure is similar to that in the exact density-based method [18] (which follows Michelsen's framework [7]), except for variable selection; in the exact method the specification variables are selected according to their sensitivity, while here the scaling factor  $\alpha$  is always the specification. High quality initial estimates required for full Newton iterations are obtained by cubic extrapolation [7,18].

The linear system

$$\mathbf{J} \frac{\partial \xi}{\partial \alpha} = - \frac{\partial \Phi}{\partial \alpha} \quad (28)$$

is solved for sensitivities of the independent variables with respect to variations of  $\alpha$ .

The Jacobian matrix is already evaluated for the solution of the last point, an LU decomposition available from the resolution of the linear system (Eq. 22) at the last iteration. Only the elements of the RHS vector in Eq. (28) are additionally required in extrapolation steps.

The partial derivatives  $\partial \ln f_i / \partial \alpha$  are calculated numerically. The derivative  $\partial P / \partial \alpha$  can be calculated analytically (it is related to  $\partial P / \partial d_i$  using the chain rule and Eq. 15).

At the first point on the phase envelope, an exact (full), dew point (DP) or bubble point (BP) temperature calculation is performed at a low pressure (e.g. 10 bar), that is at "easy" conditions where no convergence problems are expected. Compositions are initialized using Wilson's relation [43] for ideal equilibrium constants. This initial point corresponds to  $\alpha = 1$ . Afterwards, the scaling exponent is decreased. If calculations start from an initial DP,  $\alpha > 0$  on the DP side, the sign changes when the "critical point" is crossed and  $\alpha < 0$  on the BP side of the saturation curve; starting from an initial BP, the opposite sign corresponds to each part of the phase boundary.

The remaining part of the phase envelope can be easily traced starting from the reference point in the opposite direction with  $\alpha > 1$  (i.e., the lower dew point curve at low feed molar density if started from the DP side).

### 3.5. Correction

In the conventional simplified method, Michelsen [32] proposed two procedures to update results if deviations become too large.

The first one is a refinement procedure and it consists in solving a nonlinear system of  $nc+2$  equations using partial Newton iterations (exhibiting linear convergence). This kind of procedure can be readily adapted to the present density-based method, using  $nc+3$  variables (the three variables in the approximate method and  $nc$  logarithms of the equilibrium factors).

The second one (adopted in this work) is a very simple correction procedure that does not require additional calculations. It consists in updating the reference equilibrium constants using information from the last calculated point, according to

$$\ln K_i^* = \frac{1}{\alpha} [\ln \varphi_{iz}(d_z, T) - \ln \varphi_i(d, T, \alpha)] \quad (29)$$

where the fugacity coefficients are  $\varphi_i = f_i / Px_i$  and  $K_i = \varphi_{iz} / \varphi_i$ .

As will be seen later in numerical examples, this very simple correction procedure proves to be very effective in the density-based approach (as also observed in the conventional PT approach [32,33]) and a high accuracy can be obtained even when the approximate method without correction gives important deviations from the exact phase envelope.

### 3.6. Temperature and pressure extrema

The slope of the tangent to the phase boundary at any point can be easily calculated exactly, using only partial derivatives with respect to temperature and molar density. The slope of the tangent to the phase boundary in the d-T plane is

$$\frac{\partial T}{\partial d_z} = - \left( \frac{\partial D}{\partial d_z} \right)_{T,d,\alpha} \left( \frac{\partial D}{\partial T} \right)_{d,d_z,\alpha}^{-1} \quad (30)$$

where  $D = D(d_z, d, T, \alpha)$  and the condition for a temperature extremum in the d-T plane (the cricondentherm or a minimum in temperature as in some open-shaped phase envelopes; a temperature minimum, as well as a second temperature maximum can occur for mixtures with double retrograde behavior) is

$$\left( \frac{\partial D}{\partial d_z} \right)_{T,d,\alpha} = 0 \quad (31)$$

where

$$\left( \frac{\partial D}{\partial d_z} \right)_{T,d,\alpha} = \frac{\partial \Phi_1}{\partial d_z} - \frac{\partial \Phi_3}{\partial d_z} = \frac{1}{d_z} (J_{11} - J_{31}) \quad (32)$$

The pressure corresponding to a temperature extremum in the T-P plane is calculated explicitly from the EoS.

The slope of the tangent to the phase boundary in the T-P plane can be easily calculated using the available partial derivatives from

$$\frac{\partial P}{\partial T} = - \left( \frac{\partial D}{\partial T} \right)_P \left( \frac{\partial D}{\partial P} \right)_T^{-1} \quad (33)$$

The condition of pressure extrema in the T-P plane (the cricondenbar or a minimum in pressure in some open-shaped phase envelopes), that is,  $\partial P / \partial T = 0$ , is

$$\left( \frac{\partial D}{\partial T} \right)_P = 0 \quad (34)$$

where

$$\left( \frac{\partial D}{\partial T} \right)_P = \left( \frac{\partial D}{\partial T} \right)_{d_z,d,\alpha} + \left( \frac{\partial D}{\partial d_z} \right)_{T,d,\alpha} \left( \frac{\partial d_z}{\partial T} \right)_{d,\alpha} \quad (35)$$

and the required partial derivatives are

$$\left( \frac{\partial D}{\partial T} \right)_{d_z,d,\alpha} = \frac{\partial \Phi_1}{\partial T} - \frac{\partial \Phi_3}{\partial T} = \frac{1}{T} (J_{13} - J_{33}) \quad (36)$$

and

$$\left( \frac{\partial d_z}{\partial T} \right)_{d,\alpha} = - \left( \frac{\partial P_z}{\partial T} \right)_{d_z,d,\alpha} \left( \frac{\partial P_z}{\partial d_z} \right)_{T,d,\alpha}^{-1} \quad (37)$$

All the partial derivatives with respect to molar density and temperature required in the extremum criteria are already calculated in the resolution of the nonlinear system, thus the derivatives  $(\partial D / \partial d_z)_{T,d,\alpha}$  and  $(\partial D / \partial T)_P$  can be easily calculated at practically no computational cost at any point on the phase envelope. Any change of sign is recorded, and the approximate location of an extremum is calculated by cubic interpolation using two neighboring points on each side. Note that at the critical point, the numerator of  $\partial T / \partial d_z$  is also zero (for the trivial  $d_i = d_{iz}$ ) but there is no sign change; at the cricondentherm point, the sign changes for nontrivial molar densities.

## 4. Results and discussion

The proposed simplified density-based phase envelope construction method is applied to various hydrocarbon mixtures. Mixture compositions, component properties and non-zero binary interaction parameters (BIPs) are given in the supplementary material. A general form of two-parameter cubic EoS is used, including the Soave-Redlich-Kwong (SRK [39]) EoS and the Peng-Robinson (PR [40,41]) EoS. Exact phase envelopes are (or were already) calculated with the recently proposed density-based method [18].

Calculations are performed starting from both DP and BP initial (reference) points (saturation temperature at a low pressure; the initial pressure is 10 bar in all examples), without and with the simple correction procedure given by Eq. (29).

### 4.1. Usual (closed) phase envelopes

The first mixture is a seven component natural gas containing normal alkanes and nitrogen from Michelsen [14], denoted here M7. Composition, component properties, and non-zero BIPs of N<sub>2</sub> with hydrocarbon components are taken from Ref. [44] and listed in **Table S1**. The SRK EoS is used.

The phase envelopes (without correction) are plotted in **Fig. 1a** (in the d-T plane) and **Fig 1b** (in the T-P plane). At the scale of these figures, there is no distinction between exact and approximate phase boundaries. The exact and approximate (without correction) key points on the phase boundary, that is, critical, cricondentherm and cricondenbar points (obtained starting from both DP and BP reference points), are given In **Table 1**, showing an excellent agreement, as well as a

comparison with Michelsen's results [32] (given in in parenthesis; very small differences may be due to slightly different component properties and/or BIPs).

The second test mixture (denoted MY10) is a ten-component synthetic oil containing normal-alkanes (Metcalf and Yarborough [45]). Mixture composition, component properties and the non-zero BIPs (taken from Hoteit and Firoozabadi [46]) are listed in **Table S2**. The PR EoS is used.

The phase envelopes (without correction) are drawn in **Fig. 2a** (in the d-T plane) and **Fig 2b** (in the T-P plane). The approximate phase boundaries cannot be distinguished from the exact one at the scale of these figures. The critical points (exact and approximate without correction), given in **Table 2**, show a very good agreement for calculations started from both initial points (DP and BP). The deviations in the cricondentherm point temperature are 0.1 K (approximate) and 0.02 K (with correction) and deviations in the cricondenbar point pressure are 0.036 bar (approximate) and 0.015 bar (correction).

The next two mixtures (an oil and a gas-condensate) are taken from Sherafati and Jessen [47] and are denoted here SJ15 Oil and SJ15 GC. Mixture compositions are described with 15 components; component properties and non-zero BIPs can be found from Ref. [47] and are listed in **Table S3**. The SRK EoS is used. The critical points of the two mixtures are listed in **Table 3**, exact and approximate without (A-DP and A-BP) and with correction (AC-DP and AC-BP), starting from both DP and BP reference points. For the gas condensate mixture, he deviations are of about 2 K and 2 bar (A-DP) and of about 5 K and 5 bar (A-BP) for the approximate method; however, the agreement is excellent if the correction is applied.

The phase envelopes of the SJ15 Oil are drawn in **Fig. 3a** (in the d-T plane) and **Fig 3b** (in the T-P plane) and those of the SJ15 gas condensate in **Fig. 4a** (d-T plane) and **Fig 4b** (T-P plane); again, at the scale of the figures no distinction can be observed between exact and approximate phase boundaries for the two reservoir fluids. Michelsen [32] presented an example in which the approximate phase envelope of a heavy oil did not match the exact one at low temperatures (starting from DP). For the SJ15 Oil, at low temperatures, the maximum difference between exact and approximate bubble point pressures at a given temperature (starting from DP) is less than 0.8 bar (without correction) and practically identical (with correction). Note that for the SJ15 gas condensate, the three heaviest pseudo-components are present in trace amounts; it appears that neither the stability of the algorithm (because the phase envelopes are completely smooth) nor the accuracy of the results is affected.



For the SJ15 oil, without correction the cricondenthem (with 0.005 K) and the cricondenbar (with 0.03 bar) are very close to the exact ones and these points are practically identical with correction. For the SJ15 gas condensate, the deviations without correction are also small (of about 0.001 K for the cricondenthem and 0.09 bar for the cricondenbar).

## 4.2. Unusual (open-shaped) phase envelopes

Certain mixtures exhibit an unusual open-shaped phase envelope, with a bubble point branch at low temperatures extending to infinity (a minimum in pressure may exist). The application of the simplified phase envelope construction method to mixtures with an open-shaped phase envelope was not addressed by Michelsen [32]. Obviously, in this case one can easily start calculations only from a DP reference point (there is no low pressure BP temperature for such mixtures).

The Stenby et al. [48] oil mixture (denoted S10) exhibits an open-shape phase envelope with a minimum in pressure at low temperatures in the T-P plane. The mixture has 10 components. Feed compositions, component properties and non-zero BIPs are taken from Ref. [49] and listed in **Table S4**. The PR EoS is used.

The phase envelopes of the S10 Oil are plotted in **Fig. 5a** (in the d-T plane) and **Fig 5b** (in the T-P plane); the phase boundary is accurately reproduced on the dew point side and on a portion beyond the critical point. A detail in the T-P plane (around the pressure minimum) is given in **Fig. 6**, showing some deviations of the approximate method without correction and the excellent agreement with the exact phase boundary if the correction is applied.

The critical points of the S10 oil are listed in **Table 4**. Even without correction, exact and approximate critical points are in very good agreement. The differences in the cricondenthem and cricondenbar points are of 0.005 K and 0.55 bar, respectively (with correction); these points are practically identical with correction.

At about  $T= 236$  K (near the minimum in pressure in the T-P plane) divergence occurs (for  $\alpha=-2.59$ ) and calculations cannot be continued below this temperature, whether the correction is applied or not. A similar behavior of the conventional PT simplified method was reported [32] for a mixture with liquid demixing at low temperatures.

Looking at the dependence of exact equilibrium constants on feed molar density (not shown), it appears that the equilibrium constants along the phase boundary are not monotonic functions of  $d_z$  (exhibiting extrema for all components, between  $d_z=7$  Kmol/m<sup>3</sup> and  $d_z=7.3$  Kmol/m<sup>3</sup>; for some components second extrema occur at higher molar densities); thus, at high  $d_z$ , the scaling of  $K_i$ 's by Eq. (3), giving a monotonic dependence of  $K_i$  on  $\alpha$  (thus on  $d_z$ , which is a monotonic function of  $\alpha$ ), is inadequate in this case.

At the reservoir temperature,  $T=344.23$  K, bubble point pressure differences are of 0.95 bar (without correction) and 0.009 bar (with correction).

Even though the approximate method is unable to represent the branch at low-temperatures and high pressures, a large portion of the phase envelope is reproduced with high accuracy if the correction is applied.

The next mixture, denoted here MF7+ N<sub>2</sub>, taken from Mikyška and Firoozabadi [16], was obtained by combining an oil mixture described with seven components and pseudo-components with nitrogen. Feed compositions, component properties and non-zero BIPs are taken from Ref. [16] and listed in **Table S5**. The PR EoS is used.

The phase envelopes (exact and approximate without and with correction) are plotted in **Fig. 7a** (in the d-T plane) and **Fig 7b** (in the T-P plane). Significant deviations from the exact phase boundary are observed for the approximate method without correction. However, if the correction is applied, an excellent agreement is observed along the entire phase envelope, up to very high pressures (at  $\alpha=-0.329$  and  $P=5561$  bar, the difference in bubble point temperatures is less than 0.1 K). A detail of the phase boundaries around the critical region in the T-P plane is given in **Fig. 8**.

The critical points (exact and approximate without/with correction) are listed in **Table 5**. Significant deviations of the approximate critical point are observed (about 25 K and 55 bar) without correction; there is an excellent agreement if the correction is applied (the differences are 0.01 K and 0.02 bar). The approximate and exact cricondentherm points differ by only 0.03 K and are practically identical with correction.

The last mixture examined here (denoted LF12) is a North Sea (Lille Frigg field) gas-condensate fluid [50]. Mixture composition described by 12 components (5 individual components and 7 pseudo-components), as well as component properties and non-zero BIPs taken from Ref. [49]

and listed in **Table S6**. This mixture exhibits an open-shaped phase envelope (confirmed by experimental data [50]) with no critical point. The PR EoS is used.

The phase envelopes (exact and approximate without and with correction) are plotted in **Fig. 9a** (in the d-T plane) and **Fig 9b** (in the T-P plane). The difference in cricondentherm point temperatures is 0.005 K (without correction). Divergence occurs for this mixture at  $T=279$  K (without correction) and  $T=321$  K (with correction) and calculations cannot be continued below these temperatures. For this kind of mixture, equilibrium constants do not all tend to unity and  $\alpha$  remains positive along the phase envelope; the dependence of  $K_i$  vs.  $d_z$  (not shown) exhibit extrema for all components except nitrogen. While without correction important deviations are observed, the phase envelope is reasonably reproduced down to the temperature of the divergence point if the correction is applied (dew point pressure differences are not exceeding 1 bar above 335 K, for pressures up to 650 bar).

At the reservoir temperature,  $T=398.15$  K, the differences in dew point pressures with and without correction are 0.0015 bar and 22.3 bar, respectively. At a lower temperature,  $T=340$  K, the differences between exact and approximate dew point pressures are 0.55 bar with correction and 67 bar without correction.

As mentioned before, for binary mixtures, the results of the density-based approximate method are exact (as in the conventional approach). Moreover, in the binary case the number of variables is the same (three) for both exact [18] and proposed approximate methods; there is still an advantage of the simplified method, that is, the partial derivatives of fugacity with respect to mole numbers are not required. The simplified method was also tested for all binary mixtures from Ref. [18], including the  $C_1$ - $nC_4$  mixture (exhibiting double retrograde behavior) and the  $C_1$ -He mixture (with a very sharp shape in the T-P plane).

In all test examples, it is remarkable how the entire phase envelope (for closed envelopes), or at least a major part of it (for open-shaped envelopes), is reproduced with a high accuracy by solving only a [3×3] reduced system of equations and using a very simple scaling law to relate equilibrium constants at any point on the phase boundary with exact equilibrium constants calculated at some reference conditions.

The limitations of the proposed method are the same as in conventional PT Michelsen's formulation, that is, for mixtures with no critical point, mixtures with multiple critical points and mixtures with complex phase envelopes (such as envelopes exhibiting a swallowtail pattern at low temperatures) [32]; however, it was shown here that even for mixtures with no critical point, a large

part of the phase boundary (that of interest in reservoir engineering problems) can be accurately reproduced. The simplified method also fails to trace the entire phase boundary down to low temperatures for certain mixtures with open-shaped phase envelopes (e.g. mixture S10). For all these situations, the scaling relation for equilibrium constants is not adequate on the entire molar density-temperature range (as discussed for two test examples).

The results of the simplified approximate method can be seen as excellent initial guesses for exact saturation point calculations at specific points on the phase envelope; the convergence requires only a few iterations. The proposed method is recommended for mixtures with many components (as for instance hydrocarbon reservoir fluids with a detailed composition or mixed feeds with hundreds of components in refining and processing) since the dimension of the system of equations is reduced to three, irrespective of the number of components and the resolution of large systems is avoided. A general form of two-parameter cubic EoS was used in this work, but the calculation framework is not model-dependent. The simplified density-based approach may be attractive for complex EoS, for which root finding and root selection procedures can be problematic and partial derivatives can be difficult to obtain.

## 5. Conclusions

A new simple approximate density-based method is proposed for phase envelope construction of constant composition complex multicomponent mixtures, which can be seen as a density-based counterpart of Michelsen's conventional PT approximate method.

At any individual point on the phase boundary, equilibrium constants are related via a simple scaling equation to those calculated at some reference conditions. To calculate saturation points, a [3×3] reduced system of three equations must be solved for only three variables (molar densities of feed and incipient phase and temperature), irrespective of the number of components in the mixture. The specification is always the scaling factor of equilibrium constants along the phase boundary.

The EoS must not be solved for volume and the elements of the Jacobian matrix have simple forms (simpler than in the conventional PT approach and in the full density based approach); moreover, the partial derivatives of fugacity with respect to mole numbers are not required. Simple equations for calculation of maximum temperature and pressure points are presented.

Since the approximate method may introduce in some cases noticeable deviations from the exact phase boundaries for certain mixtures, a simple and computationally inexpensive correction procedure highly improves the accuracy of the method.

For open-shaped phase envelopes, the approximate method either fails or is not accurate at low temperatures (without correction), but a large portion of the envelope is very well reproduced if the correction procedure is applied. However, for certain open-shaped phase envelopes, the entire saturation curve is reproduced up to very high pressures.

For all test examples, it is remarkable how the entire phase envelope is reproduced with a high accuracy starting from exact calculations at a single point and using a simple scaling of equilibrium constants and a simple correction procedure. The simplified approximate density-based method is easy to implement and may be useful for fast generation of phase envelopes for mixtures with many components (it avoids the resolution of large linear systems) or for complex thermodynamic models.

## List of symbols

$D$	TPD function in terms of molar densities
$d$	mixture molar density (incipient phase)
$d_z$	mixture molar density (feed)
$d_i$	molar density of component $i$ (incipient phase)
$d_{iz}$	molar density of component $i$ (feed)
$F$	feed mole numbers
$f_i$	fugacity of component $i$
$h_i$	given by Eq. (2)
<b>J</b>	Jacobian matrix
$K_i$	equilibrium constants
$nc$	number of components
$n_i$	mole numbers of component $i$ (incipient phase)
$n_{iz}$	mole numbers of component $i$ (feed)
$P$	pressure
$R$	universal gas constant
$T$	temperature
$V$	volume
$v$	molar volume
$x_i$	mole fraction of component $i$ in the trial phase
$Y_i$	mole numbers of component $i$ in the trial phase
$z_i$	feed composition

## Greek letters

$\alpha$	scaling exponent of equilibrium constants
$\phi_i$	fugacity coefficient of component $i$
$\xi_i$	independent variables
$\Phi_i$	residual

## Subscripts

$i, j$	component index
$c$	critical
$spec$	specification
$z$	feed

## Superscripts

$T$	transposed
*	reference conditions

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**Table 1 Key points on phase boundary for M7 mixture (SRK EoS)**

Point on phase boundary	T/P	Exact		Approx.-DP		Approx.-BP	
Critical	T (K)	203.0	(203.1)	203.40	(203.6)	202.75	(202.9)
	P (bar)	58.84	(58.87)	59.32	(59.48)	58.47	(58.57)
Cricondentherm	T (K)	260.61	(260.3)	260.61	(260.3)	260.56	(260.1)
	P (bar)	38.80	(38.71)	38.80	(38.60)	38.76	(38.60)
Cricondenbar	T (K)	233.65	(233.4)	233.60	(233.3)	233.68	(233.6)
	P (bar)	82.71	(82.17)	82.70	(82.17)	82.60	(81.97)

**Table 2 Critical points for MY10 mixture (PR EoS)**

Critical point	Exact	A-DP	AC-DP	A-BP	AC-BP
T <sub>c</sub> (K)	570.96	570.54	570.88	569.24	570.99
P <sub>c</sub> (bar)	79.89	79.91	79.84	79.86	79.86
d <sub>c</sub> (Kmol/m <sup>3</sup> )	2.715	2.723	2.715	2.732	2.714

**Table 3 Critical points for SJ15 mixtures (SRK EoS)**

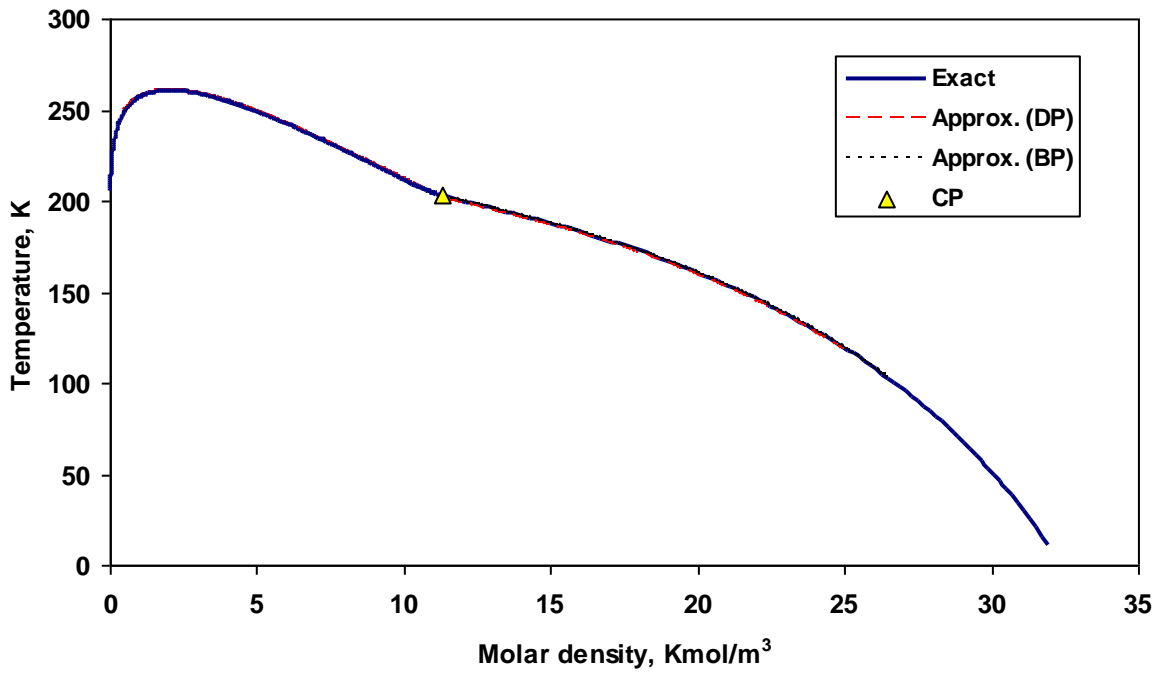
Mixture	Critical point	Exact	A-DP	AC-DP	A-BP	AC-BP
SJ15 Oil	T <sub>c</sub> (K)	721.15	719.25	721.34	720.83	721.21
	P <sub>c</sub> (bar)	114.67	115.35	114.68	114.51	114.67
	d <sub>c</sub> (Kmol/m <sup>3</sup> )	2.248	2.271	2.248	2.252	2.251
SJ15 GC	T <sub>c</sub> (K)	239.46	241.28	239.56	236.58	239.62
	P <sub>c</sub> (bar)	105.35	107.54	105.26	100.58	105.31
	d <sub>c</sub> (Kmol/m <sup>3</sup> )	13.423	13.310	13.429	13.625	13.425

**Table 4 Critical points for S10 mixture (PR EoS)**

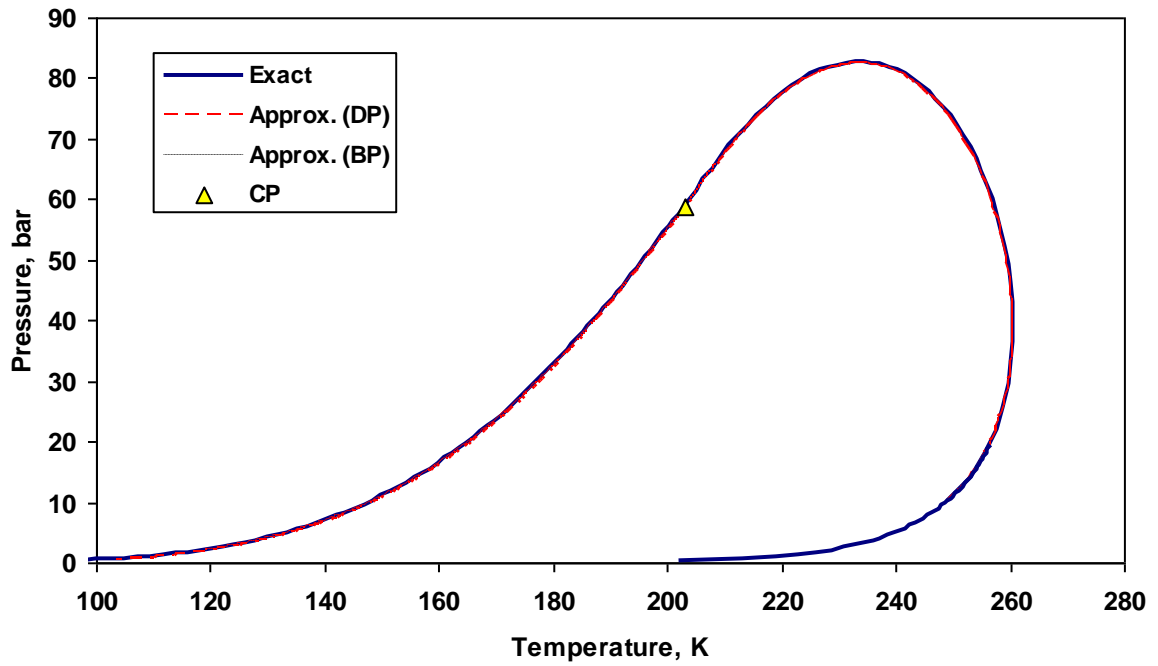
Critical point	Exact	A-DP	AC-DP
T <sub>c</sub> (K)	712.21	712.72	712.35
P <sub>c</sub> (bar)	147.96	147.29	147.96
d <sub>c</sub> (Kmol/m <sup>3</sup> )	2.912	2.898	2.912

**Table 5 Critical points for MF7-N<sub>2</sub> mixture (PR EoS)**

Critical point	Exact	A-DP	AC-DP
T <sub>c</sub> (K)	419.67	395.10	419.68
P <sub>c</sub> (bar)	705.44	760.12	705.46
d <sub>c</sub> (Kmol/m <sup>3</sup> )	12.620	13.462	12.614

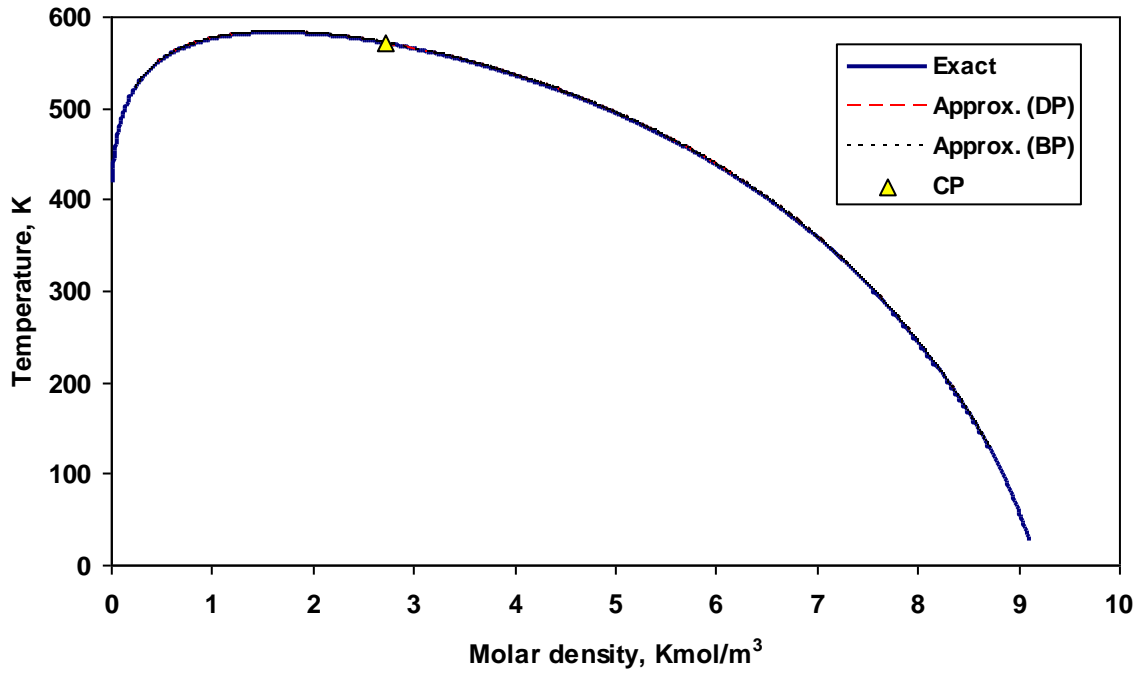


(a)

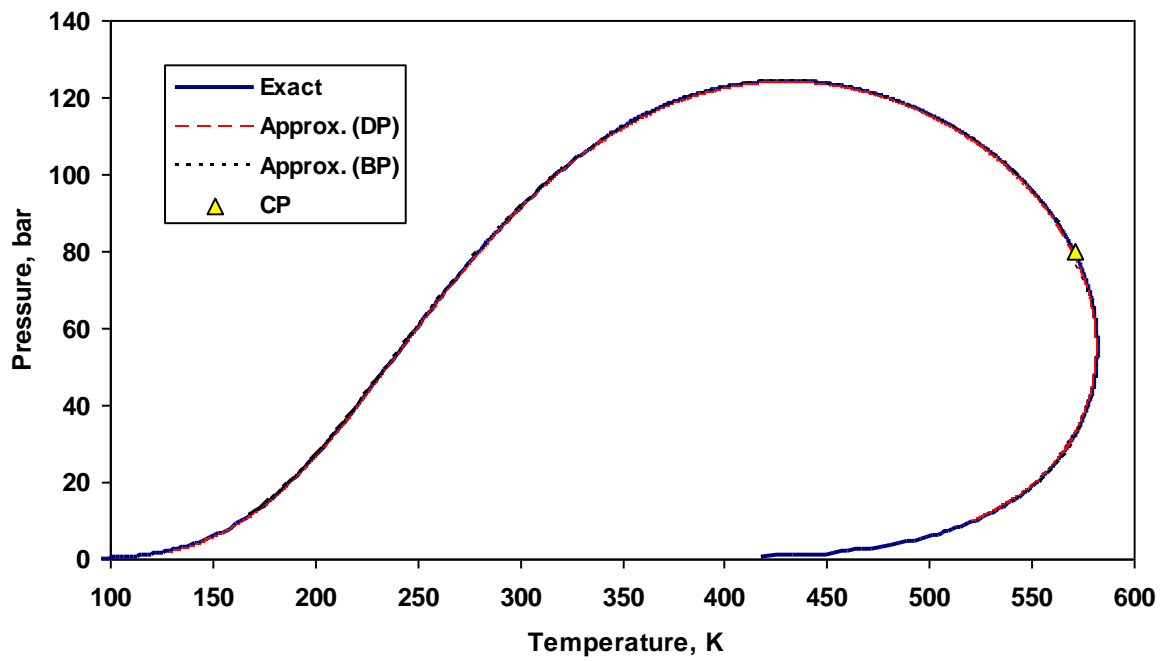


(b)

Fig. 1 Phase envelopes of M7 mixture. (a) T-d plane; (b) T-P plane

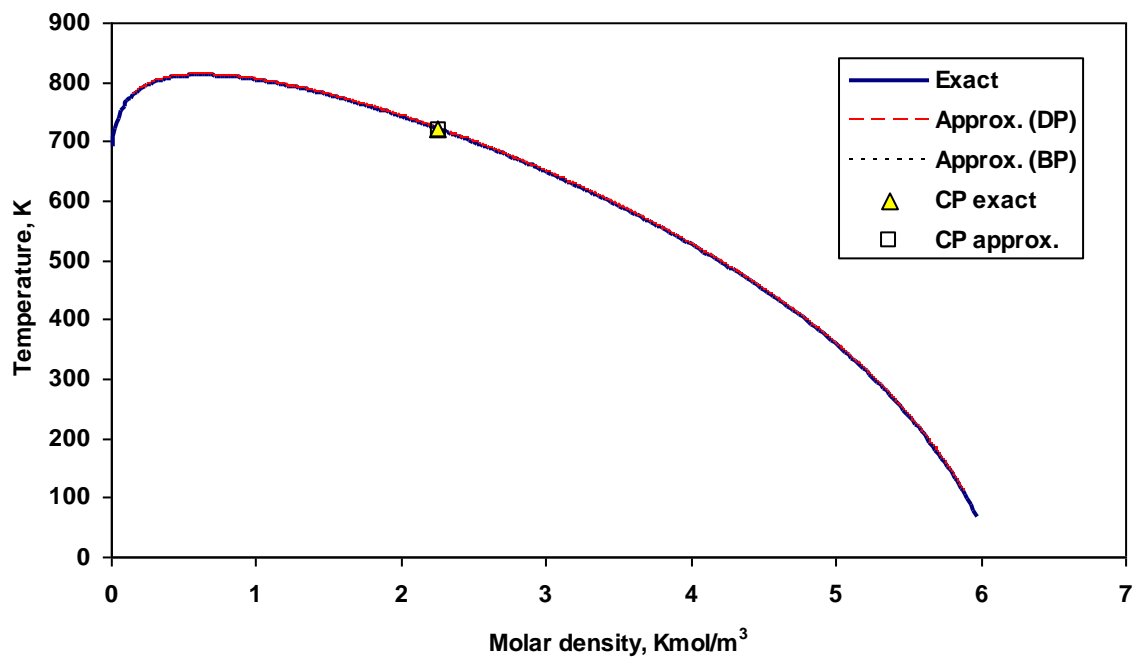


(a)

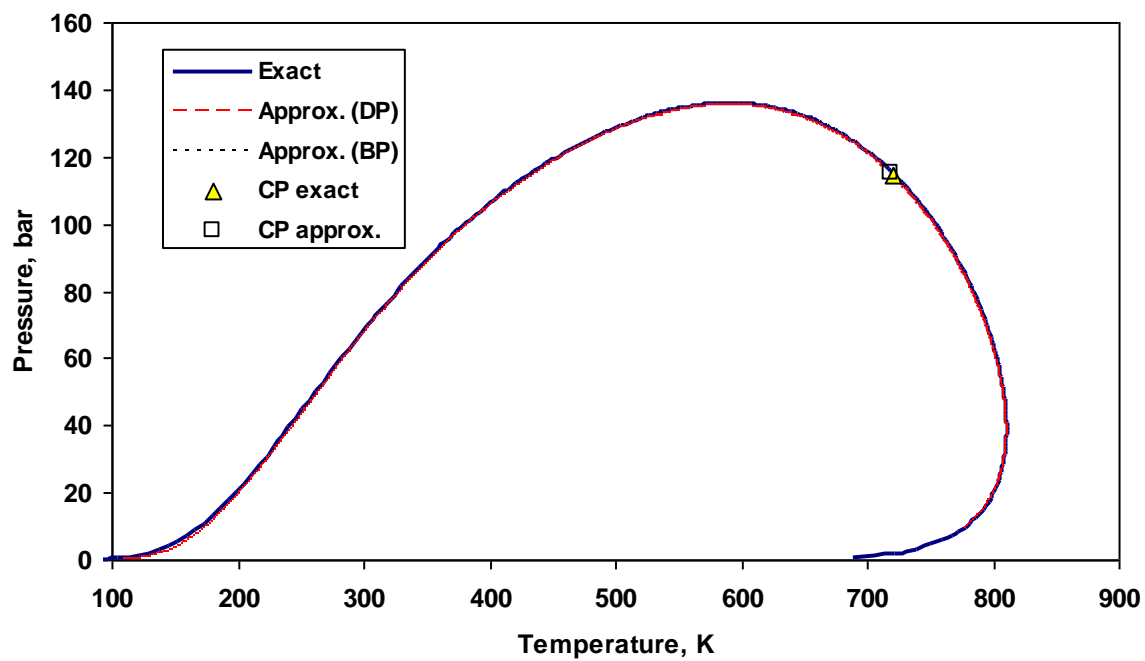


(b)

Fig. 2 Phase envelopes of MY10 mixture. (a) T-d plane; (b) T-P plane

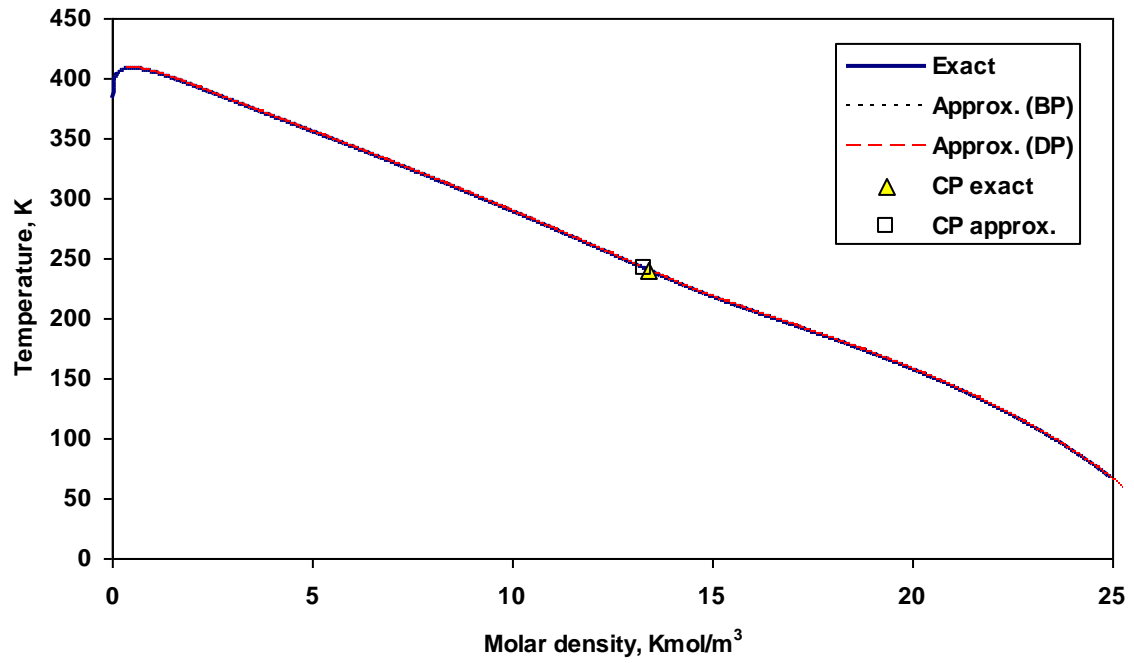


(a)

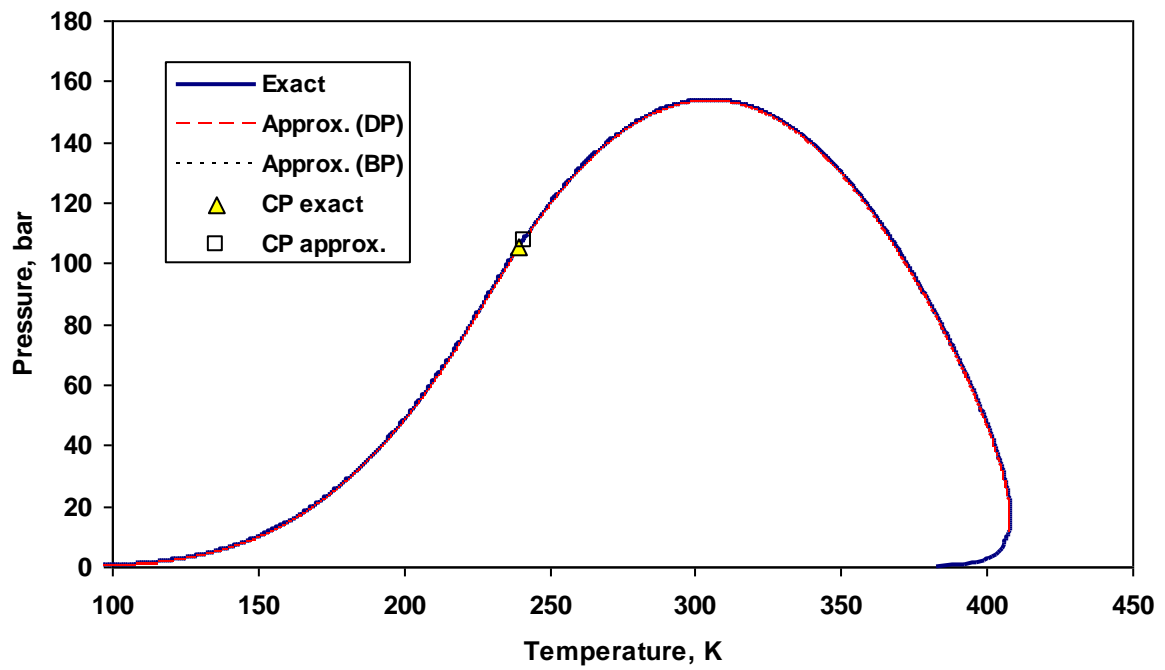


(b)

Fig. 3 Phase envelopes of SJ15 Oil. (a) T-d plane; (b) T-P plane



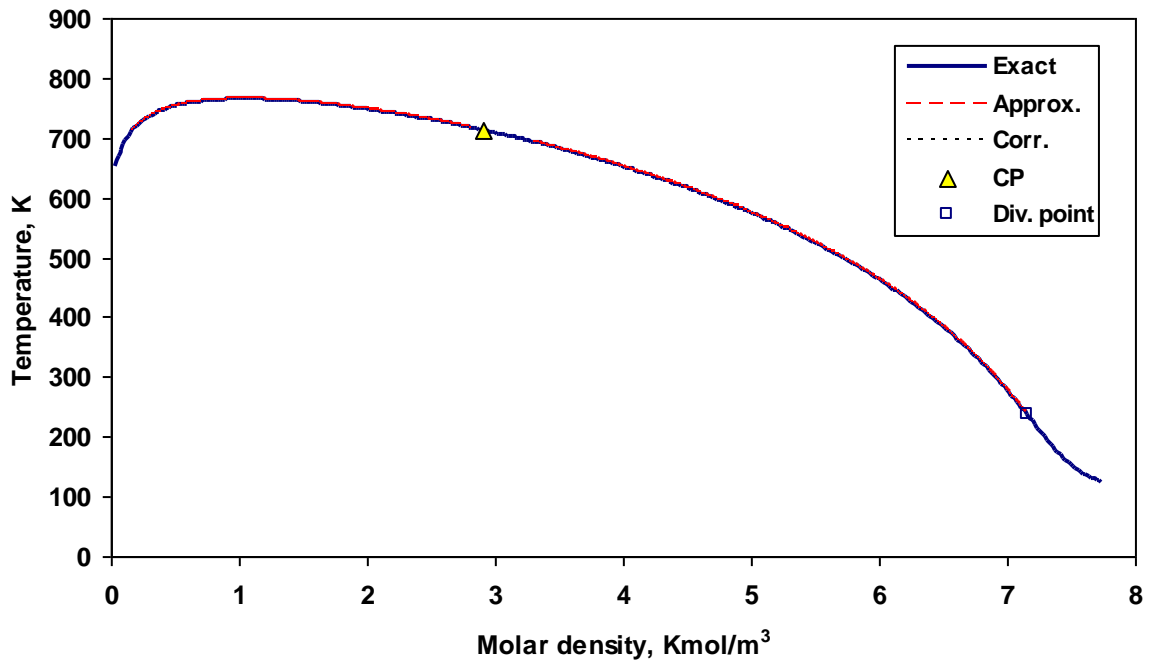
(a)



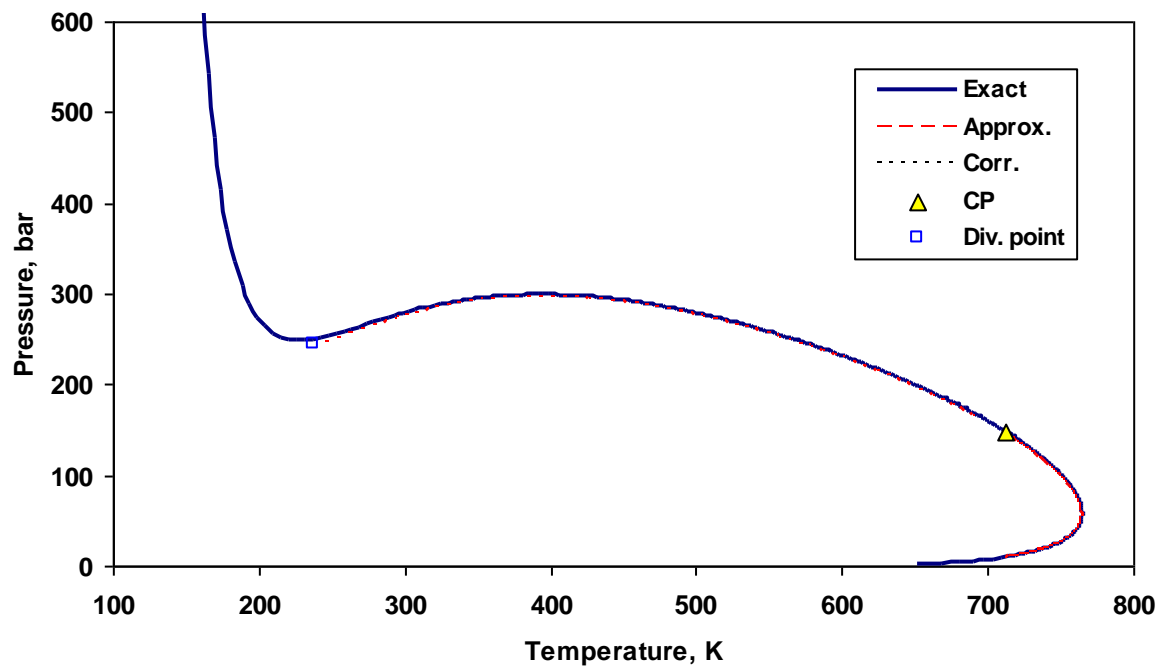
(b)

Fig. 4 Phase envelopes of SJ15 Gas condensate. (a) T-d plane; (b) T-P plane





(a)



(b)

Fig. 5 Phase envelopes of S10 Oil. (a) T-d plane; (b) T-P plane

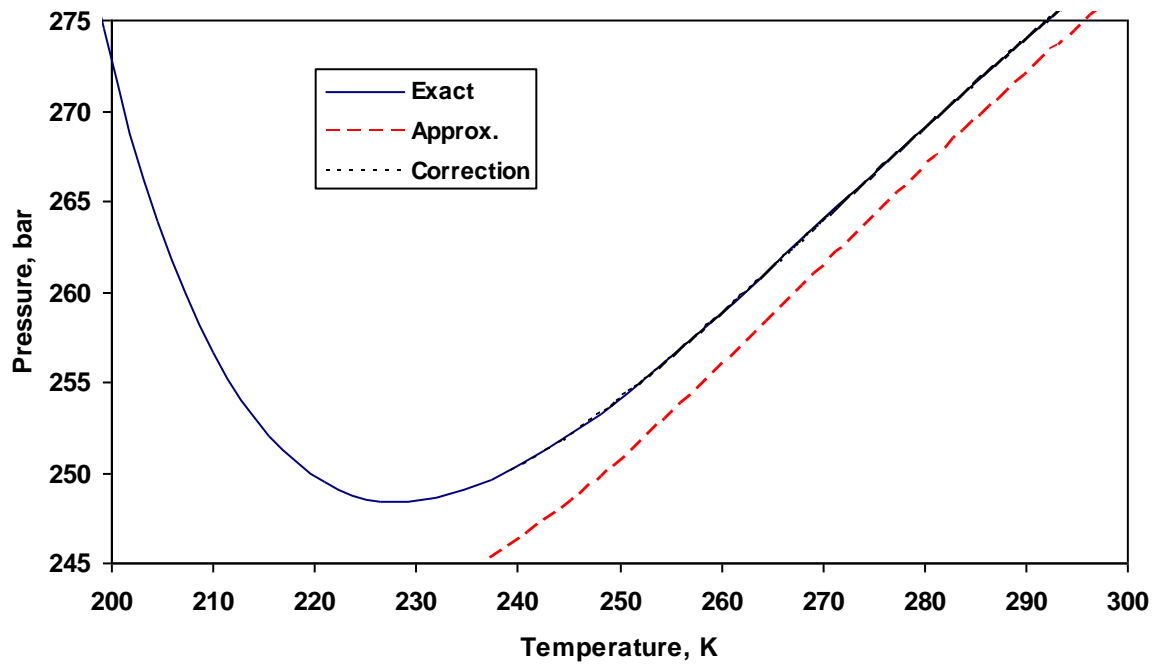
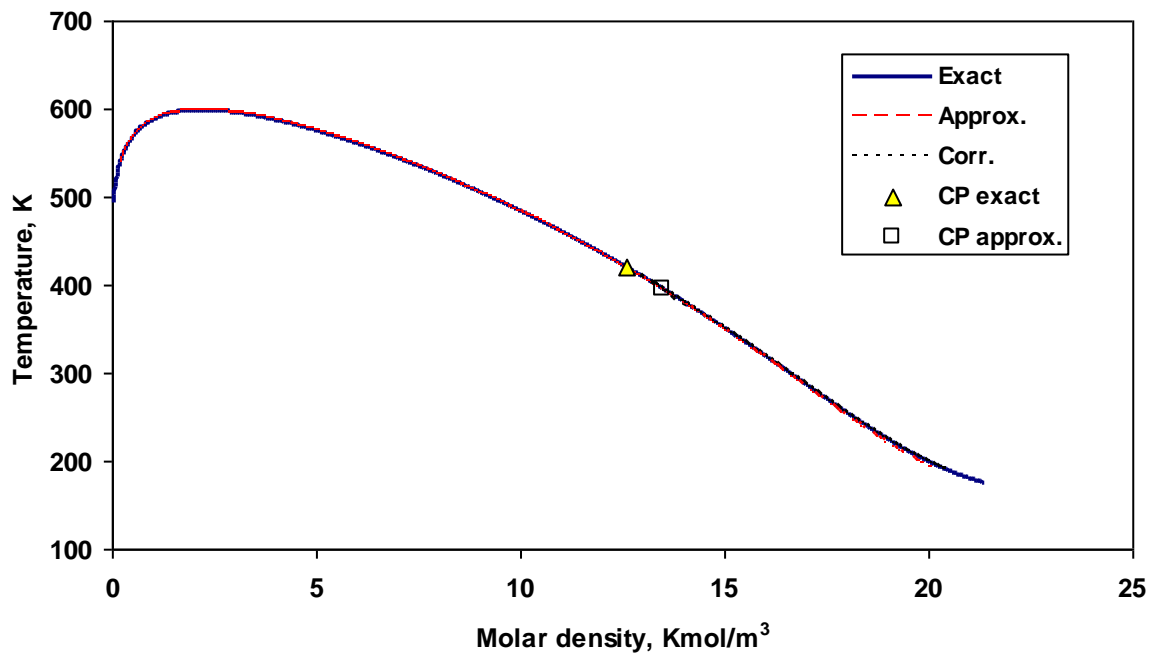
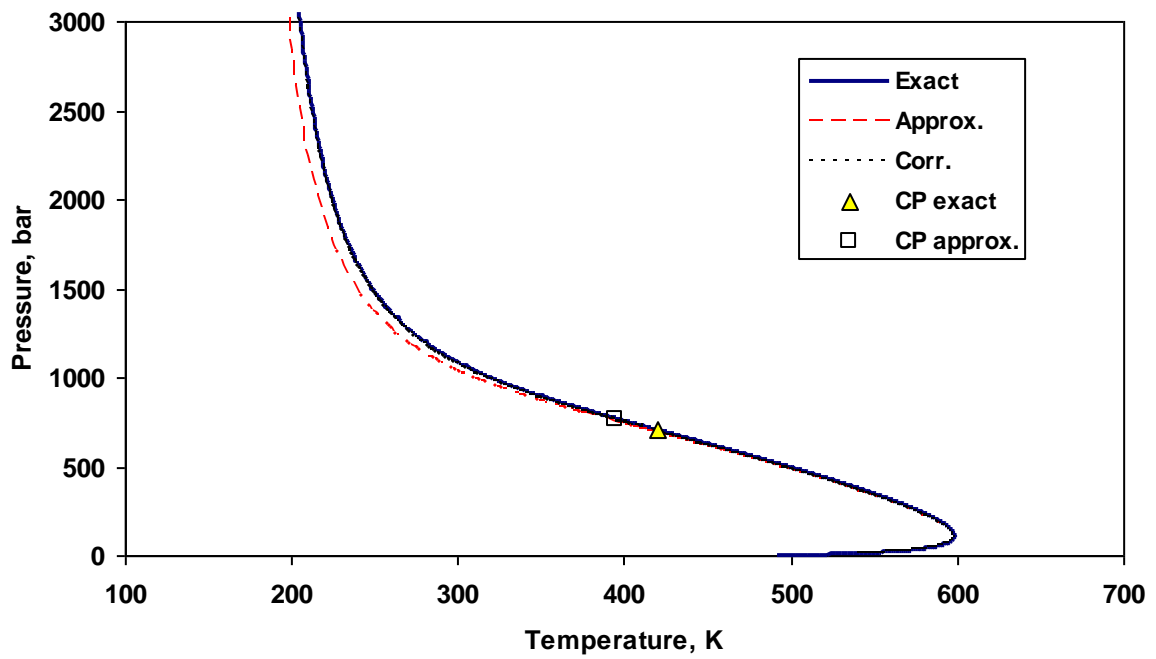


Fig. 6 Phase envelopes of S10 Oil in the T-P plane (detail)



(a)



(b)

Fig. 7 Phase envelopes of MF7 Oil+N<sub>2</sub>. (a) T-d plane; (b) T-P plane

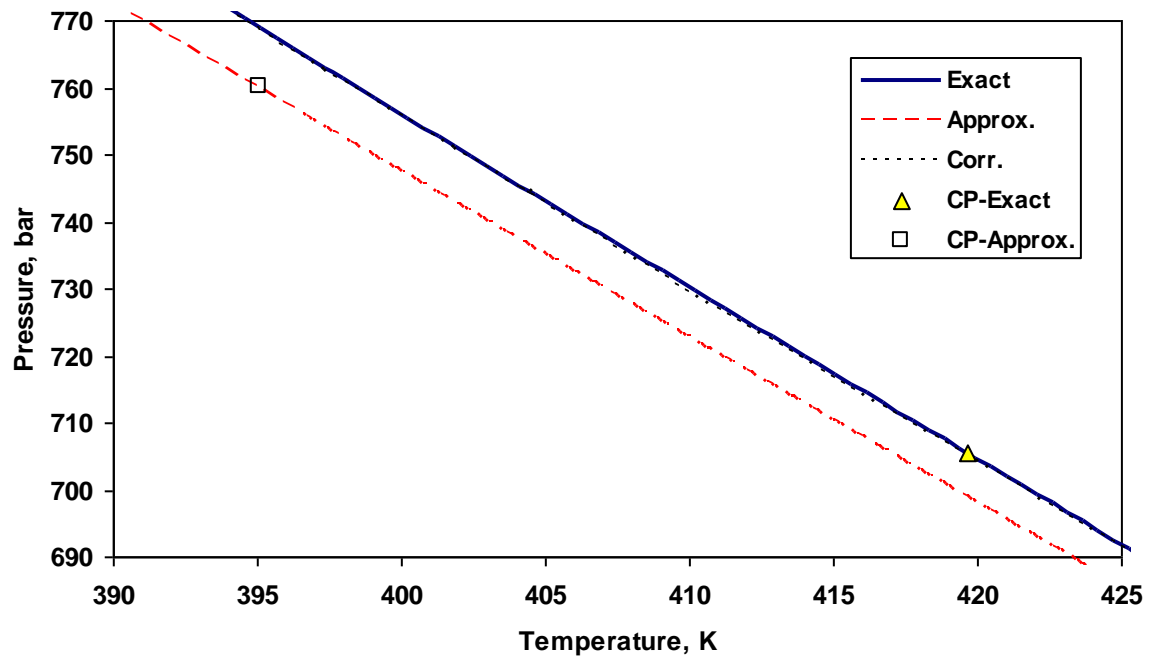
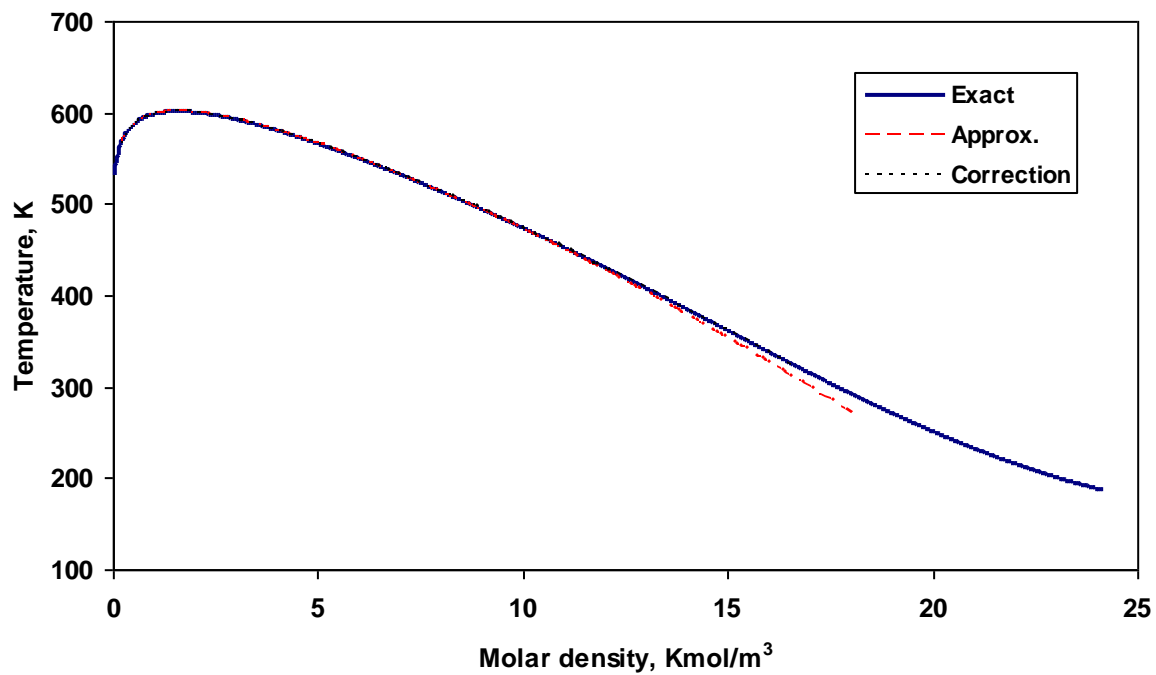
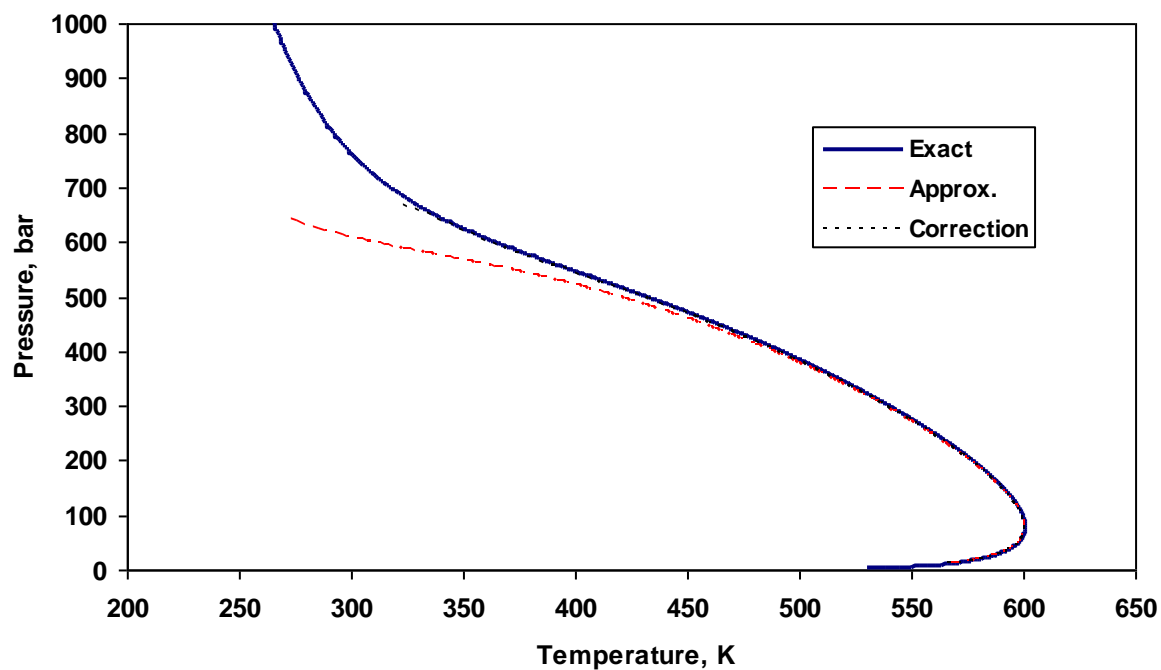


Fig. 8 Phase envelopes of MF7 Oil+N2 in the T-P plane (detail)



(a)



(b)

Fig. 9 Phase envelopes of LF12 gas condensate. (a) T-d plane; (b) T-P plane