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# Asymptotic Expansions for Constant-Composition Dew–Bubble Curves Near the Critical Locus[1]

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Explicit functional representations are developed for constant-composition dew and bubble curves near critical according to the modified Leung–Griffiths theory. The pressure and temperature increments $\Delta P = P - P_c$ and $\Delta T = T - T_c$, where c denotes critical, are linearly transformed to new variables $\Delta P'$ and $\Delta T'$. In the transformed space, the coexistence curves are no longer double-valued and can be expressed as a nonanalytic expansion, where the coefficients are functions of the critical properties and their derivatives. A similar asymptotic expansion is developed for $\Delta T$ in terms of the density increment $\Delta\rho = \rho - \rho_c$. In the approximation that the critical exponents $\alpha = 0$ and $\beta = \frac{1}{3}$, the critical point in temperature–density space is shown to be a point of maximum concave upward curvature, rather than an inflection point as previously conjectured.

**KEY WORDS:** asymptotic expansions; binary mixture; concave curvature; critical region; dew–bubble curves; Leung–Griffiths model; linear transformation; vapor–liquid equilibrium.

## 1. INTRODUCTION

Our understanding of the vapor–liquid equilibrium (VLE) of binary mixtures in the near-critical region has improved substantially in recent years. Traditional, analytic equations of state and phase equilibrium algorithms have been inaccurate or have failed to converge near the critical locus. However, the model of Leung and Griffiths [1] has provided the correct mathematical description of mixture thermodynamics near the critical state, including nonclassical, although "effective," critical exponents. The model as modified by Moldover, Rainwater, and co-workers [2–7]

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has proven efficient and successful for correlation of the VLE surfaces of a wide variety of binary mixtures.

Specific calculations of, for example, a dew–bubble curve along an isopleth (locus of constant composition) in the pressure ($P$)–temperature ($T$) or temperature–density ($\rho$) planes have required numerical solutions to sets of parametric equations [2–7]. To our knowledge, the *explicit* mathematical representations of dew–bubble curves, i.e., $P$ as a function of $T$ or $T$ as a function of $\rho$, have not been examined. The objective of the present paper is to derive such explicit representations from the modified Leung–Griffiths formalism in terms of asymptotic expansions about the mixture critical point.

The typical dew–bubble curve has a maximum pressure (maxcondenbar or cricondenbar) point and a maximum temperature (maxcondentherm or cricondentherm) point close to the critical point. Accordingly, the functions $P(T)$ and $T(P)$ are double-valued, as are similar relations between $\Delta P = P - P_c$ and $\Delta T = T - T_c$, where c denotes critical. We show that this problem can be averted by a linear transformation from $\Delta P$ and $\Delta T$ to new variables $\Delta P'$ and $\Delta T'$, defined in terms of certain characteristic directions in thermodynamic space [8].

Temperature–density representations have in general been accorded more attention, and various ancillary equations, e.g., Eq. (B1) in Ref. 6, are commonly used. However, these forms do not correctly locate the singularities at the critical point and simultaneously account for retrograde condensation. In this work, from the expansion of $\Delta T'$ as a function of $\Delta P'$, a similar expansion for $\Delta T$ in $\Delta\rho = \rho - \rho_c$ is constructed. As well as motivating a more fundamentally correct ancillary equation [9], this analysis demonstrates that the dew–bubble curves have intervals of both convex upward and concave upward curvature and shows the relationship of the critical point to these regions of different curvature. It is also shown that the change of curvature is a consequence of nonclassical critical exponents.

Our treatment has some similarities to that of Charoensombut-amon and Kobayashi [10], who expand isothermal dew–bubble curves about the critical point in an explicit function of $P$ versus mole fraction ($x$). However, the coefficients of their expansion are adjustable parameters that are fit to the data of each isotherm separately. In contrast, in our treatment we derive expressions for the coefficients in terms of Leung–Griffiths parameters and, primarily, the critical locus and its derivatives. If the components are not too dissimilar, the asymptotic forms of the dew–bubble curves and values of the coefficients may be *predicted* from the pure-fluid coexistence properties and the critical locus.

## 2. THE MODIFIED LEUNG–GRIFFITHS THEORY

The subject of our discussion is a normal (i.e., nonazeotropic) binary mixture with a continuous critical line from one pure fluid critical point to the other and with no liquid–liquid immiscibility. Our convention is that fluid 1 is the less volatile and fluid 2 is the more volatile component and that $x = 1$ is pure fluid 2. We define a coordinate system $(\zeta, t)$ in terms of "field" variables [8], by definition variables that are equal for coexisting vapors and liquids, as follows:

$$\zeta = \frac{e^{\mu_1/RT}}{K(T)\, e^{\mu_2/RT} + e^{\mu_1/RT}} \tag{1}$$

$$t = \frac{T - T_c(\zeta)}{T_c(\zeta)} \tag{2}$$

Here $\mu_i$ is the chemical potential of fluid $i$ and $R$ is the gas constant. Since $\mu_1 \to -\infty$ for pure fluid 2, and vice versa, $\zeta = 0$ when $x = 1$ (pure fluid 2) and $\zeta = 1$ when $x = 0$ (pure fluid 1). It can be shown that $K(T)$, assumed constant in earlier work [1–5], can be generalized to a temperature-dependent function without altering the formal expressions for $P$, $T$, $\rho$, and $x$. Furthermore, if $T_c(x)$ is monotonic, a particular $K(T)$ can be shown to exist such that $x = 1 - \zeta$ exactly along the critical locus.

From data for dew–bubble curves along isopleths, the critical locus may be found by constructing the envelope of the dew–bubble curves in $P$–$T$ space. Then to each value of $x$ (or $\zeta$) there corresponds a $P_c$ and $T_c$, from which $t$ is defined as in Eq. (2). Loci of constant $\zeta$ are given by

$$\frac{P}{T} = \frac{P_c(\zeta)}{T_c(\zeta)} \left[1 + C_3(\zeta)(-t)^{2-\alpha} + C_4(\zeta)t + C_5(\zeta)t^2 + C_6(\zeta)t^3\right] \tag{3}$$

and the coexisting densities along such loci are given by

$$\rho = \rho_c(\zeta)\left[1 \pm C_1(\zeta)(-t)^{\beta} + C_2(\zeta)t\right] \tag{4}$$

where plus refers to liquid, and minus to vapor.

The critical exponents $\alpha$ and $\beta$ that appear in the above equations are zero and 0.5, respectively, according to classical equations of state. Their actual limiting values [11] are 0.110 and 0.325, but for an accurate fit over a larger range around the critical locus, the "effective" values 0.1 and 0.355 are preferable [3].

The coefficients $C_i(\zeta)$, $i = 1, \ldots, 6$, for $\zeta = 0$ and $\zeta = 1$ are determined by fitting pure-fluid coexistence properties. The coexisting compositions are given by

$$x_j = (1 - \zeta)\left\{1 - \zeta\left[\frac{\bar{Q}(\zeta, t)}{\rho_j} - \frac{\bar{Q}(\zeta, 0)}{\rho_c} - \bar{H}(\zeta, t)\right]\right\} \tag{5}$$

where $j = l$ (liquid) or v (vapor), and

$$\bar{Q}(\zeta, t) = \frac{1}{R}\left[\left(\frac{\partial}{\partial \zeta}\frac{P}{T}\right)_t + T_c(\zeta)\frac{d}{d\zeta}\left(\frac{1}{T_c(\zeta)}\right)_t (1+t)\left(\frac{\partial}{\partial t}\frac{P}{T}\right)_\zeta\right] \tag{6}$$

For the choice $x = 1 - \zeta$ on the critical locus, $\bar{H}(\zeta, t = 0) = 0$. $\bar{H}$ is a function of chemical potentials but, in practice, is modeled by

$$\bar{H}(\zeta, t) = C_H(1 + C_Z\zeta)\, tT_c(\zeta)\frac{d}{d\zeta}\left(\frac{1}{T_c(\zeta)}\right) \tag{7}$$

where $C_H$ and $C_Z$ are adjustable parameters. (This was presented erroneously in some previous work [4–6].)

Two concepts central to the present work are $\alpha_2$, a measure of the relative width of a dew–bubble curve as first introduced by Onuki [12],

$$\begin{aligned}\alpha_2(\zeta) &= \lim_{t \to 0} \delta x/(\delta\rho/\rho_c)\\ &= [\rho_c(\zeta)]^{-1}\zeta(1-\zeta)\,\bar{Q}(\zeta, t=0)\\ &= [R\rho_c(\zeta)]^{-1}\zeta(1-\zeta)\left\{\frac{d}{d\zeta}\left[\frac{P_c(\zeta)}{T_c(\zeta)}\right] + C_4(\zeta)\,P_c(\zeta)\frac{d}{d\zeta}\left[\frac{1}{T_c(\zeta)}\right]\right\}\end{aligned} \tag{8}$$

where $\delta x = x_l - x_v$ and $\delta\rho = \rho_l - \rho_v$ for coexisting phases (not to be confused with $\Delta\rho = \rho - \rho_c$ along an isopleth) and $\alpha_{2m}$, a measure of the dissimilarity of the two components,

$$\alpha_{2m} = \max|\alpha_2| \tag{9}$$

With our conventions, $\alpha_2$ is negative for most normal mixtures. As already stated, we can require that $x = 1 - \zeta$ on the critical line. $C_4(\zeta)$ cannot be derived rigorously, but for mixtures for which $\alpha_{2m} \leqslant 0.25$, it has been found empirically that, for $3 \leqslant i \leqslant 6$,

$$C_i(\zeta) = C_i(0) + \zeta[C_i(1) - C_i(0)] \tag{10}$$

i.e., a linear interpolation. This implies that loci of constant $\zeta$ form a set of parallel curves terminating at the two vapor pressure curves; cf. Fig. 1 in Ref. 4. Therefore, if the components are not too dissimilar, the limiting ratio of composition change to density change across the phase boundary can be predicted from the slopes of the vapor pressure curves and the values and derivatives of the mixture critical parameters.

The expressions for $C_1$ and $C_2$ are somewhat more involved:

$$C_1(\zeta)=\frac{C_1(0)+\zeta[C_1(1)-C_1(0)]}{1+C_X(1+C_Y\zeta)\,|\alpha_2(\zeta)|} \tag{11}$$

$$C_2(\zeta)=C_2(0)+\zeta[C_2(1)-C_2(0)]+C_R\zeta(1-\zeta) \tag{12}$$

where $C_X$, $C_Y$, and $C_R$ are additional adjustable parameters; specific examples are given elsewhere [4–7]. For $\alpha_{2m}>0.25$, a sixth parameter is used [7] which allows $x$ on the critical locus to deviate from $1-\zeta$, but this is not considered here.

## 3. THE LINEAR TRANSFORMATION

We make the approximation in this work that the critical locus is linear in the vicinity of the mixture critical point, i.e., that $P_c$ and $T_c$ are linear functions of $x$, and consequently, $P_c$ is linear in $T_c$. This condition is, of course, not true in general, but is a good "local" approximation over the small range of $\zeta$ required for a relatively narrow dew–bubble curve, and simplifies the mathematics while retaining the most important general features of the analysis. For some mixtures, e.g., nitrogen + oxygen [6], the critical locus is, in fact, nearly linear.

The transformation is

$$\Delta P'=\Delta P-\Delta T\frac{dP_c}{dT_c} \tag{13}$$

$$\Delta T'=\Delta T-\Delta P\left(\frac{\partial P}{\partial T}\right)^{-1}_{\zeta,t=0} \tag{14}$$

where, from Eqs. (2) and (3),

$$\left(\frac{\partial P}{\partial T}\right)_{\zeta,t=0}\equiv\left(\frac{\partial P}{\partial T}\right)_{\zeta}=\frac{P_c}{T_c}[1+C_4] \tag{15}$$

and the $\zeta$ dependences of $P_c$, $T_c$, and $C_4$ are suppressed. A geometrical interpretation of $\Delta P'$ and $\Delta T'$ is given in Fig. 1; $\Delta P'$ is the vertical distance from a $(P, T)$ point to the sloping critical line, and $\Delta T'$ is the horizontal distance from that point to a tilted axis parallel to the constant-$\zeta$ locus at the critical point.

The dew–bubble curve in transformed space is shown in Fig. 2. To leading order, it resembles a pure fluid temperature–density coexistence curve as described by Eq. (4).

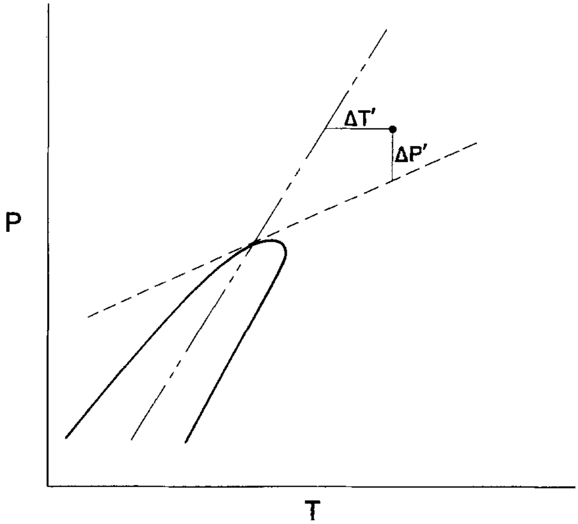

Fig. 1. A constant-composition dew–bubble curve (schematic) in the critical region (solid curve), with the locus of constant $\zeta$ (broken line) and the critical locus (dashed line).

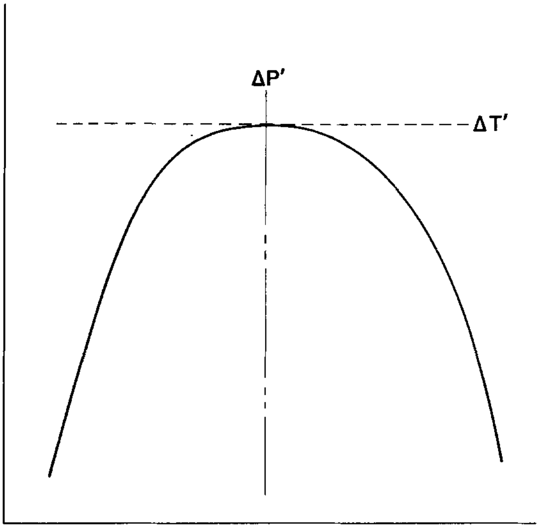

Fig. 2. The dew–bubble curve, locus of constant $\zeta$ ($\Delta P'$ axis), and critical locus ($\Delta T'$ axis) in the transformed space (schematic).

## 4. EXPANSION OF $\Delta T'$ IN TERMS OF $\Delta P'$

As shown below, the expansion of the transformed dew–bubble curve in Fig. 2 has the form

$$\Delta T' = \pm a_1 |\Delta P'|^{\beta} + a_2 |\Delta P'|^{2\beta} \pm a_3 |\Delta P'|^{3\beta} + a_4 |\Delta P'|^{1-\alpha} + a_5(\Delta P') + \cdots \tag{16}$$

where plus refers to liquid, and minus to vapor. We first construct the inverse transformation

$$\Delta P = \left(\Delta P' + \frac{dP_c}{dT_c}\Delta T'\right) \Big/ \left[1 - \frac{dP_c}{dT_c}\left(\frac{\partial P}{\partial T}\right)_{\zeta}^{-1}\right] \tag{17}$$

$$\Delta T = \left[\Delta T' + \Delta P'\left(\frac{\partial P}{\partial T}\right)_{\zeta}^{-1}\right] \Big/ \left[1 - \frac{dP_c}{dT_c}\left(\frac{\partial P}{\partial T}\right)_{\zeta}^{-1}\right] \tag{18}$$

The mixture under analysis has the composition $x_0$ and a critical point at $\zeta_0 = 1 - x_0$, and we define $\Delta\zeta = \zeta_0 - \zeta$. In Figs. 1 and 2, $\zeta$ increases to the right, and $x$ to the left. From Eq. (18), the relation $x = 1 - \zeta$ on critical, and the presumed linearity of the critical locus, we find that

$$\Delta\zeta = -\Delta T'/T_1 \tag{19}$$

$$T_1 = -\frac{dT_c}{dx}\left[1 - \frac{dP_c}{dT_c}\left(\frac{\partial P}{\partial T}\right)_{\zeta}^{-1}\right] \tag{20}$$

Furthermore, we find to leading order that

$$t = \Delta P'/P_1 \tag{21}$$

$$P_1 = T_c\left[\left(\frac{\partial P}{\partial T}\right)_{\zeta} - \frac{dP_c}{dT_c}\right] \tag{22}$$

This is an approximate relation which assumes linearity of constant-$\zeta$ loci or, in effect, neglects the terms involving $C_3$, $C_5$, and $C_6$ in Eq. (3). It is sufficient for deriving the first two terms in Eq. (16).

We first consider the liquid side or bubble curve. From Eqs. (4)–(6) and (8)

$$x_l = 1 - \zeta - \alpha_2\{-C_1(-t)^{\beta} + C_1^2(-t)^{2\beta} + O(-t)^{3\beta} + O(-t)^{1-\alpha} + O(t)\} \tag{23}$$

Starting from the critical point at $x_0$ and $\zeta_0$, we lower $\zeta$ by an amount

$\Delta\zeta$ along the critical locus, so $x = x_0 + \Delta\zeta$, and then decrease $t$ from zero until the original $x_0$ is recovered, in which case

$$\Delta\zeta = -\alpha_2\{C_1(-t)^{\beta} - C_1^2(-t)^{2\beta} + \cdots\} \tag{24}$$

with the understanding that $\alpha_2$ and $C_1$ are evaluated at $\zeta = \zeta_0 - \Delta\zeta$. To leading order

$$\Delta\zeta = -\alpha_2(\zeta_0)\, C_1(\zeta_0)(-t)^{\beta} \tag{25}$$

and from Eqs. (16), (19), and (21),

$$a_1 = \alpha_2 C_1 T_1 P_1^{-\beta} \tag{26}$$

where all quantities are evaluated at $\zeta = \zeta_0$. With our sign conventions, $a_1$ is negative as it must be according to Fig. 1.

To derive the next term, in Eq. (24) we expand $\alpha_2(\zeta_0 - \Delta\zeta)$ and $C_1(\zeta_0 - \Delta\zeta)$ in a Taylor series. We then iterate by replacing $\Delta\zeta$ on the right-hand side by its leading-order expression, Eq. (25). In converting to $\Delta T'$ and $\Delta P'$, we must also consider the $\zeta$ dependence of $P_1$, through $T_c$, in Eq. (22). The end result is

$$a_2 = \left[ -\alpha_2 C_1^2 + \alpha_2 \frac{d\alpha_2}{d\zeta} C_1^2 + \alpha_2^2 C_1 \frac{dC_1}{d\zeta} + \alpha_2^2 C_1^2 \frac{\beta}{T_c} \frac{dT_c}{dx} \right] T_1 P_1^{-2\beta} \tag{27}$$

This procedure can in principle be extended to any desired order, although the mathematical expressions rapidly become more tedious [13]. The form of the last three terms of Eq. (16) is evident from Eq. (23), and $\beta \approx \frac{1}{3}$ while $\alpha$ is very small [the difference between 2 and $2 - \alpha$ is not statistically significant when fitting vapor pressure curves to Eq. (3)]. Therefore, the last three terms are all effectively of the same order.

There are several uses for our linear transformation. First, VLE data can be checked to see that they form a smooth, continuous curve in the transformed space. The mixture critical point can be located with greater precision. Upon estimating $C_1$ and $C_4$ of the pure fluids from coexistence data or a Reidel parameter correlation [14], or using "default" values $C_1 = 2$ and $C_4 = 6$, and estimating (or neglecting) $C_X$, $C_Y$, and $C_R$, the leading-order amplitude $a_1$ and critical locus can be checked for mutual consistency. Nearly "ideal" mixtures with very small differences between pure-fluid $P_c$ and $T_c$, and thus possessing extremely narrow dew–bubble curves, can be better analyzed in $\Delta P' - \Delta T'$ space by expanding the $\Delta T'$ scale; examples are carbon dioxide + nitrous oxide [15], *n*-butanol + *i*-butanol [16], and perfluorobenzene + perfluorocyclohexane [17]. Finally, these results may prove useful in development of rapidly converging VLE algorithms for classical equations of state near the critical locus.

## 5. EXPANSION OF $\Delta T$ IN TERMS OF $\Delta\rho$

A schematic temperature–density plot for a normal binary mixture is shown in Fig. 3; see also similar plots for actual mixtures in Refs. 2–6. The pure-fluid curves, at top and bottom, obey Eq. (4) for $\zeta = 0$ or $\zeta = 1$, whereas the mixture isopleth is skewed and the critical point does not coincide with the maximum temperature or maxcondentherm point.

An important result of this work is a proper understanding of the mathematical behavior near the critical state. Similarly to Eq. (16),

$$\Delta T = b_1\,\Delta\rho + b_2(\Delta\rho)^2 + b_3(\Delta\rho)^3 + b_4\,|\Delta\rho|^{(1-\alpha)/\beta} + b_5\,|\Delta\rho|^{1/\beta} + \cdots \tag{28}$$

where, within the assumption of a locally linear critical locus and Eq. (10) or linear interpolation for $C_4$, the coefficients $b_i$ can be expressed in terms of the critical parameters and their derivatives. Again, we derive only the first two coefficients here.

We consider, as before, a lowering in $\zeta$ from $\zeta_0$ by an interval $\Delta\zeta$, followed by a lowering in $t$ from zero such that $x = x_0$ according to

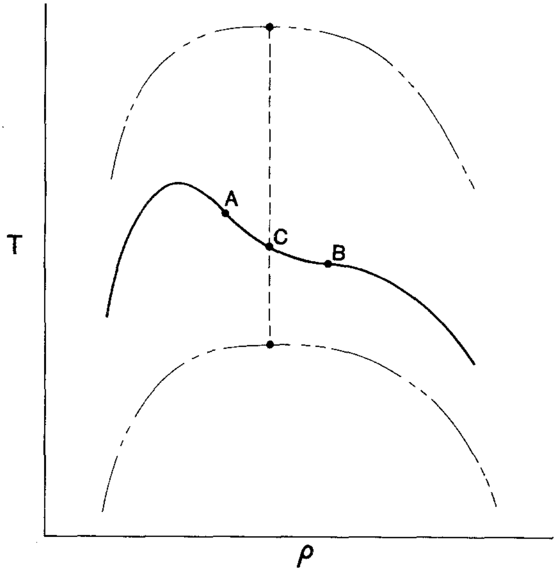

**Fig. 3.** A constant-composition dew–bubble curve (solid curve) in temperature–density space (schematic, exaggerated), with the critical locus (dashed curve) and pure-fluid coexistence loci (broken curves). The dew–bubble curve has two points of inflection at $A$ and $B$ which bracket the critical point $C$.

Eq. (23). The density change $\Delta\rho$ is expanded in $t$ from Eqs. (4) and (24) and then expressed in terms of $\Delta P'$ with Eq. (21); to leading order

$$\Delta\rho = C_1 \left[\rho_c + \alpha_2 \frac{d\rho_c}{d\zeta}\right] \left(-\frac{\Delta P'}{P_1}\right)^{\beta} \tag{29}$$

and

$$\Delta\zeta = -\frac{\Delta T'}{T_1} = -\alpha_2 C_1 \left(-\frac{\Delta P'}{P_1}\right)^{\beta} \tag{30}$$

We replace $\Delta T'$ by $\Delta T$ according to Eq. (18), where $\Delta P'$ is higher order in $t$ than $\Delta T'$ and, for the present purposes, may be neglected. We also replace $\Delta P'$ by $\Delta\rho$ according to Eq. (29). Comparison with Eq. (28) then yields

$$b_1 = -\frac{dT_c}{dx} \frac{\alpha_2}{\rho_c + \alpha_2 \dfrac{d\rho_c}{d\zeta}} \tag{31}$$

Our expansions, including nonanalytic terms, may in principle be extended to any desired order. We expand $\Delta\rho$ and $\Delta\zeta$ in terms of $t$, then iterate as necessary to get $\Delta\zeta$ in terms of $\Delta\rho$, and replace $\Delta\zeta$ by $\Delta T$ by means of Eqs. (19) and (18). The end result for $b_2$ is

$$b_2 = \frac{dT_c}{dx} \frac{\left[\rho_c\alpha_2 - \rho_c\alpha_2 \dfrac{d\alpha_2}{d\zeta} + \alpha_2^2 \dfrac{d\rho_c}{d\zeta} + \dfrac{1}{2}\alpha_2^3 \dfrac{d^2\rho_c}{d\zeta^2}\right]}{\left[\rho_c + \alpha_2 \dfrac{d\rho_c}{d\zeta}\right]^3} \tag{32}$$

A separate analysis of liquid and vapor sides shows that $b_1$ and $b_2$ are the same for liquid and vapor.

The expressions for the higher $b_i$ rapidly become more tedious [13]. But to understand the shape of the $T$–$\rho$ dew–bubble curve, we need only a qualitative analysis of the terms through $b_5$. First, for practical purposes $\beta \approx \frac{1}{3}$ and $\alpha$ is very small, so

$$\frac{1-\alpha}{\beta} \approx \frac{1}{\beta} \approx 3 \tag{33}$$

In other words, even with the highest-quality VLE data, it probably is not possible to distinguish statistically among the third, fourth, and fifth terms of Eq. (28), which we therefore can rewrite as

$$\Delta T \approx b_1\, \Delta\rho + b_2(\Delta\rho)^2 + \bar{b}_3(\Delta\rho)^3 + \cdots \tag{34}$$

where

$$\begin{aligned}\bar{b}_3 &= b_3 + b_4 + b_5 \qquad \text{(liquid side)} \\ &= b_3 - b_4 - b_5 \qquad \text{(vapor side)}\end{aligned} \tag{35}$$

Second, from Eq. (4), at the pure-fluid limits we must have the conditions

$$b_5 = -T_c(C_1 \rho_c)^{-(1/\beta)} \tag{36}$$

$$b_1 = b_2 = b_3 = b_4 = 0 \tag{37}$$

Equation (37) is obeyed by $b_1$ and $b_2$ according to Eqs. (31) and (32), since $\alpha_2 = 0$ in the pure-fluid limit.

Third, the signs of $b_1$, $b_2$, and $\bar{b}_3$ determine the shape and curvature of the $T$–$\rho$ dew–bubble isopleth. By our conventions, for most normal mixtures both $dT_c/dx$ and $\alpha_2$ are negative and $\rho_c > |\alpha_2\, d\rho_c/d\zeta|$, so from Eq. (31), $b_1$ is negative.

Since both $\alpha_2$ and the variation of $\rho_c$ with $\zeta$ are relatively small, the first two terms in the numerator of Eq. (32) usually dominate. Hence, the sign of $b_2$ is opposite from the sign of $[\alpha_2 - \alpha_2(d\alpha_2/d\zeta)]$. If we utilize Onuki's (somewhat crude but instructive) approximation that

$$\alpha_2(\zeta) \approx \alpha_c \zeta(1-\zeta) \tag{38}$$

where $\alpha_c$ is a negative constant, we find that $[\alpha_2 - \alpha_2(d\alpha_2/d\zeta)]$ is negative, and therefore $b_2$ is positive, for $0 \leqslant \zeta \leqslant 1$ if $\alpha_c > -1$, whereas if $\alpha_c < -1$, then $b_2$ is negative near $\zeta = 1$, i.e., near the less volatile component. Since $\alpha_{2m} = -\alpha_c/4$, it follows that $b_2$ is everywhere positive for $\alpha_{2m} < 0.25$ and near the more volatile component for all mixtures.

At the pure limits, $\bar{b}_3$ is negative on the liquid side and positive on the vapor side. We expect this behavior to persist into the mixture, so that $\Delta T$ is always negative for sufficiently large $|\Delta\rho|$. Combining these results, we find that the curvature of the dew–bubble curve is typically concave upward at the critical point but convex upward away from it, and there are two inflection points $A$ and $B$ where the curvature switches, as shown in Fig. 3. At the critical point, $d^3T/d\rho^3$ is discontinuous and $d^2T/d\rho^2$ reaches its maximum value. The critical point on a $T$–$\rho$ dew–bubble curve is therefore the point of maximum concave upward curvature, and not an inflection point as has been conjectured previously [18]. In the classical limit, $\alpha = 0$ and $\beta = \frac{1}{2}$, so $b_4$ and $b_5$ would combine with $b_2$ rather than $b_3$ in Eq. (28), and in most cases a change in sign of the curvature would not occur.

This region of concave upward curvature, a manifestation of nonclassical critical exponents, is most easily seen in mixtures of highly dissimilar fluids near the more volatile component, where $b_2$ is largest. Good examples are the experiments of Kay and co-workers on ethane + *n*-heptane [18], ethylene + *n*-heptane [19], ethane + benzene [20], ethane + cyclohexane [21], and propane + *n*-octane [22], as well as the measurement by Magee et al. [23] of a 5.31% solution of propane in methane. The latter authors find that the critical point is approximately in the middle of the concave upward interval, in agreement with our analysis.

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