An isomorphic Peng–Robinson equation for phase-equilibria properties of hydrocarbon mixtures in the critical region

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Abstract

The principle of isomorphism of critical phenomena asserts that the equation of state of fluid mixtures in the critical region has the same form as that of the pure components, provided that the mixture is not considered at a fixed composition but at a fixed value of a constant field variable related to the chemical potentials of the components of the mixtures. This principle has been successfully applied by various investigators to formulate nonclassical equations of state for fluid mixtures in the critical region. In this paper we show how the same principle can be applied to simple classical equations of state using the Peng–Robinson equation as a representative example. The isomorphic Peng–Robinson equation thus obtained is applied to represent phase equilibria properties of some binary mixtures of methane, butane and decane.

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1. Introduction

After more than a century since van der Waals extended his famous equation of state to the description of binary and ternary fluid mixtures [1,2], his ideas have remained an important guidance for modeling vapor–liquid equilibria. Cubic and generalized van der Waals equations are still widely used in practice [3–7]. An example of a popular cubic equation is the Peng–Robinson equation [8] often used in industry, especially for refinery and reservoir simulations. Fluid phase behavior in the near-critical region is of key importance in many process technologies at high pressures, such as supercritical fluid extraction, exploitation of rich gas condensate/volatile oil reservoirs, and gas-injected enhanced oil recovery.

However, there are two problems with the application of classical equations of state to characterize the thermodynamic properties of fluids and fluid mixtures near critical points. The first well-known problem is that classical equations neglect density fluctuations which become large near the critical point. A second and perhaps even more conceptual problem is encountered when such classical equations are used for mixtures near critical points. When a mixture with a fixed composition is represented by a classical equation, the critical point of the classical equation is located at the top of the coexistence curve implied by the classical equation, while in reality the critical point is no longer located at the top of the dew–bubble curve. As a result, the critical point of the classical equation no longer corresponds to a real critical point but becomes a pseudocritical point. It is the latter issue that will be addressed in the present publication.

Van der Waals understood this problem and saw the solution in the extension of the modern theory of critical phenomena to mixtures which need to be reformulated upon the increase of number of thermodynamic variables [9]. In fact, the extension of the modern theory of critical phenomena to mixtures is based on a principle of isomorphism of critical phenomena [10–13] which utilizes the van der Waals formulation of stability conditions. This principle asserts that the equation of state of a mixture in the critical region is isomorphic to that of a one-component fluid provided that the mixture is not considered at a fixed composition, but at a fixed value of a suitable chosen field variable. For binary mixtures with a simple phase diagram in which the critical points of the two components are connected by a continuous critical locus, an appropriate field variable ζ is commonly taken to be a function of the chemical potentials μ1 and μ2 of the two components [14–16]:

\[
ζ = \frac{1}{1 + \exp[(μ_1 - μ_2)/RT]}
\]

where T is the temperature and R is the universal molar gas constant. The advantage of the definition of the field variable is that...
0 ≤ ζ ≤ 1, where the values ζ = 0 and ζ = 1 correspond to the pure components.

To illustrate the principle of isomorphism of critical behavior we show in Fig. 1 phase boundaries for mixtures of methane and ethane in the critical region calculated from a scaled equation of state developed by Povodyrev et al. [17,18]. The dashed curves represent vapor–liquid phase boundaries of the mixtures at various values of the field variable ζ, with the coexistence curves of pure methane (ζ = 0) and of pure ethane (ζ = 1), which represent the mole fraction of ethane. The solid curve in Fig. 1 represents the phase boundary of the equimolar mixture (x = 0.5), commonly referred to as a dew–bubble curve [16]. While the coexistence curves at constant ζ are all similar to the coexistence curves of the pure components (ζ = 0 and ζ = 1), the dew–bubble curve is qualitatively different from the coexistence curves of the pure components. While the classical one-fluid model, which assumes that the mixture at fixed composition can be described by an equation of state similar to that of a one-component fluid, breaks down in the critical region, the one-fluid model is valid when considered at constant ζ.

Many investigators have applied the principle of isomorphism of critical phenomena to characterize thermodynamic properties of fluid mixtures in the critical region in the context of nonanalytical equations of state [16,19–49]. However, the principle of isomorphism of critical behavior should also be applicable to classical equations of state. Hence, it is of interest to investigate whether application of the isomorphism principle to simple cubic equations will lead to an improved capability of such equations for representing the thermodynamic properties of fluid mixtures in the critical region. We shall do this by adopting the classical Peng–Robinson (PR) equation as an example. An earlier attempt towards a similar goal was made by Fox and Storvick [50–52].

We shall proceed as follows. In Section 2 we consider the classical PR equation and the corresponding Helmholtz energy for one-component fluids made dimensionless in a form suitable for our analysis. We shall then formulate a corresponding isomorphic Helmholtz energy for fluid mixtures in Section 3. In Section 4 we consider a so-called critical-line condition to simplify the relationship between the isomorphic field variable ζ and the concentration of the mixture. In Section 5 we then apply the isomorphic PR equation to some mixtures of alkanes in the critical region. Concluding remarks are presented in Section 6.

2. Peng–Robinson equation for pure fluids

The original PR equation for the pressure P has the following form in terms of the molar density ρ:

\[ P = \frac{RT\rho}{1-b\rho} - \frac{a(T)\rho^2}{1+b\rho+br(T)\rho(1-b\rho)}. \]  (2)

The system-dependent parameters \( a(T) \) and \( b \) are given by [8]:

\[ a(T) = 0.45724 \frac{[1+k(1-T_{c}/T)^{0.5}]}{T_{c}} \frac{R^2 T_c^2}{P_c}, \]  (3)
\[ b = \frac{0.0778RT_c}{P_c}, \]  (4)
\[ k = 0.37464 + 1.54226\omega - 0.26992\omega^2, \]  (5)

where \( T_c = T/T_c \) is a reduced temperature, \( \omega \) the acentric factor and where \( T_c \) and \( P_c \) are the critical temperature and pressure, respectively. Eq. (2) yields for the compression factor at the critical point:

\[ Z_0 = \frac{P_c}{RT_c\rho_0} = 0.30745. \]  (6)

In the classical PR equation one conventionally adopts an incorrect classical critical density \( \rho_0 = P_c/RT_cZ_0 \) which differs from the actual experimentally observed value of the critical density \( \rho_c \).

Expressing the critical parameters through the coefficients \( a = a(T_c) \) and \( b \) one obtains:

\[ T_c = 0.17015 \frac{a}{R}, \quad P_c = 0.01324 \frac{a}{T_c}, \quad \rho_0 = 0.25305 \frac{1}{b}. \]  (7)

All thermodynamic properties and the system-dependent parameters can be made dimensionless with the aid of the critical parameters [53]:

\[ \hat{\rho} = \frac{\rho}{\rho_0}, \quad \hat{T} = -\frac{T_c}{T}, \quad \hat{p} = \frac{P_c T_c}{P_c T}, \quad \hat{\mu} = \frac{\rho_0 T_c \mu}{P_c T}, \quad \hat{b} = b\rho_0, \]
\[ \hat{\alpha} = \frac{a\rho_0}{RT_c}. \]  (8)

In terms of dimensionless variables, the PR equation becomes:

\[ \hat{p}(\hat{\rho}, \hat{T}) = \frac{1}{Z_0} \left[ \frac{\hat{\rho}}{1-b\hat{\rho}} - \left( \frac{\hat{\alpha}(\hat{T})\hat{\rho}^2}{1+(2\hat{b} - \hat{b}\hat{\rho})^2} \right) \right], \]  (9)

where the temperature-dependent function \( \hat{\alpha}(\hat{T}) \) is:

\[ \hat{\alpha}(\hat{T}) = -Z_1 \hat{T} \left[ 1 + k \left( 1 - \left( \frac{1}{\hat{T}} \right)^{0.5} \right) \right]^2, \]  (10)

with:

\[ Z_1 = \frac{0.45724}{Z_0} = 1.4874, \]  (11)

and:

\[ \hat{b} = \frac{0.0778}{Z_0} = 0.25308. \]  (12)

An equation of state does not specify uniquely the temperature dependence of caloric properties like the specific heat capacities. In the theory of critical phenomena it is advantageous to consider the Helmholtz–energy density, i.e., the molar Helmholtz energy \( A \) divided by the molar volume \( V \) [54]. The reduced Helmholtz–energy density \( \bar{A} = \rho \bar{A}_c/T \) is related to the pressure, density and chemical potential by:

\[ \bar{A} = -\bar{p} + \bar{\rho} \bar{\mu}. \]  (13)
and it satisfies a differential relation of the form:
\[
d\tilde{A} = -\tilde{U}d\tilde{T} + \tilde{\mu}d\tilde{\rho},
\]
where \(\tilde{U} = \rho U_\text{Pi}\) is the reduced energy density \([55, 56]\). Since:
\[
\tilde{\chi} = \left(\frac{\partial \tilde{\chi}}{\partial \tilde{T}}\right)_\tilde{\rho} = \left(\frac{\partial \tilde{\chi}}{\partial \tilde{\rho}}\right)_\tilde{T},
\]
it follows that the chemical potential \(\tilde{\chi}\) can be obtained by integrating the equation of state for \(P(\tilde{\rho}, \tilde{T})\):
\[
\tilde{\chi} = \int \tilde{\rho} \left(\frac{\partial \tilde{\chi}}{\partial \tilde{\rho}}\right)_\tilde{T} d\tilde{\rho}.
\]
We thus obtain for the Helmholtz-energy density associated with the PR equation:
\[
\tilde{\chi}(\tilde{\rho}, \tilde{T}) = \tilde{\rho} \ln \left(\frac{\tilde{\rho}}{\tilde{\rho}_0}\right) + \tilde{\rho}_0 \tilde{\chi}_\text{deg} + \tilde{\chi} \tilde{\rho}^2.
\]
The function \(\tilde{\chi}_\text{deg}(\tilde{T})\) in Eq. (17) arises from the integration constant in Eq. (16). It is not specified by the PR equation, but it does yield a temperature-dependent contribution to the specific heat capacities independent of the density. In practice, one represents \(\tilde{\chi}_\text{deg}(\tilde{T})\) by a truncated Taylor series expansion around the critical temperature in terms of \(\Delta T = (T - T_c)/T_c\):
\[
\tilde{\chi}_\text{deg}(\Delta T) = \tilde{\rho}_0^2 \tilde{\chi}_\text{deg} + \tilde{\rho}_0 \Delta \tilde{T} + \ldots.
\]
The first two coefficients, \(\tilde{\chi}_\text{deg}^0\) and \(\tilde{\chi}_\text{deg}^1\), in this expansion determine the zero points of entropy and energy. Hence, they do not affect the calculation of any of the thermodynamic properties and they can be given arbitrary values for one-component fluids.

It is convenient to separate the Helmholtz-energy density into a critical contribution \(\Delta \tilde{A}\) and a regular background contribution \(\tilde{A}_\text{deg}\) \([55]\):
\[
\tilde{A} = \Delta \tilde{A} + \tilde{A}_\text{deg}
\]
with:
\[
\tilde{A}_\text{deg} = -\tilde{P}_0(\tilde{T}) + \tilde{\mu}_0(\tilde{T}),
\]
where \(\tilde{P}_0(\tilde{T})\) and \(\tilde{\mu}_0(\tilde{T})\) represent the pressure \(\tilde{P}\) and the chemical potential \(\tilde{\mu}\) at the critical density \(\tilde{\rho} = \tilde{\rho}_0\). The contribution \(\Delta \tilde{A}\) is defined so as to satisfy the following two conditions: first, \(\Delta \tilde{A} = 0\) at the critical point and, second, \(\chi^{-1} = (\tilde{\rho}^2 \Delta \tilde{A}/\tilde{\rho}^2)^2\), since \(\chi\) is the physical quantity directly related to the strength of the critical fluctuations \([54]\). From Eqs. (9), (16) and (17) we find:
\[
\tilde{P}_0(\tilde{T}) = \frac{1}{Z_0} \left[ \frac{\tilde{a}(\tilde{T})}{1 - b} - \frac{\tilde{a}(\tilde{T})}{1 + 2b - b^2} \right],
\]
and:
\[
\tilde{\mu}_0(\tilde{T}) = \Delta \tilde{\mu}_0(\tilde{T}) + \tilde{\mu}_0^0(\tilde{T}),
\]
with:
\[
\Delta \tilde{\mu}_0(\tilde{T}) = \tilde{P}_0(\tilde{T}) + \frac{1}{Z_0} \left[ -\ln(1 - b) + \frac{\tilde{a}(\tilde{T})}{\sqrt{2b}} \arctan \frac{\sqrt{\frac{b}{2}}}{\sqrt{2}} \right].
\]
We note that \(\tilde{P}(\tilde{\rho}, \tilde{T})\), \(\tilde{P}_0(\tilde{T})\) and \(\Delta \tilde{\mu}_0(\tilde{T})\) only depend on temperature through \(\tilde{a}(\tilde{T})\). If we expand \(\tilde{P}_0(\tilde{T})\) and \(\Delta \tilde{\mu}_0(\tilde{T})\) around the critical temperature in terms of \(\Delta T\) we obtain:
\[
\tilde{P}_0(\tilde{T}) = \tilde{P}_{00} + \tilde{P}_{01} \Delta T,
\]
\[
\Delta \tilde{\mu}_0(\tilde{T}) = \tilde{\mu}_{00} + \tilde{\mu}_{01} \Delta T,
\]
with:
\[
\tilde{P}_{00} = 1,
\]
\[
\tilde{P}_{01} = \frac{Z_1(1 + k)}{Z_0(1 + 2b - b^2)},
\]
\[
\tilde{\mu}_{00} = 1 + \frac{1}{Z_0} \left[ -\ln(1 - b) + \frac{Z_1}{\sqrt{2b}} \arctanh \frac{\sqrt{\frac{b}{2}}}{\sqrt{2}} \right],
\]
\[
\tilde{\mu}_{01} = \tilde{P}_{01} - \frac{Z_1(1 + k)}{Z_0 \sqrt{2b}} \arctanh \frac{\sqrt{\frac{b}{2}}}{\sqrt{2}}.
\]
The resulting expression for the critical part \(\Delta \tilde{A}\) of the Peng–Robinson equation is then readily obtained as:
\[
\Delta \tilde{A}(\Delta \tilde{\rho}, \Delta \tilde{T}) = \tilde{\mu}(\tilde{\rho}, \tilde{T}) - \tilde{\mu}_0(\tilde{T}) + \tilde{P}_0(\tilde{T})
\]
as a function of \(\Delta \tilde{\rho} = \tilde{\rho} - 1\) and \(\Delta \tilde{T} = \tilde{T} - 1\). \(\Delta \tilde{A}\) is the critical contribution to the Helmholtz-energy density. It is this part which needs to be renormalized if one wants to incorporate the effects of the critical fluctuations \([55, 56]\). In the classical approximation adopted here the compact expression (17) for \(\tilde{A}\) and the decomposed expression (19) for \(\tilde{A}\) remain equivalent.

3. Isomorphic Peng–Robinson equation for fluid mixtures

For mixtures the critical parameters \(P_c, T_c\) and \(\rho_c\) depend on the composition. To deal with this additional complication we find it convenient to adopt for mixtures a modified set of thermodynamic variables \([14, 19]\):
\[
\tilde{T} = \frac{1}{RT}, \quad \tilde{P} = \frac{P}{RT}, \quad \tilde{\mu}_1 = \frac{\mu_1}{RT}, \quad \tilde{\mu}_2 = \frac{\mu_2}{RT}, \quad \tilde{A} = \frac{\Delta A}{RT}, \quad \tilde{U} = \rho U.
\]
The choice of \(\tilde{\mu}_1\) and \(\tilde{\mu}_2\) as the field variables is not convenient in practice, since \(\tilde{\mu}_1\) or \(\tilde{\mu}_2\) diverge in the pure component limits. Instead one defines two fields, \(h\) and \(\zeta\), that are related to the activities \(e^{\tilde{\mu}_1}\) and \(e^{\tilde{\mu}_2}\) by:
\[
h = \ln(e^{\tilde{\mu}_1} + e^{\tilde{\mu}_2}), \quad \zeta = \frac{1}{1 + e^{(\tilde{\mu}_1 - \tilde{\mu}_2)}},
\]
so that:
\[
\tilde{\mu}_1 = h + \ln(1 - \zeta), \quad \tilde{\mu}_2 = h + \ln \zeta.
\]
The pressure \(\tilde{P}\) considered as a function of \(\tilde{T}, h\) and \(\zeta\) satisfies the differential relation:
\[
d\tilde{P} = -\tilde{U}d\tilde{T} + \rho dh + \rho d\zeta
\]
with:
\[
w = \frac{\rho(x - \zeta)}{\zeta(1 - \zeta)}.
\]
where \(x\) is the mole fraction of component 2, so that \(\rho x\) is the partial density of component 2 (solute). A modified isomorphic Helmholtz-energy density \(\tilde{A}\), defined as:
\[
\tilde{A}_\text{iso}(\tilde{T}, \rho, \zeta) = \rho h - \tilde{P},
\]
which satisfies the differential relation:
\[
d\tilde{A}_\text{iso} = d\tilde{T} + h d\rho - \rho d\zeta
\]
is more useful, since it has a measurable property (overall molar density \(\rho\)) as a canonical variable. On comparing Eq. (37) with Eq. (14) we see that for the mixture \(h\) is the ordering field, like \(\mu\) for the one-component fluid, which is conjugate to the density as the order parameter. The isomorphic field variable \(\zeta\) is often called the hidden field (i.e., irrelevant field) and \(w\) is the density variable conjugate to \(\zeta\). The mole fraction \(x\) of the solute is related to \(\zeta\) by:
\[
x = \frac{\zeta}{1 - \zeta}, \quad \frac{d\tilde{A}_\text{iso}}{d\zeta} = \tilde{T}_{\rho}.
\]
To implement the principle of isomorphism of critical behavior we consider $\Delta A_{\text{iso}}$ as a function of:

$$\Delta T = \left[ \frac{T - T_c(\xi)}{T} \right], \quad \Delta \tilde{\rho} = \frac{[\rho - \rho_0(\xi)]}{\rho_0(\xi)}. \quad (39)$$

The isomorphism principle states that for a mixture at constant $\xi$, $A_{\text{iso}}$ has the same dependence on $\Delta T$ and $\Delta \tilde{\rho}$ as $\tilde{A}$ of a one-component fluid. Since in the one-component limit $\Delta A_{\text{iso}} \rightarrow \tilde{A} = (P/R)\Delta T$, we may write:

$$\Delta A_{\text{iso}}(\Delta \tilde{T}, \Delta \tilde{\rho}, \xi) = \frac{P_c}{RT_c(\xi)}\Delta A(\Delta \tilde{T}, \Delta \tilde{\rho}, \xi), \quad (40)$$

where $\tilde{A}$ is again given by the Peng–Robinson Eq. (17). First of all, $\Delta A_{\text{iso}}$ depends on $\xi$ through the critical parameters $P_c(\xi)$, $T_c(\xi)$ and $\rho_c(\xi)$. Furthermore, $\Delta A_{\text{iso}}$ also depends on $\xi$ through the system-dependent parameter $k(\xi)$ in the definition (10) of $\Delta T$ for which we adopt a quadratic mixing rule:

$$k(\xi) = k_1(1 - \xi) + k_2\xi + k_{\text{mix}}\xi(1 - \xi). \quad (41)$$

In Eq. (41) $k_1$ and $k_2$ represent the values of $k$ for the two pure components through the values $a_{o1}$ and $a_{o2}$ of the two components in Eq. (5), while $k_{\text{mix}}$ will be treated as an adjustable coefficient for the mixtures. With Eq. (10) the $\xi$ dependence of the critical parameter $\rho_c(\xi)$ and of the coefficients in the expansion (18) for the background contribution $\tilde{A}(\xi)$, as well as that of the coefficients $P_{o1}$ and $P_{o2}$ in Eqs. (24) and (25), is now completely specified. A procedure for handling the $\xi$ dependence of the critical parameters and of the coefficients in the expansion (18) for the background contribution $\tilde{A}(\xi)$ to the chemical potential will be presented in the subsequent section. The variable $\xi$ varies from 0 to 1 when the mole fraction $x$ varies from 0 to 1. However, unlike the mole fraction $x$, the field variable $\xi$ will have the same value in the two coexisting phases.

The isomorphic Helmholtz–energy density $\Delta A_{\text{iso}}$, as defined by Eq. (40), satisfies the differential relation:

$$d\Delta A_{\text{iso}} = \bar{w}d\Delta T + h(\xi)d\Delta \tilde{\rho} - \bar{w}d\xi \quad (42)$$

with:

$$\bar{w} = \left( \frac{\partial A_{\text{iso}}}{\partial \Delta T} \right)_{\Delta \tilde{\rho}, \Delta \tilde{\rho}}. \quad (43)$$

We note that $(\partial \Delta A_{\text{iso}}/\partial \xi)_{\Delta \tilde{T}, \Delta \tilde{\rho}}$ in Eq. (38) and $(\partial \Delta A_{\text{iso}}/\partial \xi)_{\Delta \tilde{\rho}, \Delta \tilde{\rho}}$ in Eq. (43) are related by:

$$\left( \frac{\partial \Delta A_{\text{iso}}}{\partial \xi} \right)_{\tilde{\rho}, \tilde{\rho}} = \left( \frac{\partial \Delta A_{\text{iso}}}{\partial \xi} \right)_{\Delta \tilde{T}, \Delta \tilde{\rho}} - \frac{d}{\partial \xi} \left( \frac{\partial \Delta A_{\text{iso}}}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{\rho}, \xi} \Delta \tilde{\rho} - \rho \frac{\partial \rho_c(\xi)}{\partial \xi} \frac{d\rho_c}{\partial \xi} \left( \frac{\partial \Delta A_{\text{iso}}}{\partial \Delta \tilde{\rho}} \right)_{\Delta \tilde{T}, \xi}. \quad (44)$$

### 4. Relationship between mole fraction $x$ and field variable $\xi$

The isomorphic Peng–Robinson equation, defined by Eq. (40), yields the thermodynamic properties of mixtures as a function of $\Delta T$, $\Delta \tilde{\rho}$, and $\xi$. In order to represent experimentally measured thermodynamic–property data, we need to evaluate the relationship between the mole fraction $x$ and the field variable $\xi$. Eq. (32) does not specify this relationship uniquely, since it depends on the choices made for the zero points of energy and entropy through the values of the coefficients $\tilde{\mu}_1^0$ and $\tilde{\mu}_1^1$ in Eq. (18) for the two components [14]. It is convenient to specify this transformation so that $\xi$ equals $x$ on the critical locus:

$$P_c(\xi) = P_c(x), \quad T_c(\xi) = T_c(x), \quad \rho_0(\xi) = \rho_0(x). \quad (45)$$

Condition (45) is commonly referred to as “critical line condition” (CLC) [15–17,26–30]. From Eq. (38) we conclude that the CLC requires that at the critical locus:

$$\frac{\partial A_{\text{iso}}}{\partial \xi} = \frac{\partial A_{\text{reg}}}{\partial \xi} = 0. \quad (46)$$

where:

$$\bar{A}_{\text{reg}} = \frac{P_c(\xi)}{RT_c(\xi)} A_{\text{reg}} \quad (47)$$

with $A_{\text{reg}}$ given by Eq. (20). On the critical locus $\Delta \tilde{A}$ and its first derivatives are zero, so that only the regular background contribution to the Helmholtz–energy density appears in the condition given by Eq. (46). We note again that the coefficients in the expansions (18), (24), and (25) for $P_{o1}(\tilde{T})$ and $P_{o2}(\tilde{T})$ in Eq. (20) depend on $k$ and, hence, on $\xi$, except for $P_{o0}$ and $\rho_{o0}$. To formulate the CLC explicitly, we need to substitute the $\xi$-dependent expression (20) for $A_{\text{reg}}$ into Eqs. (47) and (46) and use Eq. (44). As earlier shown by Povodyrev et al. [19], condition (46) is satisfied if we demand that:

$$dP_{\text{o0}}(\xi) - \left[ \frac{1}{T_c(\xi)} \right] \frac{dT}{d\xi} - \tilde{P}_{o1}(\xi) + \tilde{P}_{o2}(\xi) + \tilde{P}_{o3}(\xi) + \left[ \frac{R T_c(\xi)}{P_c(\xi)} \right] \frac{d}{d\xi} \left( \frac{P_c}{RT_c} \right). \quad (48)$$

The $\xi$ dependence of $\tilde{P}_{o1}(\xi)$ and $\tilde{P}_{o2}(\xi)$ is specified through Eqs. (27), (29), and (41). In addition we try to specify $\tilde{P}_{o3}(\xi)$ so as to satisfy Eq. (48). As mentioned in Section 2, the coefficients $\tilde{P}_{o3}(\xi)$ and $\tilde{P}_{o2}(\xi)$ can be assigned arbitrary values for $\xi = 0$ and $\xi = 1$; however, for intermediate values $\tilde{P}_{o3}(\xi)$ and $\tilde{P}_{o2}(\xi)$ are no longer arbitrary, since they affect such quantities as the enthalpy of mixing [58,60]. There are a number of ways to implement the CLC. The simplest way is to select $\tilde{P}_{o3}(\xi)$ and $\tilde{P}_{o2}(\xi)$ such that:

$$\tilde{P}_{o3}(\xi) = \tilde{P}_{o1}(\xi) - \tilde{P}_{o2}(\xi) \quad (49)$$

and:

$$dP_{\text{o0}}(\xi) - \left[ \frac{1}{T_c(\xi)} \right] \frac{dT}{d\xi} + RT_{c}(\xi) \frac{d}{d\xi} \left( \frac{P_c}{RT_{c}} \right). \quad (50)$$

We refer to Eqs. (49) and (50) as CLC1, which is equivalent to the assumption that the internal energy $U$ can be taken to be zero everywhere on the critical locus [58]. CLC1 has the advantage that the isomorphic Peng–Robinson equation of state (IPREOS) will contain only one (adjustable) mixing parameter, namely $k_{\text{mix}}$ in Eq. (41). This simple one-parameter version of the IPREOS turns out to give a realistic representation of dew–bubble curves in a $P$–$T$ diagram as shown in the Appendix. However, to retain more flexibility, in particular to represent vapor–liquid curves in a $P$–$x$ diagram, we retain the complete Eq. (48) and satisfy it for $dP_{\text{o0}}(\xi)/d\xi$ by adopting a quadratic interpolating formula for $\tilde{P}_{o3}(\xi)$:

$$\tilde{P}_{o3}(\xi) = \tilde{P}_{o3}^0(1 - \xi) + \tilde{P}_{o3}^1\xi + \tilde{P}_{o3}^2(1 - \xi, \xi), \quad (51)$$

using $\tilde{P}_{o3}^0$, $\tilde{P}_{o3}^1$, and $\tilde{P}_{o3}^2$ as adjustable coefficients for the mixture in addition to $k_{\text{mix}}$. We refer to this more flexible version of the CLC as CLC2. We remark that for the calculation of pressure, specific heat capacities and speed of sound, one does not need $\tilde{P}_{o3}(\xi)$, but only its first and second derivatives with respect to $\xi$ which can be readily calculated from Eq. (48). However, if we were to calculate excess enthalpies we would need $\tilde{P}_{o3}(\xi)$ to be obtained by integrating Eq. (48) [19,40]. Having satisfied the CLC, we can replace $dP_{\text{o0}}(\xi)/d\xi$, $dT_{c}(\xi)/d\xi$, and $d\rho_{o0}(\xi)/d\xi$, by $dP_{\text{o0}}(x)/dx$, $dT_{c}(x)/dx$, and $d\rho_{o0}(x)/dx$, respectively.
Table 1

System-dependent parameters (critical temperature, \(T_c\); critical pressure, \(P_c\); critical density, \(\rho_c\); molecular weight, \(M\); acentric factor, \(\omega\)) for the pure fluids.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>(T_c) (K)</th>
<th>(P_c) (MPa)</th>
<th>(\rho_c) (kg/m(^3))</th>
<th>(M) (g/mol)</th>
<th>(\omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>190.564</td>
<td>4.5992</td>
<td>162.66</td>
<td>16.0428</td>
<td>0.008</td>
</tr>
<tr>
<td>Butane</td>
<td>425.20</td>
<td>3.796</td>
<td>227.85</td>
<td>58.125</td>
<td>0.193</td>
</tr>
<tr>
<td>Decane</td>
<td>617.6594</td>
<td>2.120</td>
<td>235.9635</td>
<td>142.489</td>
<td>0.489</td>
</tr>
</tbody>
</table>

\(^a\) Refs. [61–63].  
\(^b\) Refs. [63,64].  
\(^c\) Ref. [65].

5. Applications

As an illustration we apply the isomorphic Peng–Robinson equation of state (IPREOS) to represent experimental vapor–liquid \(P–T\) and \(P–x\) data for mixtures of methane, butane, and decane. In the previous section we considered two versions of an IPREOS, depending on the actual implementation of the critical line condition to assure that \(\xi\) equals \(x\) on the critical locus: one simple version of the IPREOS with CLC1, given by Eqs. (49) and (50), containing only one adjustable parameter \(k_{\text{mix}}\) and a more general version with the less restrictive CLC2, given by Eqs. (48) and (51) containing three additional adjustable parameters through Eq. (51). We prefer to use the IPREOS with CLC2, since it yields a better representation of the experimental data over a wider range of temperatures. The results obtained by adopting the simple IPREOS with CLC1 are presented in the Appendix.

To implement the IPREOS in practice, we need equations for the critical temperature \(T_c(x)\) and the critical pressure \(P_c(x)\) as a function of the composition. Like in the case of one-component fluids, the critical density is then taken as \(\rho_c(x) = z_0^1 P_c(x)/RT_c(x)\). The information needed to specify the Peng–Robinson equation for the pure fluids is presented in Table 1.

5.1. Methane + butane

In practice we represent the critical temperature and pressure of this mixture by polynomials of the form [17,19]:

\[
T_c(x) = T_{c1}(1-x) + T_{c2}x + (T_1 + T_2x + T_3x^2 + T_4x^3 + T_5x^4)x(1-x),
\]

\[
P_c(x) = P_{c1}(1-x) + P_{c2}x + (P_1 + P_2x + P_3x^2 + P_4x^3 + P_5x^4)x(1-x),
\]

(52)

where \(x\) is the mole fraction of butane and where \(T_{ci}\) and \(P_{ci}\) are the critical temperatures and pressures of methane \((i = 1)\) and of butane \((i = 2)\). We have determined the coefficients \(T_j\) and \(P_j\) \((j = 1–5)\) from a fit of Eqs. (52) and (53) to experimental data for the critical temperatures and pressures for the mixture [66,67]. The values thus obtained are presented in Table 2. A comparison of the values calculated from Eqs. (52) and (53) with the experimental values reported by Sage et al. [66] is shown in Fig. 2.

In applying the IPREOS with CLC2 to mixtures of methane \((C_1)\) and butane \((C_2)\) we adopted the following values for the coefficients in Eqs. (41) and (51):

\[
k_{\text{mix}} = -1.7, \quad \mu_{0,1}^1 = 14.30, \quad \mu_{0,2}^1 = 12.828, \quad \mu_{\text{mix}} = -5.045,
\]

(54)

deduced from a fit to experimental \(P–x\) data measured by Sage et al. [66]. In Fig. 3 we show \(P–x\) curves at the temperatures corresponding to the experimental data of Sage et al. In Fig. 4 we show \(P–T\) curves for three selected mole fractions \(x\) of butane. Note that, in order to make a comparison of the \(P–T\) curves with experimental values, we had to extract such data from the experimental \(P–x\) data. We conclude that the IPREOS yields a reasonable representation of the phase-equilibria data except for a range corresponding to small \(P\) and small \(x\).

5.2. Methane + decane

The system methane + decane exhibits a phase diagram designated as Type V in the classification of Scott and Van Konynenburg [68,69], so that the vapor–liquid critical locus does not exist for all values of the mole fraction \(x\) of decane. The vapor–liquid critical locus corresponds to [67,70] (Fig. 5).

\[
x \geq x_{\text{min}} = 0.095,
\]

(55)

so our calculations are also limited to this concentration range. For a description of the critical temperature and pressure we have adopted the following equations:

\[
T_c(x) = \frac{T_{\text{min}} - T_{c2}x_{\text{min}}(1-x)}{(1-x_{\text{min}})} + T_{c2}x + T_1(1-x)(1 + t_4x)
\]

\[
\exp\left[\frac{T_2}{(x-x_{\text{min}})^{1/14}}\right]
\]

(56)

\[
P_c(x) = \frac{P_{c2}(1-x)}{(1-x_{\text{min}})} + P_{c2}(1-x_{\text{min}})(1-x_{\text{min}}) + P_{c2}(x) \left[\frac{P_c(x)}{RT_{c2}(x)}\right]
\]

\[
+ P_1(1-x)(1 + P_4x) \exp\left[\frac{P_2}{(x-x_{\text{min}})^{1/14}}\right],
\]

(57)
where $T_{c2}$ and $P_{c2}$ are the critical temperature and pressure of decane, while $T_{\text{min}} = 277.6$ K and $P_{\text{min}} = 36.13$ MPa are the critical temperature and pressure corresponding to the cutoff composition $x = x_{\text{min}} = 0.095$. The experimental values reported by Reamer et al. [70] correspond to mole fractions below $x = 0.3$. To obtain additional values for the critical parameters we also extrapolated near-critical experimental data reported by Lin et al. [71]. The values obtained for the coefficients in Eqs. (56) and (57) for $T_c(x)$ and $P_c(x) / RT_c(x)$ are presented in Table 3. The actual values of $T_c(x)$ and $P_c(x) / RT_c(x)$ are shown in Fig. 5.

It turns out that the experimental $P-T$ data reported by Reamer et al. [70] and by Lin et al. [71] are not consistent with each other. Specifically, the mole fractions of methane obtained by Lin et al. in the liquid phase differ by about 4% from those obtained by Reamer et al. [70]. From a comparison of the two data sets we have concluded that the bubble pressures reported by Lin et al. [71] are too low compared to those reported by Reamer et al. [70]. Nevertheless we are able to predict the phase-equilibria data for mixtures of methane and decane, at least qualitatively, in terms of one mixing parameter $k_{\text{mix}} = -0.97$ as shown in the Appendix. Here we show in Fig. 6 $P-x$ curves calculated from the IPREOS with CLC2 adopting the following values for the coefficients in Eqs. (41) and (51):

$$k_{\text{mix}} = 0.96, \quad \tilde{\mu}_{1,1} = -45.08, \quad \tilde{\mu}_{1,2} = -17.96, \quad \tilde{\mu}_{\text{mix}} = 17.91$$

It should be noted that the values for the critical parameters of this mixture are not very accurate, which affects the predictive capability of the IPREOS.

### Table 3

| $T_1$ | 825.89 K |
| $P_1$ | $-0.03905$ MPa mol/kJ |
| $t_2$ | 0.70 |
| $p_2$ | 0.30 |
| $t_3$ | $-0.27313$ |

### 6. Discussion

The principle of isomorphic thermodynamic behavior of mixtures asserts that mixtures including the critical region can be described by a one-fluid model provided that the one-fluid model is taken at constant chemical potentials and not at constant compositions. In this paper we have shown how one can apply this principle in terms of the Peng–Robinson equation of state. For an accurate representation of the thermodynamic properties of the mixture...
Fig. 6. Vapor–liquid phase boundaries in terms of $P$ versus $x$ at constant $T$ for mixtures of methane and decane ($x > x_{\text{min}} = 0.095$). The curves represent values calculated from the IPREOS (with CLC2). The symbols indicate experimental data obtained by Reamer et al. [70] at $T = 477$ K and $T = 511$ K and Lin et al. [71] at $T = 542$ K.

near the critical point, one would need an additional transformation so as to incorporate asymptotic scaling laws with nonclassical critical exponents [36,57,72–75]. However, even by applying the principle of isomorphic thermodynamic behavior based on a one-fluid model field to a classical equation of state, one is able to get already a reasonable description of phase-equilibria properties, as illustrated for mixtures of methane, butane, and decane.

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Appendix A. A simpler version of the isomorphic Peng–Robinson equation

As was shown in Section 4, a simple version of the isomorphic Peng–Robinson equation of state is obtained by adopting CLC1, as given by Eqs. (49) and (50). The advantage of this simple version of the IPREOS is that it specifies an equation for mixtures in terms of only one mixing parameter, namely $k_{\text{mix}}$ in Eq. (41). In practice we have used a more general IPREOS by adopting CLC2, as given by Eqs. (48) and (51). This more general IPREOS contains three additional adjustable parameters, namely $\mu_{11}^0$, $\mu_{12}^0$ and $\mu_{\text{mix}}$ in Eq. (51), in part to compensate for incorrect values of the critical density $\rho_0(x)$ implied by the Peng–Robinson equation and its effect upon the calculation of phase boundaries in a $P$–$x$ diagram. However, one may not have sufficient experimental data to determine four adjustable coefficients for the mixtures. In that case one may want to use the simpler version of the IPREOS. Hence, it is interesting to also consider results obtained with this simple IPREOS, in particular for dew–bubble curves in a $P$–$T$ diagram.

In Fig. A1 we present a comparison between the dew–bubble curves for mixtures of methane and butane, calculated from the simple version of the IPREOS with $k_{\text{mix}} = -1.7$, and the experimental data obtained by Sage et al. [66]. For comparison we also show the dew–bubble curves calculated from the simple version of the IPREOS without using any mixing parameter i.e., $k_{\text{mix}} = 0$. In Fig. A2 we present a comparison between the dew bubble curves calculated from the simplified version of the IPREOS with $k_{\text{mix}} = -0.97$ and experimental data obtained by Reamer et al. [70] and Lin et al. [71]. We conclude that the simplified IPREOS gives a realistic estimate of the pressure–temperature dew-bubble curves. However, for a calculation of the vapor–liquid phase boundaries in the $P$–$x$ diagram, we prefer to use the more general version of the IPREOS adopted in this paper.

Fig. A1. Pressure–temperature dew-bubble curves for mixtures of methane and butane. The solid curves represent values calculated from the simple version of the IPREOS with $k_{\text{mix}} = -1.7$ for various values of the mole fraction of butane ($C_4$). The dashed curve shows the critical locus. The symbols indicate experimental data obtained by Sage et al. [66].

Fig. A2. Pressure–temperature dew-bubble curves for mixtures of methane and decane. The curves represent values calculated from the simple version of the IPREOS with $k_{\text{mix}} = -0.97$ for various values of the mole fraction of decane ($C_{10}$). The dashed curve shows the critical locus. The symbols indicate experimental data obtained by Reamer et al. [70].
References


