A Phenomenological Correction to an Equation of State for the Critical Region

This work presents a phenomenological correction to improve a classical equation of state for representing phase equilibria and densities in the vapor-liquid critical region. This correction consists of two steps. The first step is a volume translation which locates the correct critical point; this volume translation also improves density predictions for pure fluids and mixtures. The second step provides a near-critical contribution to the residual Helmholtz energy which accounts for anomalous behavior near the critical point. For pure fluids, the near-critical contribution flattens the coexistence curve and pressure-density isotherms near the critical point. For mixtures, the near-critical contribution has only a small effect on the calculated coexistence curve; this effect is often masked by the choice of binary parameters in the classical equation which have a more profound effect on the calculated results.

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Introduction

For chemical process design, we need molecular-thermodynamic models which accurately represent the thermodynamic properties of fluids and fluid mixtures. Toward that end, much effort has been spent on the development of equations of state; since these are continuous in the entire fluid-density range, they can be used to represent phase equilibria for mixtures containing both subcritical and supercritical fluids. Most commonly used equations of state are of the van der Waals type (e.g., Redlich-Kwong and Peng-Robinson). These so-called "classical" equations of state predict the existence of a vapor-liquid critical point, but fail to represent correctly thermodynamic properties in the vicinity of the critical point. In particular, they predict coexistence curves and pressure-density isotherms that are insufficiently flat in the critical region.

Anomalous or nonclassical behavior of fluids in the critical region follows from large-scale fluctuations of the order parameter; for pure fluids near their vapor-liquid critical points, the order parameter is the fluid density. A rigorous theory which describes nonclassical behavior of fluids in the critical region is the powerful renormalization-group theory by Wilson (1983), which provides critical exponents in scaling laws proposed by Widom (1965) for a pure fluid. For binary mixtures, critical exponents and scaling have been extensively discussed by Scott (1972, 1978). Sengers and Levelt Sengers (1978, 1986) have presented comprehensive reviews of theories for fluids and fluid mixtures near critical points. The scaling laws and the resulting scaled equation of state for pure fluids (Schofield, 1969) and for binary mixtures (e.g., Leung and Griffiths, 1973; D'Arrigo et al., 1975; Moldover and Gallagher, 1978; Rainwater and Williamson, 1986) give correct limiting properties at the critical point, but they are valid only very near the critical point.

To establish an equation of state which is useful both near and remote from critical, various techniques have been suggested (e.g., Chapela and Rowlinson, 1974; Fox, 1983; Erickson and Leland, 1986; Albright et al., 1986). These techniques attempt to solve the crossover problem, i.e., to construct an equation of state which represents both singular scaling behavior and analytical classical behavior. Such an equation is unattractive for engineering applications, because it is mathematically complex and often requires a large number of system-dependent parameters. Moreover, an equation often uses thermodynamic field variables (T, P, μ) rather than directly measurable equation-of-state variables (T, P, ρ).

Our goal here is not to solve the crossover problem rigorously, but to develop an analytical equation of state which reasonably represents thermodynamic properties and phase equilibria both near and far from the critical region. Toward that end, we propose a phenomenological correction to a classical equation of the van der Waals form which accounts for critical-region effects. To determine quantitatively the critical-region effects on phase behavior, however, the classical equation must first predict rea-

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sonably accurate phase equilibria outside the critical region, and it must locate the true critical point correctly.

For a pure fluid, the critical point is identified by three coordinates: T_c, P_c, and v_c. For equations of the van der Waals type, the two adjustable parameters for the critical isotherm correctly represent the critical temperature and one of the other two coordinates. As shown in Figure 1, if the equation-of-state parameters are obtained from the experimental critical temperature and critical volume, the predicted critical pressure is too high. Similarly, if the parameters are obtained from the experimental critical temperature and critical pressure, the predicted critical density is too low.

We propose a two-step correction for these classical equations. The first step uses a linear transformation in the volume coordinate (also called volume translation) to enable the equation to locate the critical point correctly. The second step provides a near-critical contribution to the residual Helmholtz energy which flattens the coexistence curve and pressure-density isotherms in the critical region. Our work differs from that of Brandani and Prausnitz (1981) who used a single empirical correction which is not easily extended to mixtures. For illustration, we apply our correction to the Soave-Redlich-Kwong (SRK) equation (Soave, 1972). Application is here directed at mixtures encountered in petroleum and natural-gas technology.

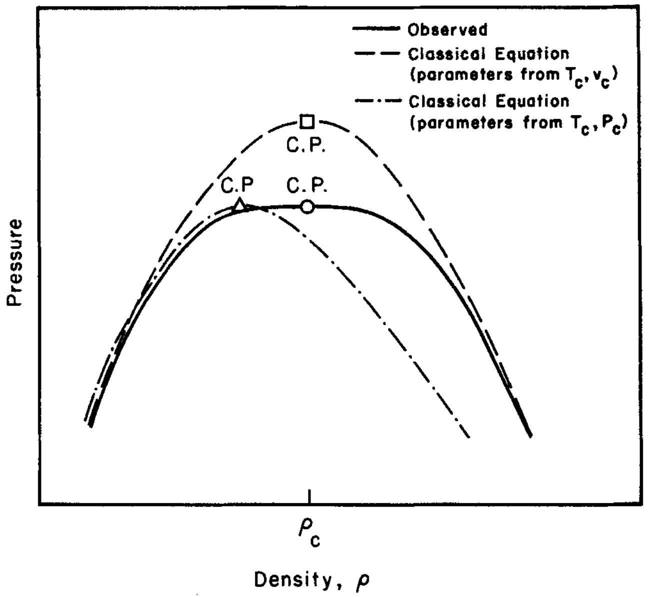

Figure 1. Coexistence curve in the critical region: classical vs. observed.

Volume Translation for a Pure Fluid

Volume translation was first proposed by Martin (1967) to improve critical-compressibility predictions for the van der Waals equation; Martin's proposal was revived by Péneloux et al. (1982) for improving liquid-density prediction for the SRK equation for reduced temperatures below 0.7. Our procedure is a refinement of that of Péneloux et al. (1982); we also consider temperatures above 0.7, including the critical region. Mathias et al. (1989) recently proposed a volume-translation procedure similar to ours for improving density predictions from the Peng-Robinson equation of state.

The SRK equation is

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \tag{1}$$

where $a(T)$ and b are adjustable parameters, and R is the gas constant. Experimental critical temperature and critical pressure are used to calculate parameters b and $a(T_c)$. The effect of temperature on parameter $a(T)$ is determined from correlations proposed by Soave (1972, 1979).

Saturated liquid volumes (densities) predicted from the SRK equation are displaced from the experimental values; for a pure component, this displacement increases as conditions approach critical and reaches a maximum near the critical point. The volume translated, therefore, must be a function of the "distance" between a state point and the critical point. For a pure component, a suitable variable for characterizing this distance is the slope of the pressure-density isotherm, $(\partial P/\partial \rho)_T$; this slope also determines if the system is intrinsically stable in a homogeneous phase. The locus of the limit of intrinsic stability, $(\partial P/\partial \rho)_T = 0$, is the spinodal curve; the critical point is a stable state on the spinodal curve. Based on the intrinsic stability, we define a dimensionless distance

$$d = \frac{1}{RT_c}\left(\frac{\partial P^{SRK}}{\partial \rho}\right)_T \tag{2}$$

where T_c is the experimental critical temperature, and ρ is the molar density. To avoid iterative solutions, d is calculated from the original SRK equation, P^{SRK}. To preserve vapor pressures predicted from the original SRK equation, we constrain distance d to depend only on temperature. For subcritical temperatures, d is evaluated at the saturated liquid density; for supercritical temperatures, d is evaluated at the critical isochore. Distance d is zero at the critical temperature and positive elsewhere.

Once an appropriate distance variable is chosen, the true volume v is then translated from the "apparent" volume $\hat{v}$ predicted from the SRK equation as a function of the distance variable. A one-parameter inverse-linear function describes this translation:

$$v = \hat{v} - c - \delta_c\left(\frac{\eta}{\eta + d}\right) \tag{3}$$

where c is the constant translation used by Péneloux et al. (1982) to correct for densities remote from critical, η is a universal constant determined from regression of coexistence data for pure fluids, $\eta = 0.35$. The volume shift at the critical temperature, δ_c, is given by

$$\delta_c = \frac{RT_c}{P_c}(z_c^{SRK} - z_c) \tag{4}$$

where T_c, P_c, and z_c are the experimental critical temperature, pressure, and compressibility factor, respectively; z_c^{SRK} has the universal value $1/3$.

Since the distance variable chosen is only temperature-dependent, the translation of the SRK equation is linear in volume. This linearity provides a useful advantage; as pointed out by Péneloux et al. (1982), linear translation preserves the vapor-pressure curve predicted from the original SRK equation. Preservation of vapor pressures allows use of the original temperature dependence $a(T)$ proposed by Soave.

Near-Critical Contribution to Residual Helmholtz Energy for a Pure Fluid

Once volume translation locates the true critical point, we introduce a near-critical contribution to flatten the coexistence curve in the vicinity of the critical point. The near-critical contribution is for the residual Helmholtz energy; derivatives of the residual Helmholtz energy provide the equation of state, residual chemical potential, and residual enthalpy.

The molar residual Helmholtz energy, a^r, is the difference between the molar Helmholtz energy of the real fluid and that of an ideal gas at the same temperature and density: $a^r = a - a^{id}$. We assume that the true residual Helmholtz energy is the sum of a classical contribution, a^C, and a near-critical contribution, a^{NC}:

$$a^r = a^C + a^{NC} \tag{5}$$

where we obtain a^C from integrating the volume-translated SRK equation.

Since a^{NC} represents critical-region effects, it should be a maximum at the true critical point and decay to zero according to a characteristic distance from the true critical point. Upon studying the observed curvature of the critical isotherm for carbon dioxide, we find that distance d in volume translation does not adequately characterize the distance for both vapor and liquid due to asymmetry in the curvature. Upon dividing d by the reduced density, ρ/ρ_c, we obtain a dimensionless distance variable, D:

$$D = \frac{1}{\rho}\left(\frac{\partial P^{SRK-VT}}{\partial \rho}\right)_T \left(\frac{\rho_c}{RT_c}\right) \tag{6}$$

where P^{SRK-VT} is the volume-translated SRK equation. Since D is an explicit function of both temperature and density, it can be calculated without iterations. Distance D is zero at the true critical point and positive elsewhere in all physically meaningful PVT space.

For the near-critical contribution, we assume an exponential function which satisfies the necessary boundary conditions and provides good decay properties:

$$\frac{a^{NC}}{RT_c} = a_m^{NC} \exp(-wD^2) \tag{7}$$

where a_m^{NC} is a constant representing the maximum contribution at the true critical point, and w is a constant reflecting how fast the function decays as a system moves away from the true critical point. To fix both a_m^{NC} and w, we have correlated coexistence data for ten pure fluids indicated in Table 1: $a_m^{NC} = 7 \cdot 10^{-4}$ and $w = 90$. Appendix A gives details on data reduction.

The use of an exponential function to describe near-critical anomalies has been proposed by other researchers (e.g., Haar et al., 1984; Schreiber and Pitzer, 1988). These previously proposed near-critical corrections, however, use separate distances for temperature and density which require several system-dependent parameters; it is not clear how these equations can be generalized to mixtures.

Results for Pure Fluids

We compare experimental results for the coexistence curve and the critical isotherm with those calculated from: 1) the original SRK equation, 2) SRK equation with volume translation (SRK-VT), and 3) SRK equation with volume translation and near-critical Helmholtz energy (SRK-VT-NC). For all figures shown here, pressure and density are reduced by the respective criticals.

Table 1. Deviations in Calculated Saturated Liquid Densities for Ten Pure Fluids

Component	Reduced Temp. Range	% Avg. Abs. Dev. in Liq. Dens. SRK*	SRK-VT-NC**
Methane	0.48–0.997	6.1	2.6
Ethane	0.42–0.999	8.8	2.1
Propane	0.26–0.987	8.2	2.0
n-Butane	0.32–0.988	9.6	1.7
Ethene	0.56–0.998	8.7	3.1
Propene	0.51–0.998	7.2	1.4
Carbon Dioxide	0.72–0.999	13.1	1.1
Nitrogen	0.51–0.998	5.7	2.4
Water	0.45–0.997	28.2	3.0
Hydrogen Sulfide	0.77–0.992	12.1	0.9

*SRK – original SRK EOS

**SRK-VT-NC – SRK EOS with volume translation and near-critical Helmholtz energy

Figures 2, 3, and 4 show coexistence curves for methane, water, and n-butane, respectively; volume translation shifts the top of the coexistence curve from the apparent critical point to the true critical point. Since volume translation preserves the vapor pressure curve, the length of the vapor-liquid volume tie line is unchanged as a result of volume translation. However, since linear transformation in volume implies nonlinear trans-

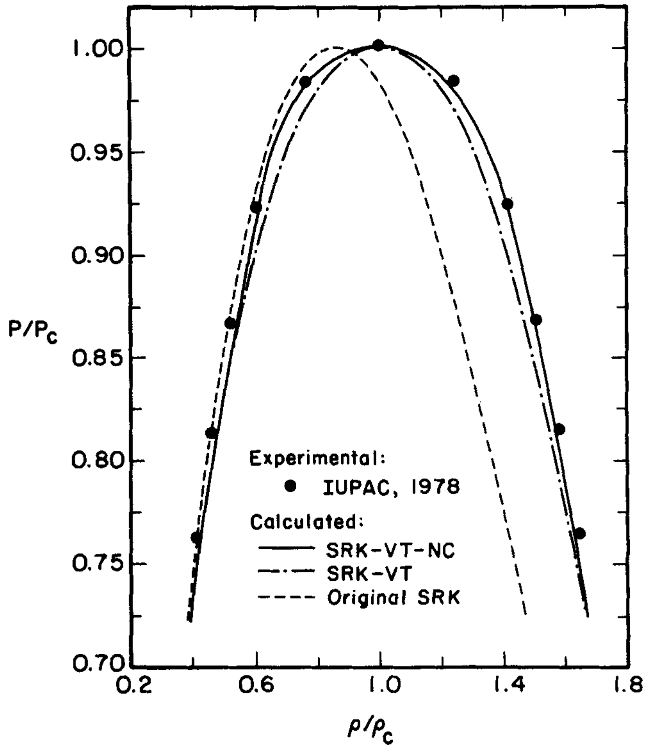

Figure 2. Coexistence curve for methane in the region 0.96 < T_r < 1.0.

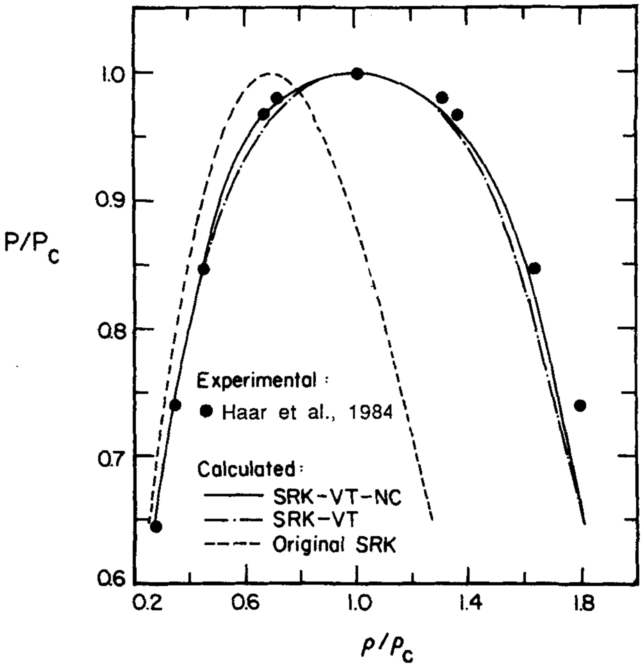

Figure 3. Coexistence curve for water in the region 0.94 < T_r < 1.0.

Calculations based on modified temperature dependence for SRK parameter "a" for polar and quantum fluids (Soave, 1979).

formation in density, volume translation results in lengthened tie lines in the two-phase region of a pressure-density diagram. The near-critical contribution further flattens the coexistence curves, giving good agreement with experiment in the critical region.

Table 1 presents deviations in calculated saturated liquid densities for ten components over temperature ranges both within and outside the critical region. Since the critical region comprises only a small fraction of the temperature range shown, the deviations reflect mostly the noncritical region; it is evident that volume translation not only locates the correct critical point, but significantly improves liquid-density predictions over a wide temperature range. Since vapor volumes are much larger than liquid volumes, volume translation has a much smaller effect on vapor densities.

Figure 5 shows a plot for estimating critical exponent β over a small reduced-temperature range. Critical exponent β is defined along the coexistence curve in the asymptotic limit of the critical point:

$$|\rho_r - 1| \propto |T_r - 1|^{\beta} \tag{8}$$

where T_r and ρ_r are reduced temperature and reduced density, respectively.

The renormalization-group theory predicts $\beta \approx 0.33$ for all systems that belong to the 3-D Ising-like universality class. Experimental observations give similar values for β. Since the definition of β applies only in the singular asymptotic limit of the critical point, Figure 5 gives only an "apparent" β for the temperature range indicated; this apparent β reflects the flatness of the coexistence curve.

Figure 6 compares calculated and experimental critical isotherms for carbon dioxide. Volume translation shifts the inflection point of the isotherm from the apparent critical point to the true critical point and also somewhat flattens the isotherm. The near-critical contribution further flattens the isotherm by providing a positive pressure correction to the vapor-like region and a negative pressure correction to the liquid-like region; the near-

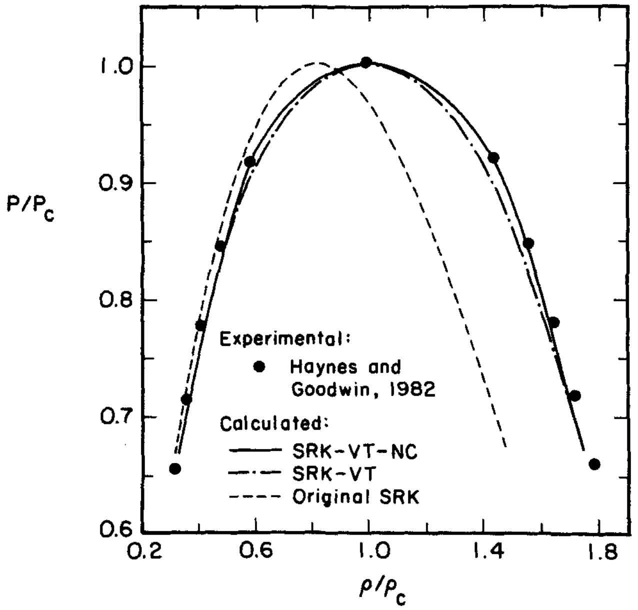

Figure 4. Coexistence curve for *n*-butane in the region 0.94 < T_r < 1.0.

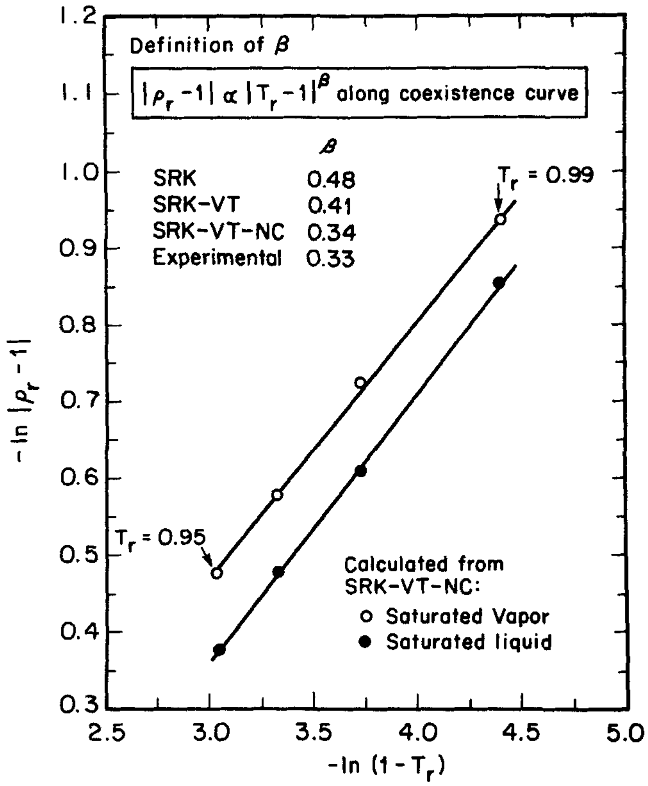

Figure 5. Apparent critical exponent β for *n*-butane in the region 0.95 < T_r < 1.0.

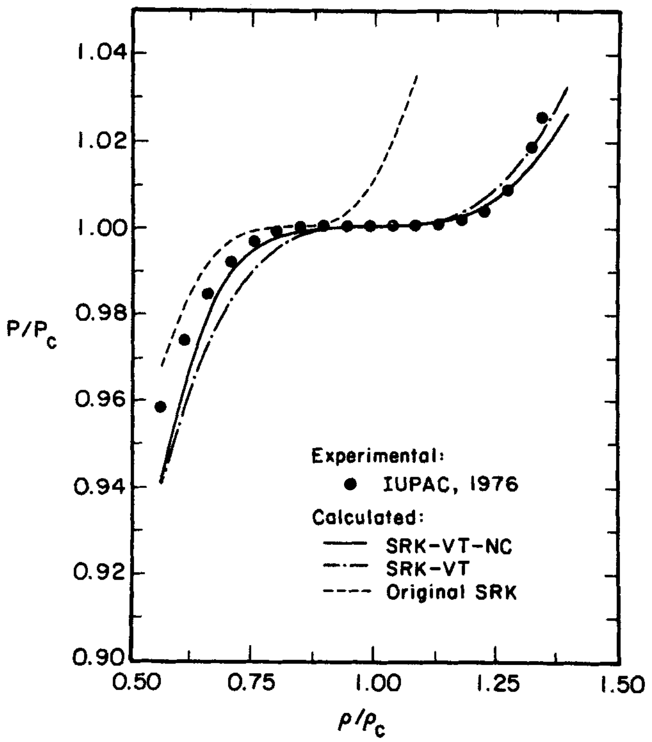

Figure 6. Critical isotherm for carbon dioxide.

critical contribution to pressure is zero at the true critical point.

Extension to Mixtures

For a simple mixture, the critical-temperature locus and the critical-pressure locus predicted by the SRK equation are reasonably accurate. (See, for example, Heidemann and Khalil, 1980.) The predicted critical-volume locus, however, is usually displaced from the experimental data. We now apply our two-step correction for pure fluids to mixtures.

Mixture distance function for volume translation

To extend the proposed correction to mixtures, we must first choose an appropriate variable which characterizes the distance between a state point and a point on the critical locus. To obtain a direct extension from pure fluids, we use the intrinsic-stability limit for a mixture (e.g., Modell and Reid, 1983) as a guide to define the distance variable.

The limit of intrinsic stability for a binary mixture is often expressed in terms of a Gibbs-energy derivative (Rowlinson and Swinton, 1982). However, when a pressure-explicit equation of state is used to correlate fluid properties, the most convenient form for the stability criterion uses the Helmholtz energy. Beegle et al. (1974) showed that, by considering different ordering of independent variables in the fundamental equation of thermodynamics and by taking different Legendre transforms of the fundamental equation, the stability criterion may be expressed in terms of other thermodynamic functions, including the Helmholtz energy. Further, depending on the choice of composition variables in the fundamental equation, the stability criterion may use either mole fractions or mole numbers as working variables.

To illustrate, we describe here the distance variable for a binary mixture. As described in Appendix B, we write the fundamental equation for a binary with the following ordering of independent variables:

$$U = U(S, V, n_1, n) \tag{9}$$

where U, S, V and n are the total internal energy, total entropy, total volume, and total number of moles, respectively; n_1 is the number of moles of component 1.

Based on the first-order Legendre transform of Eq. 9 with respect to entropy, the stability criterion may be expressed in terms of derivatives of the molar Helmholtz energy $\boldsymbol{a}$ (Modell and Reid, 1983):

$$\begin{vmatrix} a_{vv} & a_{v1} \\ a_{v1} & a_{11} \end{vmatrix} = 0 \tag{10}$$

where the subscripts denote differentiation variables; subscript v indicates the molar volume, and subscript 1 indicates the mole fraction of component 1.

Based on this stability criterion, we define a dimensionless distance variable for a binary mixture which, in the pure-component limit, properly reduces to that for a pure fluid, as shown in Appendix B:

$$d_M = \frac{1}{RT_{cM}}\left(\frac{\partial P^{SRK}}{\partial \rho}\right)_T - \left(\frac{1}{RT_{cM}\,\rho^2}\right)\frac{a_{v1}^2}{a_{11}} \tag{11}$$

where T_{cM} is the critical temperature of the mixture. As for pure fluids, to avoid iterative solutions, d_M is calculated from the original SRK equation. In the limit of either pure 1 or pure 2, a_{11} becomes infinite; in that event, d_M reduces to distance d for a pure fluid.

Volume translation for mixtures

As a direct extension from pure fluids, volume translation for a mixture is a function of distance d_M:

$$v = \tilde{v} - c_M - \delta_{cM}\left(\frac{\eta}{\eta + d_M}\right) \tag{12}$$

where we use a linear mixing rule for c_M, $c_M = \Sigma\, x_i c_i$, as proposed by Péneloux et al. (1982); δ_{cM}, as discussed subsequently, is the constant needed to locate the correct critical volumes for a mixture.

To determine δ_{cM}, we must first consider the path (i.e., isotherm or isochore or isopleth) along which thermodynamic states approach critical; in other words, we must specify the particular point on the critical line or surface from which the distance (from critical) is measured. Upon studying deviations in calculated volumes for several binary mixtures, it appears that the isopleth is the most suitable path. For a given state, the relevant critical point is the one having the same composition as that of the given state. Therefore, δ_{cM} is a function only of composition, $\underline{x}$:

$$\delta_{cM} = \tilde{v}_{cM}(\underline{x}) - v_{cM}(\underline{x}) - c_M \tag{13}$$

where $\tilde{v}_{cM}(\underline{x})$ is the apparent mixture critical volume predicted from the SRK equation and $v_{cM}(\underline{x})$ is the true critical volume.

For a given composition, the apparent critical volume, $\hat{v}_{cM}$, is calculated using computational algorithms developed by Heidemann and Khalil (1980). To estimate the true critical volume, v_{cM}, we use a correlation proposed by Chueh and Prausnitz (1967):

$$v_{cM} = \sum_i \theta_i v_{c_i} + \sum_i \sum_j \theta_i \theta_j v_{ij} \tag{14}$$

where v_{c_i} is the critical volume of pure i; v_{ij} is a binary parameter characteristic of the i-j interaction where $v_{ii} = v_{jj} = 0$; and θ_i is the surface fraction of i defined by

$$\theta_i = \frac{x_i v_{c_i}^{2/3}}{\sum_i x_i v_{c_i}^{2/3}}. \tag{15}$$

where x_i is mole fraction.

As for pure fluids, to preserve the original vapor-liquid equilibria, the contribution from volume translation to the chemical potential of each component must be the same for the coexisting phases. Therefore, both δ_{cM} and d_M are evaluated at liquid-phase conditions only.

Near-critical Helmholtz energy for mixtures

To account for critical-region effects in mixtures, we represent the near-critical Helmholtz energy by the same expression as that for pure fluids:

$$\frac{a^{NC}}{RT_{cM}} = a_m^{NC} \exp\left(-wD_M^2\right) \tag{16}$$

where T_{cM} is the critical temperature of the mixture; a_m^{NC} and w are the same universal constants as those for pure fluids. As a direct extension from pure fluids, distance D_M is related to distance d_M (Eq. 11) used in volume translation:

$$D_M = \frac{\rho_{cM}}{\rho RT_{cM}} \left[\left(\frac{\partial P^{SRK-VT}}{\partial \rho} \right)_T - \frac{1}{\rho^2} \frac{a_{v1}^2}{a_{11}} \right] \tag{17}$$

where ρ_{cM} is the critical density of the mixture, $\rho_{cM} = 1/v_{cM}$; the volume-translated SRK equation is used to evaluate D_M.

Equation-of-state parameters for mixtures

To calculate phase equilibria for mixtures, the equation-of-state parameters for mixtures, a_m and b_m, are calculated using conventional mixing rules:

$$a_m = \sum_i \sum_j z_i z_j (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) \tag{18}$$

and

$$b_m = \sum_i \sum_j z_i z_j \left(\frac{b_{ii} + b_{jj}}{2} \right) (1 - l_{ij}) \tag{19}$$

where z is mole fraction; a_{ii}, a_{jj}, b_{ii}, and b_{jj} are pure-component parameters; and k_{ij} and l_{ij} are binary parameters characteristic of i-j interaction; $k_{ii} = k_{jj} = 0$ and $l_{ii} = l_{jj} = 0$.

Results for Mixtures

We compare phase equilibria and densities calculated from the corrected equation of state with those calculated from the original SRK equation and with experimental data. In general, as for pure fluids, volume translation improves predicted liquid densities both within and outside the critical region, and has little effect on vapor densities. In most cases, however, the near-critical contribution does not have an appreciable effect on calculated results; as shown in the following, binary parameters k_{ij} and l_{ij} have a more profound effect.

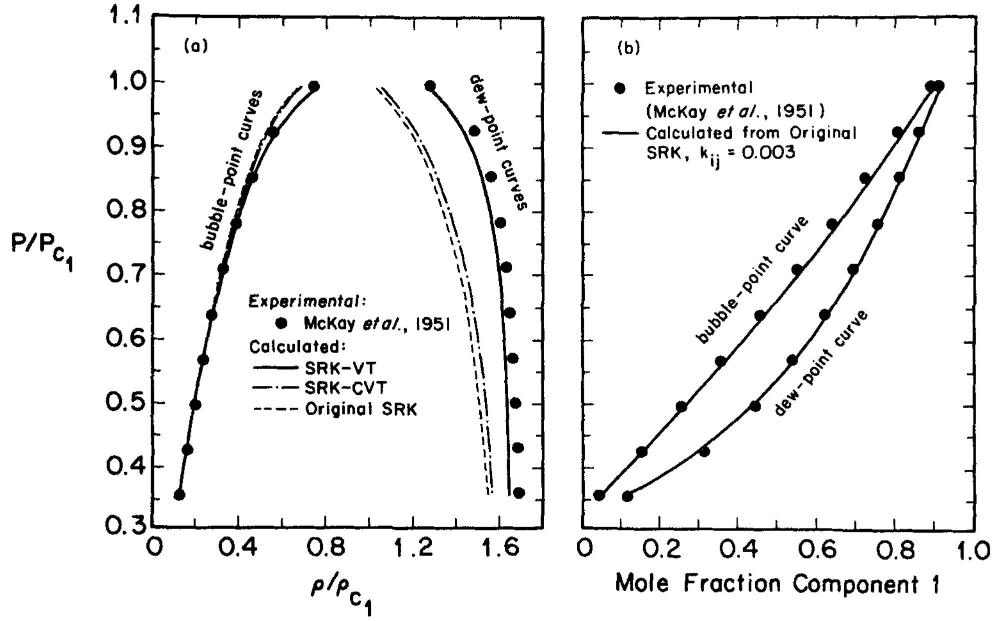

Figure 7. Vapor-liquid equilibria for ethane(1)/propene at 311 K.
a. Pressure-density diagram
b. Pressure-composition diagram.

Figure 7a compares a calculated and experimental pressure-density isotherm for the ethane/propene binary at 311 K. Figure 7a illustrates the typical results from volume translation for a simple mixture containing components that are similar in size. The constant volume translation (CVT) proposed by Péneloux et al. (1982) slightly improves the predicted liquid densities. The distance-dependent translation further improves predicted densities both near and far from the critical point; it also shifts the mixture critical point toward better agreement with experiment. Figure 7b shows this isotherm in pressure-composition ($P - x - y$) coordinates; for this simple mixture, the SRK equation adequately represents phase equilibria with a near-zero k_{ij}. For this mixture, the near-critical contribution does not have any significant effect on the calculated results.

Figure 8 shows the calculated $P - x - y$ isotherm for the methane/carbon dioxide binary at 230 K. As for most mixtures studied here, the effect of the near-critical contribution on phase equilibria is evident only very near the critical point. Figure 9 shows an enlargement of the critical region for this system; the near-critical contribution lengthens the $x - y$ tie line, giving slightly better agreement with experiment.

For a highly asymmetric mixture, such as a light gas/heavy hydrocarbon system, calculated phase equilibria and densities depend strongly on the binary parameters. Figure 10 illustrates the effect of k_{ij} and l_{ij} on the calculated $P - x - y$ diagram for the carbon dioxide/n-decane binary at 344 K. Using only k_{ij}, the calculated $P - x$ curve is able to represent the experimental data either remote from or near the critical region, but not both. A small negative l_{ij}, however, alters the slope of the calculated $P - x$ curve and makes it possible to represent data both near and far from the critical point. Since calculated phase equilibria are sensitive to the choice of binary parameters, a near-critical contribution here is superfluous.

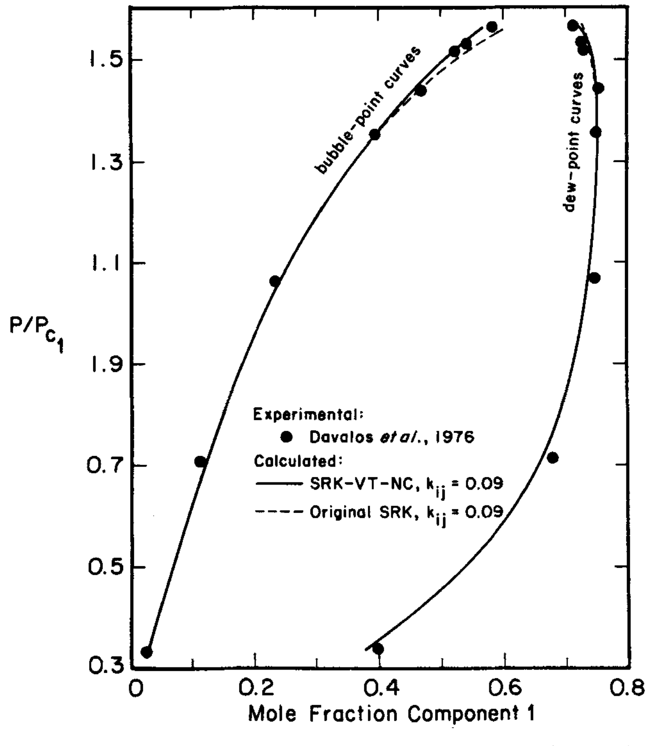

Figure 8. Pressure-composition diagram for methane(1)/carbon dioxide at 230 K.

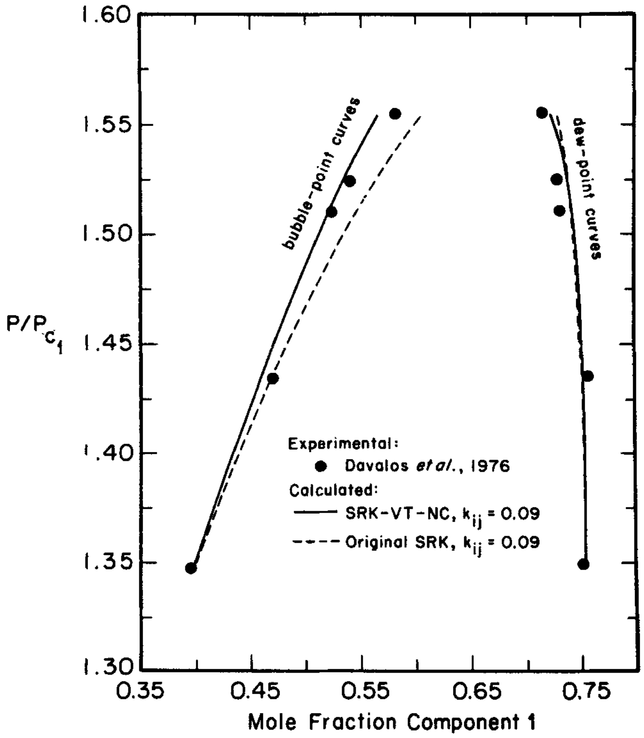

Figure 9. Pressure-composition diagram for methane(1)/carbon dioxide at 230 K in the vicinity of the critical point.

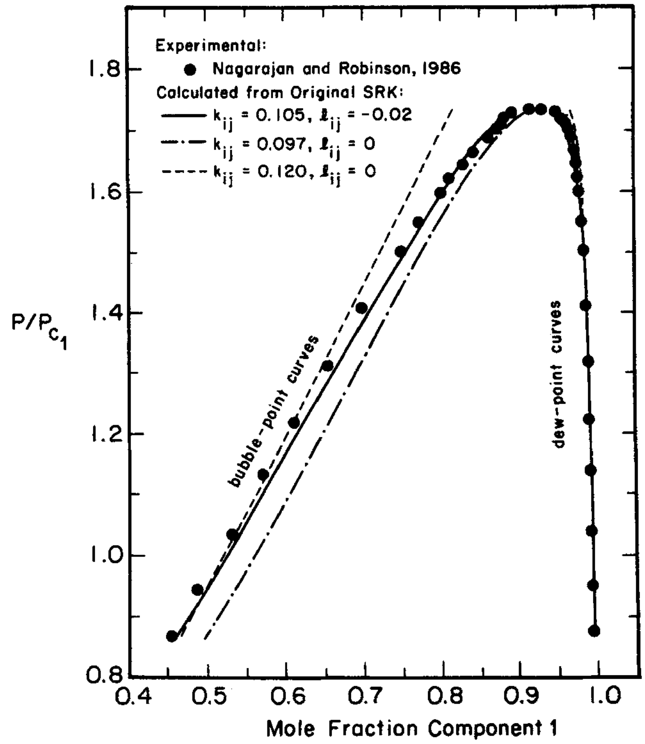

Figure 10. Pressure-composition diagram for carbon dioxide(1)/n-decane at 344 K: effect of binary parameters.

To demonstrate the effect of volume translation on the calculated densities for an asymmetric mixture, Figure 11 compares experimental pressure-density curves for the carbon dioxide/*n*-decane system at 344 K with those calculated from the SRK and SRK-VT equations. As for simple mixtures, volume translation significantly improves liquid-density prediction both near and far from the critical region; it also shifts the predicted critical density toward the experimental critical density. However, as indicated in Figure 11, there is still a slight discrepancy between the predicted and the experimental critical density. This discrepancy may be attributed to limitations in Chueh's correlation for estimating critical volume. Unless critical-volume data are available, the critical points for a mixture cannot be exactly located because their locations depend on the correlation used to estimate them.

Conclusions

A phenomenological correction is proposed for a classical equation of state of the van der Waals form to improve representation of thermodynamic properties in the critical region. The correction uses volume translation to locate the critical point more accurately and a near-critical Helmholtz energy to account for anomalies in the neighborhood of the critical point. The proposed correction uses universal parameters applicable to pure fluids and mixtures. For illustration, the correction has been applied to the SRK equation; however, the correction described here may be applied to any equation of state of the van der Waals form.

For pure fluids, the corrected equation reproduces the experimental critical point exactly and provides more accurate densities both near and remote from the critical region. Near the critical point, the corrected equation gives coexistence curves and pressure-density isotherms flatter than those obtained from the original classical equation.

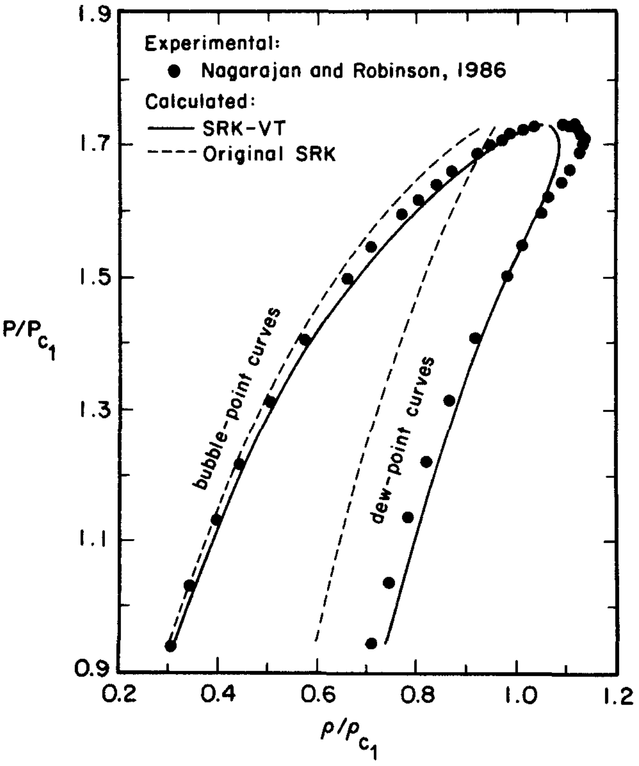

Figure 11. Pressure-density diagram for carbon dioxide(1)/*n*-decane at 344 K.

For mixtures, volume translation improves density predictions both near and far from the critical region; it also locates the critical density of a mixture more accurately than does the original equation. In general, however, the near-critical contribution does not have an appreciable effect on calculated phase equilibria, because the choice of binary parameters in the classical equation has a dominant effect on calculated results. For highly asymmetric mixtures, where the SRK equation is seriously deficient (indicated by the large values of the binary parameters), the near-critical contribution is superfluous.

In addition to the deficiencies of the classical equation, the rather small effect of the near-critical contribution for mixtures may be partly a result of our choice for the distance parameter. The critical region for mixtures is probably larger than that indicated here if some other distance parameter is used in terms of relevant thermodynamic field variables.

For engineering applications, however, it is important that in addition to attempts to correct a classical equation for critical-region effects, the uncorrected equation must accurately represent fluid properties in regions remote from critical. Classical equations that are deficient in regions other than critical tend to give a large extended "critical" region where deficiencies are not due to density fluctuations. Once these "classical" deficiencies are removed, the critical region, measured in terms of engineering-oriented thermodynamic density variables (T, P, x), appears to be small.

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Notation

a = molar Helmholtz energy
a^r = molar residual Helmholtz energy
A = total Helmholtz energy
$a(T)$ = temperature-dependent energy parameter in SRK equation
a_m^{NC} = near-critical Helmholtz energy at the critical point
b = size parameter in SRK equation
c = constant volume translation for pure fluids
c_M = constant volume translation for mixtures
d = pure-component distance for volume translation
d_M = mixture distance for volume translation
D = pure-component distance for near-critical contribution
D_M = mixture distance for near-critical contribution
R = gas constant
T_{cM} = critical temperature of a mixture
v_{cM} = true critical volume of a mixture
$\hat{v}_{cM}$ = apparent mixture critical volume calculated from the original SRK equation
$\hat{v}$ = apparent molar volume calculated from the original SRK equation
w = decay constant in the near-critical contribution
z_c = critical compressibility factor of a pure fluid

Greek letters

β = critical exponent in Eq. 8
δ_c = volume translation at the pure-fluid critical point

δ_{cM} = volume translation at a mixture critical point
η = universal constant in volume-translation function
ρ_c = critical density of a pure component
ρ_{cM} = critical density of a mixture
θ_i = surface fraction of i in Chueh's correlation
v_{ij} = binary parameter in Chueh's correlation

Superscripts and subscripts

SRK = SRK equation
$SRK - VT$ = volume-translated SRK equation
C = classical
NC = near-critical

Appendix A: Data Reduction for Pure Fluids

Before determining parameter η for volume translation and parameters a_m^{NC} and w for the near-critical correction from experimental data, we first consider the possibility of obtaining these parameters from criteria for criticality. For a pure component, criticality requires

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0. \qquad (A1)$$

For the corrected equation of state, these two derivatives include terms containing distance d and density-derivatives of d which all vanish at the critical point. Since critical-state criteria are automatically satisfied due to the definition of distance d, the parameters must be determined from regression of experimental data.

To avoid arbitrary definition of the critical-region boundary, parameters η, a_m^{NC}, and w are fitted simultaneously to coexistent vapor and liquid density data over a wide temperature range. To place emphasis on phase-equilibrium properties, PVT data are not included in the fit; inclusion of PVT data may distort the parameters depending on the range and distribution of the data.

The value and the goodness-of-fit for η is found to be independent of parameters a_m^{NC} and w. However, a_m^{NC} and w, as expected, are correlated and they do not exist as a unique pair. Fortunately, calculated results are not sensitive to small, simultaneous changes in parameters a_m^{NC} and w. The use of universal parameters for volume translation and for the near-critical contribution eliminates the need for arbitrary mixing rules in Eqs. 12 and 16.

Appendix B: Mixture Distance Function from the Stability Criterion

Depending on the set of variables used in the thermodynamic fundamental equation, a stability criterion employing the Helmholtz energy may be expressed in terms of either mole numbers or mole fractions (Modell and Reid, 1983). We derive here distance d_M from the stability criterion that utilizes mole fractions and discuss the reason for selecting this criterion. To illustrate, we consider only a binary mixture.

When the fundamental equation uses the total mole number, n, as one of its independent variables (Eq. 9), the stability criterion consists of mole-fraction derivatives of the molar Helmholtz energy (Eq. 10):

$$\begin{vmatrix} a_{vv} & a_{v1} \\ a_{v1} & a_{11} \end{vmatrix} = 0. \qquad (B1)$$

In the limit of pure 1 or pure 2, a_{11} becomes infinite. If the determinant of this matrix is divided by a_{11}, we obtain the quantity Q:

$$Q = a_{vv} - \frac{a_{v1}^2}{a_{11}}. \qquad (B2)$$

In either pure-component limit, Q reduces to a_{vv} which is related to the pure-component distance variable, $(\partial P/\partial \rho)_T$:

$$a_{vv} = \rho^2(\partial P/\partial \rho)_T \qquad (B3)$$

We divide Q by $RT_{cM}\rho^2$ to obtain the dimensionless distance d_M for a binary mixture (Eq. 11):

$$d_M = \frac{1}{RT_{cM}}\left(\frac{\partial P^{SRK}}{\partial \rho}\right)_T - \left(\frac{1}{RT_{cM}\rho^2}\right)\frac{a_{v1}^2}{a_{11}} \qquad (B4)$$

To investigate the possible use of the stability criterion in mole-number derivatives, we rewrite the fundamental equation employing mole numbers of all individual components:

$$U = U(S, V, n_1, n_2). \qquad (B5)$$

The stability limit derived from Eq. B5 consists of mole-number derivatives of the total Helmholtz energy A:

$$\begin{vmatrix} A_{VV} & A_{V1} \\ A_{V1} & A_{11} \end{vmatrix} = 0 \qquad (B6)$$

where subscript 1 refers to differentiation with respect to the number of moles of component 1, and subscript V refers to differentiation with respect to the total volume.

A_{11} represents the change of chemical potential of component 1 with respect to its mole number, $(\partial\mu_1/\partial n_1)_{T,n_2}$, which diverges in the limit of pure 1. However, in the limit of pure 2, A_{11} remains finite. The distance variable derived from Eq. B6 is not suitable, since it reduces to the pure-component distance only at one end of the binary mixture.

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