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ABSTRACT

Classical constitutive equations for equilibrium properties of fluids and fluid mixtures fail near a critical point. To improve the performance of classical models near the critical point of a pure fluid, Fox (1983) proposed a method for transforming the coordinates of a classical equation of state to nonclassical coordinates. In this work, the method of Fox is extended and applied to binary liquid mixtures at constant pressure, and to ternary liquid mixtures at constant temperature and pressure. A conventional activity-coefficient model is used to represent mixture properties; mixture parameters are determined primarily from the experimental (or estimated) critical point and stability conditions. Results are shown for binary and ternary liquid mixtures. The method proposed here gives good representation of liquid-liquid equilibria, including the critical region. However, the required calculations are complex and therefore, a phenomenological method presented earlier may be preferred for engineering calculations.

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I INTRODUCTION

Liquid-liquid equilibria (LLE) play an important role in the modern chemical industry. As new, temperature-sensitive specialty chemicals are developed, liquid-liquid extraction is becoming an increasingly popular alternative to distillation as a means of purification. In addition, LLE are often encountered in petroleum recovery operations. While it is desirable to conduct extractions remote from critical conditions, prevailing conditions in an oil well are often near critical.

At the critical point of a pure fluid, the properties of the coexisting vapor phase and the liquid phase become identical. Liquid mixtures can also exhibit critical points; as the consolute point of a partially miscible binary mixture is approached, the properties of the coexisting phases become identical. Similarly, as the plait point of a partially miscible ternary mixture is approached, coexisting phases become identical.

It is well known that classical (mean-field) models cannot describe the non-classical behavior of a pure fluid or a fluid mixture near its critical point. On the other hand, scaled equations of state are limited to a vicinity close to the critical point. For practical purposes, it is desirable to have a single model capable of representing all regions, critical and remote from critical. Thus, as the critical point is approached, an equation of state should gradually cross over from classical behavior to non-classical behavior.

Albright et al.(1985) have proposed a formal theory for the cross-over behavior of pure fluids. Recently, this work has been formally extended to mixtures (Chen and Sengers, 1988). That work, however, is not as yet suitable for practical applications. For the global representation of a fluid, as required for engineering-oriented calculations, we need to devise methods that are simple to use and that require few adjustable parameters.
To describe the non-classical behavior of a pure fluid near its gas-liquid critical point, Fox (1979,1983) presented a method for transforming a classical equation of state (EOS). When applied to a van-der-Waals type EOS, correct non-classical behavior is obtained near the critical point, while regions remote from critical are not adversely affected.

Systems that have the same critical exponents and follow the same scaling laws are said to belong to the same universality class (Sengers and Levelt Sengers; 1978). Critical points in pure fluids, consolute points in binary liquid mixtures at constant pressure, or plait points in ternary liquid mixtures at constant pressure and temperature, belong to the same universality class. Universality implies that the properties of all of these systems, which at first glance may appear very different, follow similar scaled equations of state. Here, we have applied Fox’s method for pure fluids to excess Gibbs energy models for binary and ternary liquid mixtures. We present results for a few liquid mixtures, and we show how an improved description of the critical region can be obtained without loss of accuracy in the region remote from critical.

II ANALOGIES: THE CRITICAL REGION OF A LIQUID MIXTURE IS RELATED TO THAT OF A PURE FLUID

The properties of fluids near their critical points are best described using scaling laws with critical exponents. As the critical point of a pure fluid is approached, some thermodynamic properties diverge and others go to zero according to well-defined powers of the scaling fields. For example, the isothermal susceptibility \( \chi_T \) defined by Equation (1), diverges along the critical isochore (above critical temperature \( T_c \)) according to
The molar constant-volume heat capacity also diverges along the critical isochore, above $T_c$, according to

$$\chi_T = \left( \frac{\partial^2 P}{\partial \mu^2} \right)_T = \Gamma |\Delta T|^{-\gamma} . \quad (1)$$

The difference between the equilibrium density, along the coexistence curve, and the critical density, goes to zero according to

$$c_v = A |\Delta T|^{-\alpha} . \quad (2)$$

where $\Delta T = (T - T_c)/T_c$. Exponents $\gamma$, $\alpha$ and $\beta$ in Equations (1), (2) and (3) are positive universal critical exponents. Amplitudes $\Gamma$, $A$ and $B$ are substance-dependent parameters. Subscript $c$ denotes a property at the critical point, and subscript $\text{exc}$ denotes a property at coexistence (i.e. on the coexistence curve).

Three different exponents are used in Equations (1) to (3). While still other thermodynamic properties may diverge according to additional critical exponents, thermodynamics tells us that only two of these exponents can be chosen independently; the remaining can be obtained from relations given elsewhere (Rowlinson and Swinton, 1982).

While Equations (1), (2) and (3) refer to a pure fluid, similar analogous relations can be obtained for a binary fluid mixture (Scott, 1978). To establish an analogy between a pure fluid and a binary fluid mixture, we turn to a description of the thermodynamic surface as given by the Gibbs-Duhem equation. For a pure fluid, the Gibbs-Duhem equation inter-relates temperature $T$, pressure $P$, and chemical potential $\mu$:

$$\left( \frac{S}{V} \right) dT - dP + \rho \; d\mu = 0 . \quad (4)$$

where $(S/V)$ is the entropy density and $\rho$ is the molar density.
For a binary mixture containing components 1 and 2, the Gibbs-Duhem equation inter-relates temperature, pressure, and two chemical potentials $\mu_1$ and $\mu_2$:

$$s\,dT - v\,dP + x_1\,d\mu_1 + x_2\,d\mu_2 = 0,$$

(5)

where $s$ is the molar entropy, $v$ is the molar volume, and $x_i$ is the mole fraction of component $i$. For a system at constant pressure, Equation (5) can be written as

$$s\,dT + d\mu_2 + x_1\,d\Delta_{12} = 0,$$

(6)

where $\Delta_{12} = \mu_1 - \mu_2$. We now compare Equations (4) and (6). Both of these are Gibbs-Duhem equations which inter-relate the field variables of the system. [Field variables are equal in coexisting phases, as opposed to "densities", which have different values in coexisting phases.] Through a transformation of variables, Equation (4) for a pure fluid becomes formally identical to Equation (6) for a binary liquid mixture at constant pressure. Because of this transformation, those power laws which describe the critical behavior of a pure fluid, also describe, through transformation of variables, the critical region of a binary mixture at constant pressure.

From Equations (4) and (6), we see that $P$ in a one-component system corresponds to $-\mu_2$ in a binary liquid mixture at constant pressure. Similarly, $\mu$ for the pure fluid corresponds to $\Delta_{12}$ in Equation (6), $\rho$ in Equation (4) corresponds to $x_1$ in Equation (6), and $S/V$ in Equation (4) corresponds to $s$ in Equation (6).

As shown by Griffiths and Wheeler (1970), the behavior of a multicomponent mixture near a critical point can be deduced from that of a pure fluid, provided the system is described in terms of field variables. To illustrate this point, Figure (1a) shows the familiar coexistence surface of a binary mixture, in $(P,T,x)$ space, near the gas-liquid critical line. Figure (1b) shows the same surface in "field space", that is $(P,T,a_2)$, where $a_2$, the activity of component 2, has the same value in coexisting phases. Figure (1b) also shows that if one of the fields is held constant, say $a_2$, then sections of constant activity have the same topology as that of the pure-fluid $P-T$ diagram (i.e. $a_2=0$ or $a_2=1$), regardless of the value of $a_2$. 
If, however, we take a constant-composition section in the \((P,T,x)\) diagram, the topology of the surface changes drastically. On a \((P,T,a_2)\) surface, a pure-fluid formalism is essentially equivalent to that of a binary mixture where one of the fields is held constant; the number of field variables is irrelevant because any field can be held constant with the same value in coexisting phases (Scott, 1978). In general - and this is the essence of the theory of Griffiths and Wheeler (1970) - a pure-fluid formalism can be extended to multicomponent mixtures provided the thermodynamic space is extended only by adding field variables (Rowlinson and Swinton, 1982).

We now consider a \(T-x\) diagram for a binary liquid mixture at constant pressure. The consolute (critical) point is at \(T_c\) and \(x_{1c}\). We note the transformation of variables indicated by comparing Equations (4) and (6). As the consolute point of a binary liquid mixture is approached along the coexistence curve at constant pressure, the binary-liquid-mixture analogue to Equation (3) is

\[ x_{1ce} - x_{1e} = B \Delta T \Gamma \beta \tag{7} \]

For a binary mixture, we can obtain a relation analogous to Equation (1); the binary-liquid-mixture analogue of the isothermal susceptibility \(\chi_T\) is \(-\frac{\partial^2 \mu_2}{\partial \Delta_{12}^2}\)\(_{T,p}\). Thus, along the path \(x_1 = x_{1c}\), analogous to Equation (1), we have

\[-\left( \frac{\partial^2 \mu_2}{\partial \Delta_{12}^2} \right)_{T,p} = \Gamma \Delta T \Gamma \gamma \tag{8} \]

Scott (1978) and Levelt Sengers (1983) give a complete account of the analogies between binary liquid mixtures and pure fluids.

A similar analogy can be applied to ternary systems. In that case, the Gibbs-Duhem equation at constant pressure and constant temperature can be written as

\[ x_1 \, d\Delta_{12} + d\mu_2 + x_3 \, d\Delta_{32} = 0 \tag{9} \]

where \(\Delta_{32} = \mu_3 - \mu_2\) and \(\Delta_{12} = \mu_1 - \mu_2\). Comparing with Equation (4), \(x_1\) in Equation (9) corresponds to the pure-fluid entropy density \((S/V)\), \(x_3\) corresponds to the pure-fluid density \(\rho\), and \(-\mu_2\) corresponds to the pure-fluid pressure. In the ternary
mixture, \( \Delta_{12} \) corresponds to the temperature \( T \) in the pure fluid, and \( \Delta_{32} \) corresponds to the pure-fluid chemical potential \( \mu \).

Following these transformations, as the plait point of a ternary liquid system is approached along the coexistence curve at constant pressure and temperature, we can expect power laws of the form

\[ x_3 - x_{3e} = B | \Delta_{12} - \Delta_{12e}|^\beta \]  

Based on the analogies described above, the expected asymptotic power laws for binary or ternary mixtures can be derived from those found for pure fluids, for which significant experimental and theoretical evidence is available. More important for our purposes here, through appropriate transformation of variables, we can extend previous results for pure fluids to binary and ternary liquid mixtures; in this work we extend to mixtures the method for pure fluids described by Fox (1983). To do so, we first review Fox's method in the next section. Extension to mixtures is shown in Section IV.

III EQUATION OF STATE FOR A PURE FLUID, INCLUDING THE CRITICAL REGION

Based on Widom's homogeneity hypothesis (Widom, 1965), Fox (1979, 1983) developed a mathematical technique for modifying a classical equation of state for a pure fluid such that it gives correct results in the critical region. This procedure incorporates into a classical EOS the correct non-classical behavior near the critical point. In Fox's method, the cross-over from the classical region to the non-classical region is imposed on two scaling fields, temperature and chemical potential. Appendix A gives a brief overview of the theoretical foundations that support Fox's method.
Consider the vapor-liquid diagram of a pure fluid shown in Figure (2). Critical point $c$ is located at (experimental) temperature $T_c$ and density $\rho_c$. Suppose now that we move to a near-by point $d$, at temperature $T'$ and pressure $P'$, not necessarily on the coexistence curve. We want to evaluate the thermodynamic properties (e.g. density $\rho'$) at point $d$. If we do so using a classical EOS, with independent variables $T'$ and $P'$, our calculated result will be in error.

To obtain the correct thermodynamic properties, here called "non-classical", we use a classical EOS but, instead of variables $T'$ and $P'$, we use "effective" variables $T$ and $P$. Following Fox, we must relate the (correct) non-classical properties $T'$, $P'$ and $\mu'$ to the (incorrect) classical properties $T$, $P$ and $\mu$. These relations are given by

\begin{align}
T' &= (T - T_c) [g(\psi')]^\theta + T_c, \quad (11a) \\
\mu' &= (\mu - \mu(\rho_c,T)) [g(\psi')]^\phi + \mu(\rho_c,T') \quad (11b)
\end{align}

and

\begin{equation}
P' = P + \rho_c(\mu' - \mu) + s_c(T' - T) \quad (11c)
\end{equation}

where $g(\psi')$ is a damping function of some positive distance $\psi'$ measured from the critical point ($\psi^* = 0$ at the critical point). Constants $\theta$ and $\phi$ are given by

\begin{equation}
\theta = \frac{2\alpha}{2-\alpha} \quad (12a)
\end{equation}

where $\alpha = 0.11$, and

\begin{equation}
\phi = 1 - 2\beta \left( 1 + \left( \frac{\alpha}{2-\alpha} \right) \right) \quad (12b)
\end{equation}

where $\beta = 0.35$. Here $\alpha$ and $\beta$ are the critical exponents appearing in power laws (e.g. Equations (1) and (2)). Appendix A discusses the basis for Equations (11) and (12).

Damping function $g(\psi^*)$, not to be confused with the molar Gibbs energy, must obey the boundary condition
In other words, \( g(\psi^*) \) vanishes at the critical point. Similarly, as \( \psi^* \) increases, \( g(\psi^*) \) approaches unity.

For a pure fluid, Fox defined \( \psi \) as the distance from the \( P(\mu,T) \) surface, to a plane tangent to that surface at the critical point. To satisfy stability criteria, the \( P(\mu,T) \) surface must be concave, and this geometrical construction makes \( \psi \) positive everywhere. According to Fox's definition, \( \psi \) has units of pressure. The equation describing such a distance is

\[
\psi = P - P_c - \left( \frac{\partial P}{\partial \mu} \right)_T (\mu - \mu_c) - \left( \frac{\partial P}{\partial T} \right)_\mu (T - T_c)
\]

(13a)

where the symbol \( _c \) indicates that the derivatives must be evaluated at the critical point. Equation (13a) can be rewritten

\[
\psi = P - P_c - \rho_c(\mu - \mu_c) - s_c(T - T_c)
\]

(13b)

Here and in Equation (11c), \( s_c \) and \( \mu_c \) are, respectively, the entropy and the chemical potential at the critical point, relative to the ideal gas at the same temperature and pressure. For convenience, we normalize \( \psi \) according to

\[
\psi^* = \frac{\psi}{P_c}
\]

(13c)

Function \( g(\psi^*) \) is an arbitrary, positive damping function. Fox used

\[
g(\psi^*) = \left( \frac{(\psi^*)^{\lambda/4}}{W + (\psi^*)^{\lambda/4}} \right)^{1/\lambda}
\]

(14)

where \( \lambda \) and \( W \) are adjustable parameters. Fox's function obeys the two desired boundary conditions.

Other forms of \( g(\psi^*) \) could be used. As shown by Erickson and Leland (1986), an exponentially decaying damping function may yield results better than those obtained from Equation (14). Further, the damping function used for Equation (11b) doesn't necessarily have to be the same as that used for Equation (11a).
We now return to Equations (11) for calculating effective variables, given non-classical variables. In a uni-phase system, with two degrees of freedom, only two of these properties can be specified (e.g. \( P \) and \( T \)); the third one (e.g. \( \mu \)) can be calculated provided the corresponding classical, "effective" state is known. In the language of critical phenomena (Griffiths and Wheeler, 1970), in a system having \( m + 1 \) degrees of freedom, only \( m \) field variables can be chosen independently. The \((m + 1)^{th}\) field, which is a function of the others, is called a potential. Derivatives of a potential with respect to the independent fields are called densities.

Suppose that pressure \( P' \) and temperature \( T' \) of a pure fluid are specified [point \( d \) in Figure (2)]. We want to calculate \( \mu' \) (at point \( d \)), the potential field. The corresponding classical properties, \( T, P, \mu \) and \( \rho \) appearing in Equations (11) are also unknown. To calculate these five unknowns, five independent equations are needed. Equations (11) provide three of the necessary equations. The remaining two are provided by an arbitrarily-chosen classical EOS (e.g. the van der Waals equation gives \( P \) and \( \mu \) as a function of \( T \) and \( \rho \)). Solution of these five simultaneous equations yields \( \mu', T, P, \mu \) and \( \rho \). These calculations are shown schematically in Figures (3a) and (3b).

Once \( T', P' \) and \( \mu' \) are known, other thermodynamic properties at point \( d \) can be obtained by numerical differentiation. For example, to calculate non-classical density \( \rho' \), we use

\[
\rho' = \left( \frac{\partial P'}{\partial \mu'} \right)_{T'} = \left( \frac{\Delta P'}{\Delta \mu'} \right)_{T'}
\]

To obtain \( \rho' \), we set a small increment \( \Delta P' \) keeping \( T' \) constant. We then repeat the procedure outlined in Figure (3b) and find \( \Delta \mu' \). The derivative of Equation (15) can then be calculated numerically.

As shown in Section V, the procedure outlined in Figure (3b) can be extended to binary mixtures at constant pressure and to ternary mixtures at constant pressure and temperature. The calculation procedure for binary and ternary mixtures is analogous to that for pure fluids.
IV EXTENSION OF FOX’S METHOD TO BINARY AND TERNARY LIQUID MIXTURES

A Binary Liquid Mixture at Constant Pressure

Upon using the transformations discussed in Section III, Equations (11) for a pure fluid can be rewritten for a binary liquid mixture at constant pressure:

\[ T' = (T - T_c) \left[ g(\psi_b^*) \right]^\theta + T_c \]  

\[ \Delta_{12} = (\Delta_{12} - \Delta_{12}(x_{1c}, T)) \left[ g(\psi_b^*) \right]^\phi + \Delta_{12}(x_{1c}, T') \]  

\[ -\mu_2 = -\mu_2 + x_{1c} (\Delta_{12} - \Delta_{12}) + \sigma_{mc} (T' - T) \]  

where subscript \( mc \) denotes a property of mixing, evaluated at the critical coordinates (consolute point, \( x_{1c} \) and \( T_c \)), and subscript \( b \) denotes a binary distance function.

Exponents \( \theta \) and \( \phi \) are given by Equations (12). For the damping function \( g(\psi_b^*) \) we use Equation (14). Distance \( \psi_b \), however, is not the same as that in Equation (14). A suitable measure of distance from the consolute point of a binary system at constant pressure, is given by

\[ \psi_b = -\mu_2 + \mu_{2e} - \left( -\frac{\partial \mu_2}{\partial \Delta_{12}} \right)_{T, P} (\Delta_{12} - \Delta_{12c}) - \left( -\frac{\partial \mu_2}{\partial T} \right)_{\Delta_{12}, P} (T - T_c) \]  

Equation (17a) can be rewritten as

\[ \psi_b = -\mu_2 + \mu_{2e} + x_{1c} (\Delta_{12} - \Delta_{12c}) - \sigma_{mc} (T - T_c) \]  

which is normalized according to

\[ \psi_b^* = \frac{\psi_b}{\mu_{2e}} \]  

Geometrically, \( \psi_b \) represents the distance from a plane, tangent to the \( -\mu_2(\Delta_{12}, T) \) surface at the consolute point, to a point on that surface. \( \psi_b^* \) satisfies the desired
boundary conditions: it is everywhere positive; it is the same from "both sides" of the coexistence curve, and gradually decreases to zero as the consolute point is approached from anywhere on that surface.

B Ternary Liquid Mixture at Constant Pressure and Temperature

Upon using the transformation of variables discussed in Section III, Equations (11) for a pure fluid can be rewritten for a ternary liquid mixture at constant pressure and temperature:

\[
\Delta_{12}^\prime = (\Delta_{12} - \Delta_{12c}) [g(\psi_r^\prime)]^\theta + \Delta_{12c}
\]

\[
\Delta_{32}^\prime = (\Delta_{13} - \Delta_{32}(x_{3c},\Delta_{12})) [g(\psi_r^\prime)]^\phi + \Delta_{32}(x_{3c},\Delta_{12}^\prime)
\]

\[-\mu_2^\prime = -\mu_2 + x_{1c} (\Delta_{12}^\prime - \Delta_{12}) + x_{3c} (\Delta_{32}^\prime - \Delta_{32})
\]

where \(\theta\) and \(\phi\) are given, respectively, by Equations (12a) and (12b). Function \(g(\psi_r^\prime)\) is given by Equation (14). Analogous to Equations (13), \(\psi_r\) can be defined by

\[
\psi_r = -\mu_2 + \mu_{2c} + \left(\frac{\partial \mu_2}{\partial \Delta_{12}}\right)_{T,P} \Delta_{12c} + \left(\frac{\partial \mu_2}{\partial \Delta_{32}}\right)_{T,P} \Delta_{32c}
\]

which can be rewritten as

\[
\psi_r = -\mu_2 + \mu_{2c} - x_{1c} (\Delta_{12} - \Delta_{12c}) - x_{3c} (\Delta_{32} - \Delta_{32c})
\]

and which is normalized according to

\[
\psi_r^\prime = \frac{\psi_r}{\mu_{2c}}
\]

Here, \(\psi_r\) represents the distance to a point in the surface \(-\mu_2(\Delta_{12},\Delta_{32})\), from a plane tangent to this surface at the plait point. In our nomenclature components 1 and 3 form the partially-miscible pair.

With Equations (16) and (18), and a calculation analogous to that outlined in Figures 3a and 3b, we can turn our attention toward calculating phase diagrams of binary and ternary liquid systems that exhibit a critical point. But before we do so,
we briefly recall the classical procedure for calculating thermodynamic properties of liquid mixtures.

V CALCULATION OF THERMODYNAMIC PROPERTIES OF LIQUID MIXTURES

Liquid-liquid equilibria can be calculated using an EOS or an excess-Gibbs-energy model that provides activity coefficients. In practice, the latter is more convenient and, usually, more reliable. In the examples to follow, we restrict our attention to such models. Our discussion, however, is also valid for equation-of-state calculations.

To use Equations (16) or Equations (18), we require a relation (constitutive equation) which provides residual thermodynamic properties, that is, thermodynamic properties relative to some well-defined idealized state. For an EOS, that state is the ideal gas at system temperature, pressure and composition. For an activity-coefficient model, that state is the ideal mixture, at system temperature, pressure and composition.

As discussed in numerous textbooks, for any component \( i \), activity coefficient \( \gamma_i \), is obtained from a molar excess Gibbs energy model, \( g^E \), using

\[
RT \ln \gamma_i = \left( \frac{\partial n_T g^E}{\partial n_i} \right)_{n,T,P},
\]

where \( n_T \) is the total number of moles, and \( n_i \) is the number of moles of component \( i \). Liquid-liquid equilibria (LLE) can be calculated from the equilibrium conditions

\[
\left( x_i \gamma_i \right)' = \left( x_i \gamma_i \right)'' \quad i=1,N,
\]

where \( N \) denotes the number of components in the system, and superscripts \( I \) and \( II \)
denote coexisting liquid phases at equilibrium.

In engineering practice, common choices for $g^E$ include the van Laar equation, the NRTL equation, or the UNIQUAC equation (Prausnitz et al., 1986). When any one of these mean-field models is used to calculate equilibrium properties of liquid mixtures, the critical point of the system is erroneously approached according to power laws having classical critical exponents. Further, when mean-field models are used with parameters determined from the experimental critical point and stability relations, the miscibility gap is too narrow. To illustrate, Figure (4) shows (dotted line) a representative coexistence curve for a binary system calculated with the standard NRTL equation. As the consolute point is approached, Equation (7) holds, but critical exponent $\beta$ is now equal to 0.5 rather than the observed value ($\sim 0.35$).

To calculate a non-classical coexistence curve for a binary isobaric system, we use the NRTL equation. From the experimental critical point we obtain two NRTL parameters, as shown in Appendix C; the third parameter $\alpha_{12}$ is set equal to 0.2. For a specified classical temperature $T$, we use Equation (21) to obtain the corresponding classical equilibrium compositions ($x'$ and $x''$). Once these classical quantities are known, we can compute distance $\psi_{b*}$ (Equations (17)), and we can calculate the corresponding non-classical $T'$, $\Delta_{12}'$ and $\mu_2'$ using Equations (14) and (16). These three quantities completely specify the non-classical state of the system.

To calculate non-classical equilibrium compositions, we use an analogue to Equation (6):

$$x_1' = -\left(\frac{\partial \mu_2'}{\partial \Delta_{12}'}\right)_{T',P'} = -\left(\frac{\Delta \mu_2'}{\Delta (\Delta_{12}')}\right)_{T',P'}.$$  

(22)

This derivative can be determined numerically; we set an increment $\Delta (\Delta_{12}')$ and calculate the corresponding change in $\mu_2'$ at constant $T'$ and $P'$. This, in turn, can be done using a successive substitution algorithm or a Newton-Raphson method. If we denote this new non-classical state by superscript (1), we have
\[ \Delta_{12}^{(1)} = \Delta(\Delta_{12}') + \Delta_{12}' \]  
\[ T^{(1)} = T' \]  

(23a)

(23b)

The sequence of calculation is now reversed: for specified values of \( \Delta_{12}^{(1)} \) and \( T^{(1)} \), we need to calculate the corresponding classical values \( \Delta_{12}^{(1)} \) and \( T^{(1)} \), which allow calculation of \( \psi_s^* \), \( g(\psi_s^*) \), and finally \( \mu_2^{(1)} \). To proceed with a successive substitution-solution method, we start by guessing classical compositions \( x_{1(0)}^{(1)} \) and \( x_{1(0)}^{(2)} \), and classical temperature \( T^{(1)} \), which correspond to non-classical state \( (\Delta_{12}^{(1)}, T^{(1)}) \). We then compute \( \mu_2^{(1)} \) and \( \Delta_{12}^{(1)} \) from the classical model (i.e. NRTL), and \( \psi_s^* \) from Equations (17). With this value of \( \psi_s^* \), we calculate a new \( T^{(1)} \) using Equation (16a). We now calculate a new \( \Delta_{12}^{(1)} \) with Equation (16b), and solve the classical model for the classical compositions that correspond to these particular values of \( \Delta_{12}^{(1)} \) and \( T^{(1)} \). With these compositions, \( \mu_2^{(1)} \) can be calculated, and \( \mu_2^{(2)} \) can be obtained from Equation (16c). With the new classical values, the procedure is repeated until convergence.

For more accurate numerical derivatives, the procedure just outlined can be repeated using the increment \( -\Delta(\Delta_{12}') \). If we denote this subsequent non-classical state by superscript (2), we have

\[ \Delta_{12}^{(2)} = -\Delta(\Delta_{12}') + \Delta_{12}' \]  
\[ T^{(2)} = T' \]  

(24a)

(24b)

To second order in \( \Delta(\Delta_{12}') \), the derivative of Equation (22) can be calculated using standard numerical methods (Carnahan et al., 1969):

\[ x_1' = -\frac{1}{2\Delta(\Delta_{12}')} [\mu_2^{(1)} - \mu_2^{(2)}] + O[\Delta^2(\Delta_{12}')] \]  

(25)

For calculations very close to the critical point, Equation (25) might not be accurate enough; in that case, higher-order approximations must be used.
The solid curve in Figure (4) shows calculations performed with the same NRTL model as that used to compute the classical curve, but using now the non-classical transformation proposed here (Equations (16)). Figure (4) also shows some classical equilibrium points and their corresponding non-classical points.

Figure (5) shows results for the critical isotherm of a binary liquid mixture at constant pressure, calculated with the same NRTL model. Along the critical isotherm \( T = T_c \), the power law for the chemical potential \( \mu_2 \) is

\[
\mu_2 - \mu_{2c} = D \left( x_1 - x_{1c} \right)^\delta ,
\]

where \( \delta = 1 + \gamma/\beta \), and where \( D \) is a substance-dependent amplitude. Classically \( \delta = 3 \), much smaller than the observed value of \( \sim 4.5 \); however, by using the transformed equations (Equations (16)), the correct non-classical asymptotic behavior is obtained.

Ternary LLE were also calculated using the NRTL equation. The procedure to calculate non-classical equilibrium compositions is entirely analogous to that used to calculate binary non-classical compositions. The coordinates of the plait point must be known or estimated using methods described elsewhere (Fleming and Vinatieri, 1979).

Figure (6) illustrates qualitatively, on a ternary composition diagram, the nature of the transformations to a classical model that are introduced through Equations (18). Following Widom (1968), along the coexistence curve, as the plait point is approached,

\[
l = d^{\frac{\beta}{1-\alpha}} ,
\]

where \( l \) is the length of a tie-line, and \( d \) is the orthogonal distance from that tie-line to the plait point. Classically \( \beta = 1/2 \) and \( \alpha = 0 \); therefore, the classical exponent in Equation (27) is 0.5. The non-classical values of \( \beta \) and \( \alpha \) are, respectively, 0.35 and 0.11. Thus, the correct exponent for Equation (27) is 0.38. The correct asymptotic behavior is obtained when Equations (18) and (19) are used.
The exponent that determines the shape of the coexistence curve on a ternary diagram in the critical region (i.e. $\beta/1-\alpha$) is not the same as that for a pure fluid [Equation (3), or that for a binary mixture, Equation (7)]. The exponent for the ternary is different because the coordinates of pure-fluid $P-\rho$ diagrams and binary $T-x$ diagrams are, respectively, one field and one density, whereas the coordinates of a ternary isothermal-isobaric ternary diagram are two densities (Figure 6). If, however, we choose as coordinates for a ternary-system diagram a field (e.g. $\mu_1$) and a density (e.g. $x_1$), as shown in Figure 11, the limiting shape of the coexistence curve is again determined by exponent $\beta$ [i.e. Equation (10)]. In contrast to Figure 6, the tie-lines in Figure 11 are parallel to the density ($x_1$) axis.

VI ILLUSTRATIVE RESULTS AND DISCUSSION

A Binary Systems

To test the applicability of Equations (16) and (17) for binary systems, we show results for the binary system methanol-cyclohexane, which has been studied extensively by Ewing et al.(1988). For the constitutive equation we use the conventional NRTL equation.

In the conventional NRTL equation, we do not assume any additional temperature-dependence for the parameters beyond that given in the original equation. It is well known that this model is unable to reproduce experimental binary coexistence curves adequately.

The non-randomness parameter is fixed at $\alpha_{12} = 0.2$. If the two parameters of the NRTL model are calculated from the coordinates of the consolute point, using the conditions of incipient immiscibility (see Appendix C), the coexistence curve predicted by the model is too narrow. However if Equations (16) and (17) are used, the original curve is broadened; much better results are then obtained, as shown in Figure 7. Figure 8 shows a blow-up of the critical region, where the correct non-
classical behavior is observed.

Provided that the coordinates of the critical point are known, and provided that $\alpha_{12}$ is set, the method proposed here does not introduce any additional NRTL parameters. In typical conventional use, NRTL parameters are obtained by regressing mutual solubility data. However, here NRTL parameters are calculated from stability criteria at the known (or estimated) critical point. But Equation (14) requires two system-specific parameters, $\lambda$ and $w$; these are obtained by regressing mutual solubility data.

While agreement with experiment is greatly improved through the method proposed here, it is not completely satisfactory. The remaining disagreement follows from inadequacy of conventional models (such as NRTL) to represent the temperature dependence of the binary parameters at conditions remote from critical. Most commonly-used functions for $g^E$ give a good composition dependence, but the temperature dependence is usually poor. This inadequacy could be corrected by assigning an additional temperature dependence to the binary NRTL parameters (see e.g. Skjold-Jorgensen et al., 1980), but the important point here is that the need for this dependence is not a consequence of non-classical behavior in the critical region.

To some extent, the success of scaled equation for the critical region depends on the symmetry of the system. While pure-fluid chemical-potential isotherms are remarkably antisymmetric with respect to the critical isochore, $\Delta_{12}$ isotherms are often not very antisymmetric with respect to $x_{1c}$ (Simon et al., 1972). The modifications introduced by the method proposed in this work are symmetric; both branches of the coexistence curve, for example, are affected to the same degree. While this is not a significant problem in the system methanol-cyclohexane, the coexistence curves of most real binary systems are seldom that symmetric with respect to the critical composition. In a forthcoming paper, we will discuss how to deal with more asymmetric systems.

We now turn our attention to isothermal isobaric ternary systems, which are much more interesting for engineering applications.
B Ternary Systems

While the temperature dependence of conventional local-composition models is not sufficiently well known for reliable nonisothermal LLE calculations, the isothermal composition dependence often gives quantitative agreement with experiment, provided that the parameters appearing in the model are properly evaluated and provided that experimental data in the critical region are not regressed together with data remote from the critical region. Most often, binary data, coupled with only one or two ternary tie-lines are sufficient to yield parameters that allow correct representation of the entire ternary diagram, except near the plait point (see, for example, Anderson and Prausnitz, 1978).

In the example to follow, NRTL parameters are determined from the known (or estimated) coordinates of the plait point, coupled with stability criteria, as discussed in Appendix C.

Figure (9) shows results for the ternary system 1-hexene/benzene/sulpholane at 50 °C and atmospheric pressure. No binary data were used to obtain NRTL parameters. The plait point was estimated using well-established graphical methods (De Fre and Verhoeeye, 1976). The dotted line was calculated with the conventional NRTL equation; NRTL parameters were obtained from two ternary tie-lines remote from the plait point and from stability criteria at the plait point. The solid line was calculated with Equations (18), using the same NRTL equation with the same parameters. The results obtained with Equations (18) and (19) are much better than those obtained using the conventional method. The correct non-classical coexistence curve is now obtained.

To calculate parameters \( w \) and \( \lambda \), we proceed as follows. We use ternary tie-line data, remote from the plait point, and stability criteria at the known plait point to determine NRTL parameters. With these NRTL parameters, \( \lambda \) and \( w \) are obtained by regressing all available mutual solubility and tie-line data.

Figure (10) shows results for the system 2-butanone/acetic acid/water at 50 °C. Again, the NRTL equation was used. The classical method is unable to represent
accurately the coexistence curve, even when its nine parameters are adjusted to all
the available solubility data. On the other hand, if only two ternary tie-lines (remote
from the plait point) and the coordinates of the plait point are used to obtain the con-
ventional NRTL parameters (in this case only six parameters are adjusted; all the
non-randomness parameters are kept constant), the coexistence curve is too narrow
(dotted curve). However, when the NRTL equation is used with transformed coor-
dinates, accurate results can be obtained, only at the expense of two additional adju-
stable parameters, \( w \) and \( \lambda \), as shown by the solid line in Figure (10). The
exponent that determines the shape of the ternary diagram in the critical region is
indeed \( \beta/(1-\alpha) \). Figure (11) shows a chemical-potential-versus-composition diagram
for the same mixture; in the critical region, exponent \( \beta \) governs the shape of this
diagram.

Transformation of classical to nonclassical coordinates provides an important
advantage: not only is the correct non-classical coexistence curve obtained, but other
thermodynamic properties (in addition to phase equilibrium compositions) also obey
the correct non-classical critical behavior. For engineering applications such as
extractive-distillation operations, it is important to calculate phase equilibria at com-
positions close to critical but in the one phase-region. With the transformation from
classical to non-classical coordinates, the activity of each component in the liquid
mixture can be determined accurately, and the phase equilibrium problem can now
be solved, yielding improved results for the critical region and the regions remote
from critical.

While the changes introduced by transformation of coordinates in the critical
region are a step in the right direction, unfortunately there are no simple classical
models that can consistently describe all thermodynamic properties properties of
liquid mixtures in regions remote from critical. For a liquid mixture, heat capacity,
for example, must be calculated with a model other than that used to calculate LLE,
or else with the same model but different parameters.
The method proposed here provides a convenient framework to modify classical $g^E$ models, and to improve their performance in the critical region. As new and more accurate classical models are developed for conditions remote from critical, a well-established method is now available to transform such models toward obtaining also correct non-classical behavior in the critical region.

VII CONCLUSIONS

Fox has given a method for modifying classical equations of state for pure fluids to improve their performance in the critical region. That method has been extended and applied to binary and ternary liquid mixtures.

Transformation from classical to nonclassical coordinates provides a powerful method for using conventional excess-Gibbs-energy models to calculate binary isobaric phase equilibria in the critical region. However, while the method presented here yields the correct asymptotic behavior of different thermodynamic properties, the temperature dependence found in these models does not allow quantitative representation of several thermodynamic properties simultaneously. For practical applications, when only LLE must be calculated, a phenomenological method presented earlier (de Pablo and Prausnitz, 1988) gives better results and greater flexibility with less computational effort.

For ternary mixtures at constant temperature and pressure, the transformations presented here have some advantages and some disadvantages when compared to the phenomenological method presented earlier (de Pablo and Prausnitz, 1988). The success of the method presented earlier depends on the ability of a given classical model to represent accurately the regions remote from critical. In highly asymmetric phase-equilibrium diagrams, if that region is described with moderate accuracy, then a very large correction is necessary to shift the plait point coordinates to the desired position. The method proposed previously, while conceptually simpler than that proposed here, can sometimes fail to provide such a large correction. In the method
proposed here, the plait point coordinates are fixed a priori and the correction to the classical model is such that regions remote from critical are also modified, allowing accurate results everywhere. An additional advantage of the method discussed here is that the "distance" to the plait point is no longer constant (as it is in the previous method) from anywhere on a tie-line. Therefore, thermodynamic-property calculations other than LLE should also be improved by the modifications proposed here. These advantages, however, are at the expense of more complicated numerical algorithms and longer calculations. While additional calculations are an important disadvantage for routine process simulation, the ever-increasing power of computers is likely to minimize that disadvantage in the future.

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LITERATURE CITED


**APPENDIX A**

Sengers and Levelt Sengers (1978), and Rowlinson and Swinton (1982), discuss critical phenomena in fluids and fluid mixtures. This appendix gives only a brief overview of Fox’s original work.

In 1965, Widom postulated that the Helmholtz energy is a generalized homogeneous function of its arguments. A generalized homogeneous function $F$ of variables $X$ and $Y$ satisfies the relation

$$F(k^nX, k^nY) = k^nF(X,Y)$$  \hspace{1cm} (A1)
for all values of $X$, $Y$ and $k$. Here, $\xi$ and $\eta$ are two independent (but fixed) exponents, and $k$ is any positive parameter.

Let $\Phi$ be the singular part of the Helmholtz energy density $A/V$, and let $X$ and $Y$ be two independent fields (e.g. temperature and chemical potential, or some combination of them). For a system with two degrees of freedom, classical scaling can be expressed by

$$\Phi(X,Y) = k^{-4} \Phi(k^3X,k^2Y) \quad (A2)$$

The essence of Fox's method is to construct a new singular Helmholtz energy $\Phi'$, with a new scaling form that differs from the classical by the small exponents $\theta$ and $\phi$:

$$\Phi'(X,Y) = k^{-4} \Phi(k^{3+\theta}X,k^{2+\phi}Y) \quad (A3)$$

Conjugate densities to the $X$ and $Y$ fields are obtained by differentiation. If $\rho_X$ and $\rho_Y$ denote these densities, classical scaling gives

$$\rho_X(X,Y) = -\frac{\partial \Phi}{\partial X} = k^{-1} \rho_X(k^3X,k^2Y) \quad (A4a)$$

$$\rho_Y(X,Y) = -\frac{\partial \Phi}{\partial Y} = k^{-2} \rho_Y(k^3X,k^2Y) \quad (A4b)$$

The corresponding rescaled densities are

$$\rho_X'(X,Y) = -\frac{\partial \Phi'}{\partial X} = k^{\theta-1} \rho_X'(k^{3+\theta}X,k^{2+\phi}Y) \quad (A5a)$$

$$\rho_Y'(X,Y) = -\frac{\partial \Phi'}{\partial Y} = k^{\phi-2} \rho_Y'(k^{3+\theta}X,k^{2+\phi}Y) \quad (A5b)$$

The above equations hold for all values of $X$, $Y$ and $k$. If we now take $X=0$ and $k = Y^{-1/(2+\phi)}$, Equations (A5) can be rewritten as

$$\rho_X'(0,Y) = Y^{1-\phi} \rho_X'(0,-1) \quad (A6a)$$
\[ \rho_Y'(0,Y) = Y^{\frac{2-\theta}{2+\theta}} \rho_Y'(0,-1). \] (A6b)

Making the following substitutions,

\[ \beta = \frac{1-\phi}{2+\theta}, \] (A7a)
\[ 1 - \alpha = \frac{2-\theta}{2+\theta}, \] (A7b)

the desired scaling relations for the densities are obtained:

\[ \rho_X' = (Y)^\beta \] (A8a)
\[ \rho_Y' = (Y)^{1-\alpha}, \] (A8b)

where \( \alpha \) and \( \beta \) are experimental critical exponents. Note that Equations (A7) and Equations (12) are equivalent. In classical scaling, \( \phi \) and \( \theta \) are both zero; \( \beta \) and \( \alpha \) are then given by their classical values, 0.5 and 0, respectively.

Fox arrives at a rescaled Helmholtz energy \( \Phi' \) using a parametric representation of the Helmholtz energy and its arguments. Details can be found in the original paper. Here, we only point out that rescaling of the Helmholtz energy can be achieved by multiplying the independent fields \( X \) and \( Y \) by a suitable homogeneous scaling function, \( g \), raised to the \( \phi \) and \( \theta \) powers, respectively. This modification is such that the scaling form of Equation (A3) is obtained.

In Fox's method for pure fluids, \( X \) and \( Y \) correspond, respectively, to \( \Delta \mu = \mu - \mu(\rho_c, T) \) and \( \Delta T \). Function \( \Phi \) is given in terms of temperature and chemical potential (rather than temperature and pressure), because on a \( \Delta \mu \) vs \( \rho \) diagram, isotherms are remarkably antisymmetric with respect to the critical isochore (Sengers and Levelt Sengers (1978)); this antisymmetry is essential to the use of scaled equations for the critical region.
APPENDIX B

The purpose of a distance function is to provide a measure which indicates when non-classical behavior starts to dominate the thermodynamic properties of the system or, in other words, when long-range fluctuations start to control the behavior of the system. Therefore, a possible relation for $\psi_b$ might be

$$\psi_b = -\left( \frac{\partial \mu_2}{\partial x_1} \right)_{T,P}, \quad (B-1)$$

which is inversely proportional to the fluctuations in composition. Unfortunately, Equation (B-1) has a serious disadvantage: it is not equal for both branches of the coexistence curve; therefore, we prefer to use Equation (17) as a definition of distance.

APPENDIX C

In this work, conventional-model parameters (e.g. NRTL parameters) are obtained from the conditions of incipient immiscibility at the critical point.

In a binary liquid mixture, these criteria are

$$(\frac{\partial^2 \Delta g}{\partial x^2})_c = 0 \quad (C1a)$$

$$(\frac{\partial^3 \Delta g}{\partial x^3})_c = 0, \quad (C1b)$$

where $\Delta g$, the molar Gibbs energy of mixing, is given by sum of the molar excess Gibbs energy of mixing and the ideal Gibbs energy of mixing:

$$\Delta g = g^e + RT(x_1\ln x_1 + x_2\ln x_2) \quad (C2)$$

Solution of Equations (C1a) and (C1b) at the known (or estimated) coordinates of the consolute point determines the values of two conventional-model parameters. If the model contains a third parameter, it must be assumed constant or evaluated from other data.
In a ternary liquid mixture, the conditions of incipient inmiscibility at the plait point are

\[
\begin{align*}
\xi &= \begin{vmatrix} \frac{\partial^2 \Delta g}{\partial x_2^2} & \frac{\partial^2 \Delta g}{\partial x_2 \partial x_3} \\ \frac{\partial^2 \Delta g}{\partial x_2 \partial x_3} & \frac{\partial^2 \Delta g}{\partial x_3^2} \end{vmatrix} = 0 & \text{(C3a)} \\
\zeta &= \begin{vmatrix} \frac{\partial \xi}{\partial x_2} & \frac{\partial \xi}{\partial x_3} \\ \frac{\partial^2 \Delta g}{\partial x_2 \partial x_3} & \frac{\partial^2 \Delta g}{\partial x_2^2} \end{vmatrix} = 0 , & \text{(C3b)}
\end{align*}
\]

where the Gibbs energy of mixing, \( \Delta g \), is given by

\[
\Delta g = g^F + RT(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3) .
\]  

\text{(C4)}

Conventional-model parameters are obtained by minimizing the difference between calculated and experimental tie-line data, remote from the plait point, and simultaneously satisfying Equations (C3) at the known (or estimated) plait point.

For the examples shown in Figures (7)-(11), all parameters are given in Table C1.
Table C1 - NRTL and other required parameters for fitting binary and ternary LLE.

<table>
<thead>
<tr>
<th>Components</th>
<th>i</th>
<th>j</th>
<th>$\tau_{ij}$</th>
<th>$\tau_{ji}$</th>
<th>$\alpha_{ij}$</th>
<th>$T_c$</th>
<th>$x_{1c}$</th>
<th>$x_{2c}$</th>
<th>$x_{3c}$</th>
<th>$\lambda$</th>
<th>$W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Methanol</td>
<td>1</td>
<td>2</td>
<td>343.66</td>
<td>384.55</td>
<td>0.2</td>
<td>318.398</td>
<td>0.490</td>
<td>0.510</td>
<td></td>
<td>0.8</td>
<td>1.4</td>
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<tr>
<td>(2) Cyclohexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) 1-Hexene</td>
<td>1</td>
<td>2</td>
<td>162.30</td>
<td>89.17</td>
<td>0.2</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) Benzene</td>
<td>1</td>
<td>3</td>
<td>1476.43</td>
<td>484.20</td>
<td>0.2</td>
<td>-</td>
<td>0.264</td>
<td>0.444</td>
<td>0.292</td>
<td>0.9</td>
<td>0.11</td>
</tr>
<tr>
<td>(3) Sulpholane</td>
<td>2</td>
<td>3</td>
<td>110.38</td>
<td>323.29</td>
<td>0.2</td>
<td>-</td>
<td></td>
<td></td>
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<tr>
<td>(T = 313.15\ K)</td>
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<td></td>
</tr>
<tr>
<td>(1) 2-Butanone</td>
<td>1</td>
<td>2</td>
<td>1229.51</td>
<td>-917.22</td>
<td>0.2</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) Acetic Acid</td>
<td>1</td>
<td>3</td>
<td>-12.83</td>
<td>895.95</td>
<td>0.2</td>
<td>-</td>
<td>0.219</td>
<td>0.031</td>
<td>0.750</td>
<td>3.5</td>
<td>0.12</td>
</tr>
<tr>
<td>(3) Water</td>
<td>2</td>
<td>3</td>
<td>-468.67</td>
<td>-1023.50</td>
<td>0.2</td>
<td>-</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(T = 298.15\ K)</td>
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</table>

In Table C1, parameters $\tau_{ij}$ are dimensionless, and temperature $T_c$ is given in degrees Kelvin. The NRTL equation (Prausnitz et al., 1986) for the excess Gibbs energy of a mixture of $N$ components is

$$
\frac{g^E}{RT} = \sum_{i=1}^{N} \sum_{j=1}^{i=N} \frac{\tau_{ij} G_{ij} x_j}{\sum_{l=1}^{N} G_{il} x_i}
$$

(C5)

where $\tau_{ij} = (g_{ij} - g_{ji})/RT$ are binary interaction parameters for the $ij$ pair, and $G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$, with $(\alpha_{ij} = \alpha_{ji})$. 
FIGURE 1 - Schematic representation of the coexistence surface of a binary mixture near its vapor-liquid critical line, a) on a (P,T,x) diagram and b) on a (P,T,α*) (field-space) diagram.

FIGURE 2 - Schematic representation the pressure-density diagram of a pure fluid. Point c is the experimental critical point, and point d represents a point with density ρ', at pressure P' and Temperature T'.

FIGURE 3a - Equations and unknowns in the method of Fox for pure fluids

FIGURE 3b - A direct-substitution algorithm for the calculation of non-classical chemical potential, μ', when T' and P' are specified.
FIGURE 4 - Coexistence curve for a representative binary mixture. The dotted curve represents calculations with a classical model. The corresponding solid curve represents calculations with the same model but with the transformations proposed in this work. The arrows indicate correspondence between classical and non-classical states.

FIGURE 5 - Critical isotherm of a representative binary mixture. The dotted curve was calculated with a classical model, and the corresponding solid curve was calculated with the same model but with the transformations proposed in this work. The arrows indicate correspondence between classical and non-classical states.

FIGURE 6 - Coexistence curve for a representative ternary mixture at constant temperature and pressure. The dotted curve was calculated using a classical model. The solid curve was calculated with the same model but with the transformations proposed in this work. The arrows indicate correspondence between classical and non-classical states.

FIGURE 7 - Coexistence curve for the system methanol/cyclohexane at constant pressure. The dotted curve was calculated using the conventional NRTL model, with two parameters obtained from stability criteria at the consolute point (The non-randomness parameter $\alpha_{i,j}$ is set equal to 0.2.) The solid curve represents calculations with the same NRTL model with the same parameters, but with the transformations proposed in this work.
FIGURE 8 - Critical region of the methanol/cyclohexane coexistence curve. The dotted curve represents calculations with the classical model. The solid curve represents the corresponding non-classical state. Both curves were calculated using the NRTL model also used in Figure 7.

FIGURE 9 - Coexistence curve for the system 1-Hexene / Benzene / Sulpholane at 50 C. The dotted curve was calculated using the NRTL equation with six parameters obtained from two tie-lines remote from the plait point and from stability criteria at the plait point. The solid curve was calculated using the same NRTL model with the same parameters but with the transformations proposed in this work. For all binary systems $\alpha_{ij} = 0.2$.

FIGURE 10 - Coexistence curve for the system 2-butanone / acetic acid / water at 25 C. The dotted curve was obtained using the conventional NRTL equation with six parameters obtained from two tie-lines remote from the plait point, and stability criteria at the plait point. The solid curve was calculated using the same NRTL equation with the same six parameters but with the transformations proposed in this work. For all binary systems $\alpha_{ij} = 0.2$.

FIGURE 11 - Coexistence curve of the ternary system 2-butanone / acetic acid / water at 25 C (see Figure 10), plotted on a chemical potential of 2-butanone vs. mole percent of 2-butanone diagram. The coordinate axis are, respectively, a field and a density, and therefore $B$ is the exponent that governs the shape of this curve in the critical region.
FIGURE 1
Two phases

Pressure $P'$

Isotherm $T'$

Density $\rho'$

FIGURE 2
1. EQUATIONS

\[ T' = (T - T_c)[g(\psi)]^\phi + T_c \]  
\[ \mu' = (\mu - \mu(\rho_c,T))[g(\psi)]^\phi + \mu(\rho_c,T') \]  
\[ P' = P + \rho_c(\mu' - \mu) + s_c(T' - T) \]  
\[ P = F_1(\rho, T) \]  
\[ \mu = F_2(\rho, T) \]  

Where \( F_1 \) and \( F_2 \) are provided by a classical EOS.

2. SPECIFIED VARIABLES

\( P' \) and \( T' \) are specified.

3. UNKNOWNS

\( T, \mu, P, \rho \) and \( \mu' \) are the unknowns.

---

**FIGURE 3a**
1. Specify State of the System

Specify $T'$ and $P'$. We wish to calculate other thermodynamic properties, such as non-classical chemical potential $\mu'$. Non-classical density $\rho'$ can then be obtained by numerical differentiation (see text).

2. Initial Guess

To start with a direct-substitution algorithm, assume $T=T'$ and $P=P'$.

3. Calculate Distance to Critical Point

Using a classical EOS, calculate $\rho$ and $\mu$ at $T$ and $P$. Having classical values for $T$, $P$, and $\mu$, calculate distance $\psi^*$ to the critical point using Equations (13).

4. Compute Damping Function and Classical Temperature

With the distance determined in step 3, calculate $g(\psi^*)$ using Equation (14). Then use Equation (11a) to calculate $T$.

5. Calculate Non-Classical Chemical Potential

With the classical EOS, calculate the classical chemical potential $\mu$ at $T$ and $P_c$, and also at $T'$ and $P_c$. With these values, calculate $\mu'$ using Equation (11b).

6. Calculate classical Pressure

Having calculated $\mu$, $T$, and $\mu'$, calculate classical pressure $P$ from Equation (11c).

7. Convergence

If classical pressure $P$ from last step is equal to the pressure used in step 3, then convergence has been achieved. If they are not the same, return to step 3 with the pressure calculated in step 6 and the temperature calculated in step 4.

FIGURE 3b
Conventional model
- Same model with non-classical coordinates
- Consolute point

FIGURE 4
Conventional model

- - Same model with non-classical coordinates

■ Consolute point

FIGURE 5
Mole Fraction (2)

Mole Fraction (3)

FIGURE 6
Data of Eckfeldt and Lucasse (1943)

Consolute point

NRTL equation

NRTL equation with non-classical coordinates

FIGURE 7
Data of Ewing et al. (1988)
Consolute point
--- NRTL equation
— NRTL equation with non-classical coordinates

\[ \Delta T = 1.0 \, ^\circ C \]

Mole Percent Methanol

\[ \begin{array}{c|c|c|c|c|c|c|c}
30 & 40 & 50 & 60 & 70 \\
44.0 & 44.5 & 45.0 & 45.5 & 46.0
\end{array} \]
FIGURE 9

Data of De Fre and Verhoeve (1978)

NRTL equation

NRTL equation with non-classical coordinates
Data of Iguchi and Fuse (1971)

- NRTL equation

- NRTL equation with non-classical coordinates

■ Plait point

FIGURE 10
FIGURE 11