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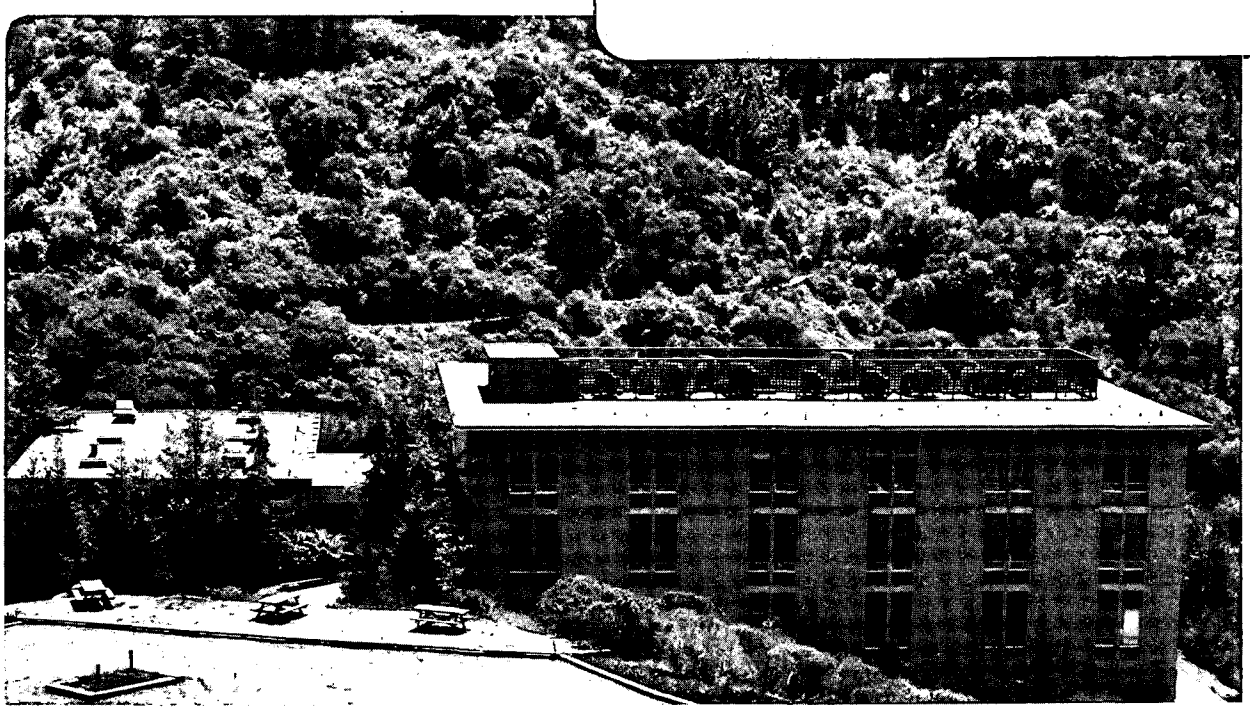

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A PHENOMENOLOGICAL CORRECTION TO AN EQUATION OF STATE FOR THE CRITICAL REGION

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ABSTRACT

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 "nonclassical" contribution to the residual Helmholtz energy which accounts for density fluctuations near the critical point. For pure fluids, the nonclassical contribution flattens the coexistence curves and pressure-density isotherms near the critical point. For mixtures, the nonclassical 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.

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, Peng-Robinson). These so-called "classical" equations of state predict the existence of a vapor-liquid critical point but the predicted coordinates of the critical point are not in agreement with experiment. Further, classical equations of state 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 and, in addition, they predict much smaller isochoric heat capacities than those observed experimentally. This work presents a phenomenological correction for an equation of state of the van der Waals form to improve representation of thermodynamic properties in the critical region. Application is here directed at mixtures encountered in petroleum and natural-gas technology.

Anomalous or "nonclassical" behavior of fluids in the critical region follows from large-scale fluctuations of the order parameter; for 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 (RG) 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 (Shoefield, 1969) and for binary mixtures (see, for example, Leung and Griffiths, 1973; D'Arrigo et al., 1975; Moldover and Gallagher, 1978; Rainwater and Williamson, 1986) give correct limiting proper-

ties at the critical point but they are valid only very near the critical point. Various procedures have been suggested to solve the crossover problem, i.e., to establish an equation of state which is useful both near and remote from critical conditions.

For pure fluids, Chapela and Rowlinson (1974) pioneered the use of a switching function to shift from a scaled equation to a classical equation; unfortunately, a switching function produces spurious behavior in derivative properties such as the heat capacity. Fox (1983) developed a critical-region scaling method which transforms an analytic classical equation of state to a nonclassical equation that gives correct scaling behavior near the critical point while preserving classical behavior outside the critical region. Erickson and Leland (1986) later modified Fox's method and applied it to a 32-constant equation of the Benedict-Webb-Rubin form. These authors concluded that accurate scaling cannot be achieved if the classical equation shows significant inaccuracies outside the critical region; further, some undesirable features of the classical equation may be enhanced by the scaling method. Albright et al (1986) developed a "crossover" formalism which joins the scaled behavior and classical behavior in a theoretically consistent manner; however, this formalism requires a large number of system-dependent constants.

The authors cited have attempted to construct an equation which represents both singular scaling behavior and analytical classical behavior. Such equations are unattractive for engineering applications because they are mathematically complex, and they often require a large number of system-dependent parameters. Moreover, it is not clear how such equations can be extended to mixtures; at present, most work in this area is limited to pure components.

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 commonly used two-parameter equation of state by taking into account the effect of density fluctuations. However, to determine quantitatively the effect of density fluctuations on phase behavior, the classical equation must first predict reasonably 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 classical equations of the van der Waals form, 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 pressure, the predicted critical density is too low.

We propose two corrections for these classical equations. To enable the equation to locate the critical point correctly, the first correction uses a linear transformation in the volume coordinate (also called volume translation). The second correction is a "nonclassical" contribution to the residual Helmholtz energy which accounts for density fluctuations in the critical region. To illustrate, we apply our corrections to the Soave-Redlich-Kwong (SRK) equation (Soave, 1972). Our work differs from that of Brandani and Prausnitz (1981) and of Larsen and Prausnitz (1980); these authors used a single empirical correction which is not easily extended to mixtures.

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 Peneloux et al (1982); we also consider temperatures above 0.7, including the critical region. Mathias et al. (1988) 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 universal 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 Peneloux et al (1982) to correct for densities remote

from critical and where η is a universal constant determined from regression of coexistence data for pure fluids: η =0.35. The volume shift at the critical temperature, δ_c, is given by

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

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 highly useful advantage. As pointed out by Peneloux 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.

Nonclassical Contribution to Residual Helmholtz Energy for a Pure Fluid

Once volume translation locates the true critical point, we introduce a near-critical correction to flatten the coexistence curve in the vicinity of the critical point. We call this near-critical correction "nonclassical" since it accounts for density fluctuations near the critical point. The nonclassical correction 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, $\mathbf{a}^r$, is the difference between the molar Helmholtz energy of the real fluid and that of an ideal gas at the same temperature and density: $\mathbf{a}^r = \mathbf{a} - \mathbf{a}^{id}$. We assume that the true residual Helmholtz energy is the sum of a classical contribution, $\mathbf{a}^C$, and a nonclassical contribution, $\mathbf{a}^{NC}$:

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

where we obtain $\mathbf{a}^C$ from integrating the volume-translated SRK equation.

Since $\mathbf{a}^{NC}$ is due to density fluctuations, it should be a maximum at the true critical point and decay to zero according to a characteristic distance from true the 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 reduced, molar nonclassical Helmholtz energy, we assume an exponential function which satisfies the necessary boundary conditions and provides good decay properties:

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

where a_m^{NC} is a constant representing the maximum nonclassical 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.

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 nonclassical Helmholtz energy (SRK-VT-NC). For all figures shown here, pressure and density are reduced by the respective

criticals.

To illustrate, Figures 2, 3, and 4 show, respectively, coexistence curves for methane, water, and n-butane; 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 transformation in density, volume translation results in lengthened tie lines in the two-phase region of a pressure-density diagram. The nonclassical contribution further flattens the coexistence curves, giving good agreement with experiment in the critical region.

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

SRK: Original SRK EOS
SRK-VT-NC: SRK EOS with volume translation and nonclassical Helmholtz energy

Component	Reduced Temperature Range	%Avg.Abs.Dev. in Liq.Dens. SRK	SRK-VT-NC
2 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

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 non-critical 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:

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

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

The renormalization-group theory predicts $\beta \approx 0.33$ for all fluids that belong to the 3-D Ising-like universality class. Experimental observations give similar values for β (Levelt Sengers, 1974). 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 nonclassical contribution further flattens the isotherm by contributing positive pressure to the vapor-like region and negative pressure to the liquid-like region; the nonclassical contribution to pressure is zero at the true critical point. Appendix B discusses the effect of volume translation and nonclassical contribution on the isochoric heat capacity.

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). However, the predicted critical-volume locus 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 corrections 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 (see, for example, Modell and Reid, 1983) as a guide to define the distance variable. To illustrate, we describe here the distance variable for a binary mixture.

The limit of intrinsic stability for a binary mixture is often expressed in terms of a Gibbs-energy derivative:

$$\left(\frac{\partial^2 \mathbf{g}}{\partial x^2}\right)_{T,P} = 0 \tag{9}$$

where **g** is the molar Gibbs energy and x is the mole fraction of one of the components.

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.

As described in Appendix C, we write the fundamental equation for a binary with the following ordering of independent variables:

$$U = U\,(S,\, V,\, n_1,\, n) \tag{10}$$

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. 10 with respect to entropy, the stability criterion may be expressed in terms of derivatives of the molar Helmholtz energy **a** (Model and Reid, 1983):

$$\begin{vmatrix} \mathbf{a}_{vv} & \mathbf{a}_{v1} \\ \mathbf{a}_{v1} & \mathbf{a}_{11} \end{vmatrix} = 0 \tag{11}$$

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 C:

$$d_M = \frac{1}{RT_{cM}} \left(\frac{\partial P^{SRK}}{\partial \rho} \right)_T - \left(\frac{1}{RT_{cM}\, \rho^2} \right) \frac{\mathbf{a}_{v1}^2}{\mathbf{a}_{11}} \tag{12}$$

where T_{cM} is the critical temperature for 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, $\mathbf{a}_{11}$ 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:

$$v = \hat{v} - c_M - \delta_{cM} \left(\frac{\eta}{\eta + d_M} \right) \tag{13}$$

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

To determine δ_{cM}, we must first consider the path traveled by a thermodynamic state as it approaches the critical state; or equivalently, we must specify the particular point on the critical line (surface) that is the end of the path. Upon studying deviations in calculated volumes for several binary mixtures, it appears that the isopleth (constant composition) path is the most suit-

able; for a given state, the end of the path is the critical point having the same composition as that of the given state. Therefore, δ_{cM} is a function only of composition, $\underline{x}$:

$$\delta_{cM} = \hat{v}_{cM}(\underline{x}) - v_{cM}(\underline{x}) - c_M \tag{14}$$

where $\hat{v}_{cM}(\underline{x})$ 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):

$$v_{cM} = \sum_i \theta_i \, v_{c_i} + \sum_i \sum_j \theta_i \, \theta_j \, v_{ij} \tag{15}$$

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

$$\theta_i = \frac{x_i \, v_{c_i}^{2/3}}{\sum_i x_i \, v_{c_i}^{2/3}}. \tag{16}$$

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.

Nonclassical Helmholtz Energy for Mixtures

To account for density fluctuations for mixtures, we represent the nonclassical Helmholtz energy by the same expression as that for pure fluids:

$$\frac{\mathbf{a}^{NC}}{RT_{cM}} = a_m^{NC} \exp\left(-wD_M^2\right) \tag{17}$$

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 the dis-

tance d_M (Eq. 12) used in volume translation:

$$D_M = \frac{\rho_{cM}}{RT_{cM}\rho}\left[\left(\frac{\partial P^{SRK-VT}}{\partial \rho}\right)_T - \frac{1}{\rho^2}\frac{\mathbf{a}_{v1}^2}{\mathbf{a}_{11}}\right] \tag{18}$$

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:

$$a_m = \sum_i \sum_j z_i\, z_j\, (a_{ii}\, a_{jj})^{1/2}\, (1 - k_{ij}) \tag{19}$$

and

$$b_m = \sum_i \sum_j z_i\, z_j\, \left(\frac{b_{ii}+b_{jj}}{2}\right) (1 - l_{ij}) \tag{20}$$

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. However, in most cases, the nonclassical correction does not have an appreciable effect on calculated results; as shown below, binary parameter k_{ij} and l_{ij} have a more profound effect.

Figure 7a compares a calculated and experimental pressure-density isotherm for the ethane/propene binary at 311K. 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 nonclassical 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 230K. As for most mixtures studied here, the effect of the nonclassical 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 nonclassical 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 344K. 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. However, a small negative l_{ij} 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 nonclassical contribution here is superfluous.

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 344K 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 located exactly because their locations depend on the correlation used to estimate them.

Conclusions

A phenomenological correction is proposed for a van der Waals-type classical equation of state to represent thermodynamic properties both near and far from the critical region. The correction uses volume translation to locate the critical point more accurately and a nonclassical Helmholtz energy to account for density fluctuations near the critical point. The proposed volume translation and nonclassical contribution use 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; it can also represent more accurately the isochoric heat capacities in the critical region.

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. However, in general, the nonclassical 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 SRK is seriously deficient (indicated by the large values of the binary parameters), the nonclassical contribution is superfluous.

To account for the effect of density fluctuations in the critical region, the uncorrected equation of state must very accurately represent the properties for both pure fluids and mixtures in

regions remote from critical. Many classical equations, including SRK, are deficient in regions other than critical; they give a large extended "critical" region where deficiencies are not due to density fluctuations. If we use an equation of state that can represent very accurately the properties of pure fluids and mixtures remote from critical, the true critical region is so small that it may not be important for engineering applications.

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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}	nonclassical 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
R	universal gas constant
T_{cM}	critical temperature of a mixture
v_{cM}	critical volume of a mixture
$\hat{v}$	apparent molar volume calculated from the original SRK equation
w	decay constant in nonclassical-Helmholtz-energy function
z_c	critical compressibility factor of a pure fluid

Greek Letters

β	critical exponent
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_{cM} critical density of a mixture

θ_i surface fraction of i in Chueh's correlation

Superscripts and Subscripts

SRK SRK equation

SRK–VT volume-translated SRK equation

C classical

NC nonclassical

Appendix A Data Reduction for Pure Fluids

Before determining parameter η for volume translation and parameters a_m^{NC} and w for 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

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0. \tag{A-1}$$

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 in nonclassical contribution. 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 nonclassical contribution eliminates the need for arbitrary mixing rules in Equations 3 and 7.

Appendix B Isochoric Heat Capacity Along the Critical Isochore

The isochoric heat capacity of a real fluid may be expressed by a sum of an ideal-gas contribution and a residual contribution: $C_v = C_v^{id} + C_v^r$. The residual heat capacity is related to the molar residual Helmholtz energy, $\mathbf{a}^r$ by

$$C_v^r = -T \left(\frac{\partial^2 \mathbf{a}^r}{\partial T^2}\right)_v \tag{B-1}$$

For the corrected equation, $\mathbf{a}^r$ is the molar residual Helmholtz energy obtained from the volume-translated SRK equation plus the nonclassical contribution. Figure B-1 shows C_v^r as a function of reduced temperature along the critical isochore for carbon dioxide. The original SRK equation, like all classical equations, predicts an essentially flat C_v^r vs. T_r curve. Volume translation gives a rise in C_v^r in the critical region. The nonclassical Helmholtz energy further increases C_v^r near the critical point, but contributes negatively at intermediate temperatures; this negative contribution is inevitable due to the existence of an inflection point in Eq. 7.

In the asymptotic limit of the critical point, the isochoric heat capacity diverges weakly along the critical isochore according to the power law:

$$C_v \approx |T_r - 1|^{-\alpha} \tag{B-2}$$

where $\alpha = 0.1$ for real fluids. For classical fluids, $\alpha = 0$, and thus C_v is finite at the critical point.

If it is desirable for C_v to have the proper divergence at the critical point, the nonclassical Helmholtz energy may be multiplied by an exponential function which has a divergent second derivative at the critical point, i.e., Eq. 7 may be modified to

$$\frac{\mathbf{a}^{NC}}{RT_c} = a_m^{NC}\, exp[-wD^2]\, exp[-w_1 |T_r - 1|^{2-\alpha}]. \tag{B-3}$$

where w_1 is an adjustable parameter and where $\alpha = 0.1$.

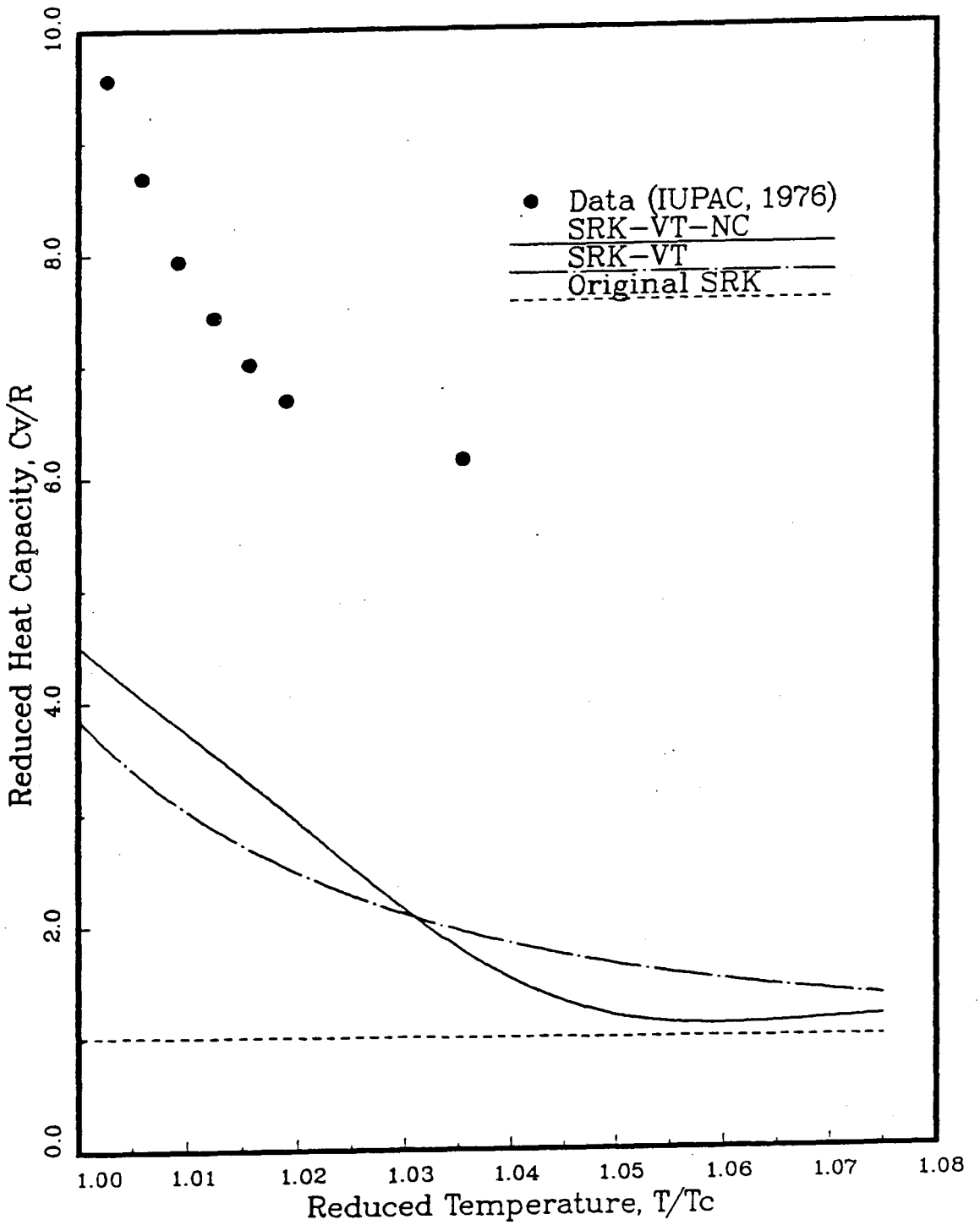

Figure C-1. Isochoric heat capacity for carbon dioxide at reduced density 0.992.

The nonclassical contribution to C_v^r now contains a singular term which diverges at the critical point according to α. With $w_1 = w$, the additional exponential function contributes only very near the critical point; it does not affect significantly C_v^r away from the critical point nor does it affect coexistent and PVT properties.

Appendix C 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. (10)], the stability criterion consists of mole-fraction derivatives of the molar Helmholtz energy [Eq. (11)]:

$$\begin{vmatrix} \mathbf{a}_{vv} & \mathbf{a}_{v1} \\ \mathbf{a}_{v1} & \mathbf{a}_{11} \end{vmatrix} = 0. \tag{C-1}$$

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

$$Q = \mathbf{a}_{vv} - \frac{\mathbf{a}_{v1}^2}{\mathbf{a}_{11}}. \tag{C-2}$$

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

$$\mathbf{a}_{vv} = \rho^2 \, (\partial P/\partial \rho)_T \tag{C-3}$$

We divide Q by $RT_{cM}\,\rho^2$ to obtain the dimensionless distance d_m for a binary mixture [Eq. (12)]:

$$d_M = \frac{1}{RT_{cM}} \left(\frac{\partial P^{SRK}}{\partial \rho} \right)_T - \left(\frac{1}{RT_{cM}\rho^2} \right) \frac{\mathbf{a}_{v1}^2}{\mathbf{a}_{11}} \tag{C-4}$$

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:

$$U = U\,(S, V, n_1, n_2\,). \tag{C-5}$$

The stability limit from Eq. (C-5) consists of mole-number derivatives of the total Helmholtz energy A:

$$\begin{vmatrix} \mathbf{A}_{VV} & \mathbf{A}_{V1} \\ \mathbf{A}_{V1} & \mathbf{A}_{11} \end{vmatrix} = 0 \tag{C-6}$$

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.

$\mathbf{A}_{11}$ 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, $\mathbf{A}_{11}$ remains finite. The distance variable derived from Eq. C-6 is not suitable, since it reduces to the pure-component distance only at one end of the binary mixture.

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

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

Figure 3. Coexistence curve for water in the region $0.94 < T_r < 1.0$. *Modified temperature dependence for SRK parameter "a" for polar and quantum fluids (Soave, 1979).

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

Figure 5. Critical exponent β for n-butane in the region $0.95 < T_r < 1.0$.

Figure 6. Critical isotherm for carbon dioxide.

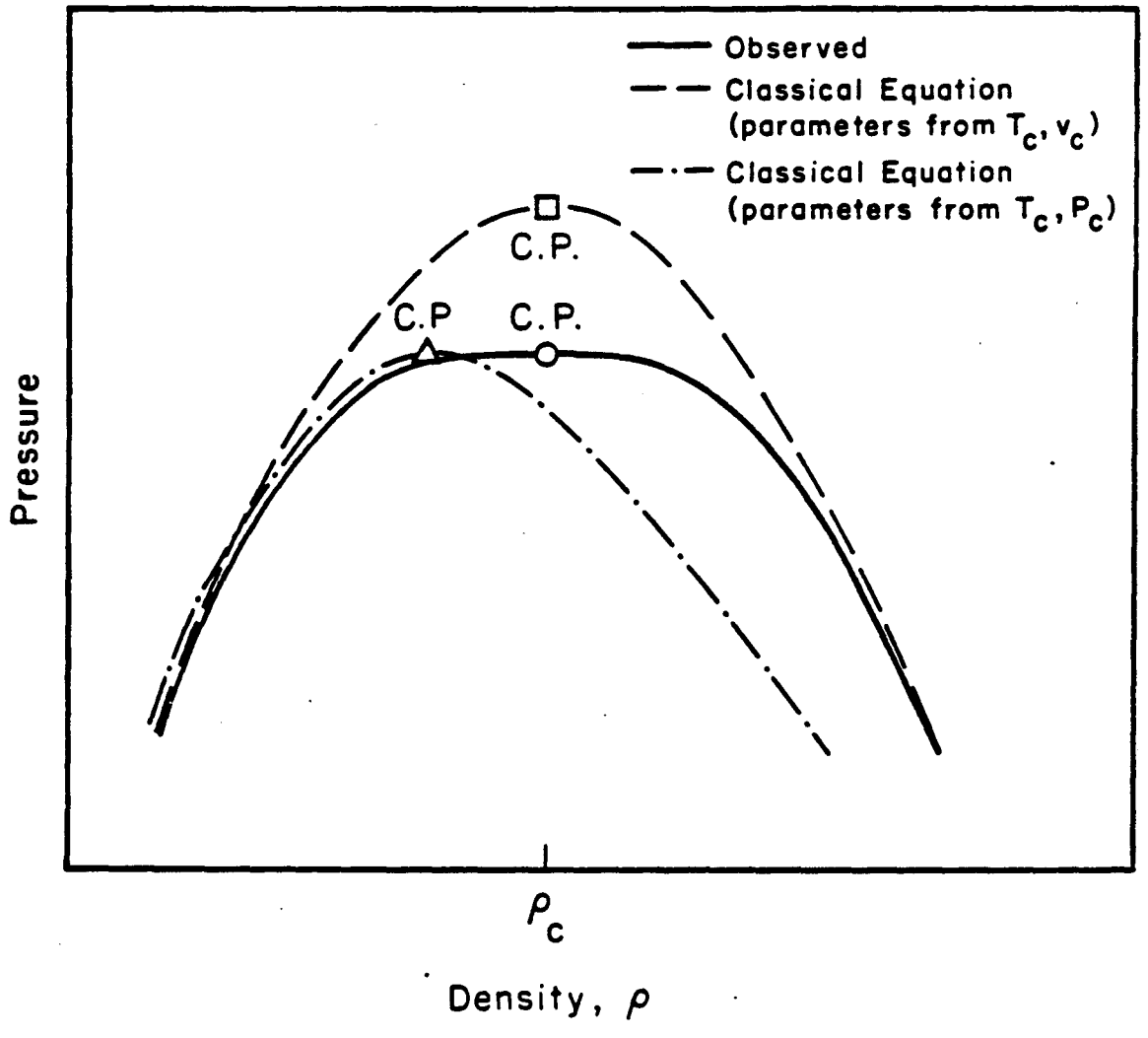
Figure 7. Vapor-liquid equilibria for ethane(1)/propene at 311K. (a) Pressure-density diagram; (b) pressure-composition diagram.

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

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

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

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



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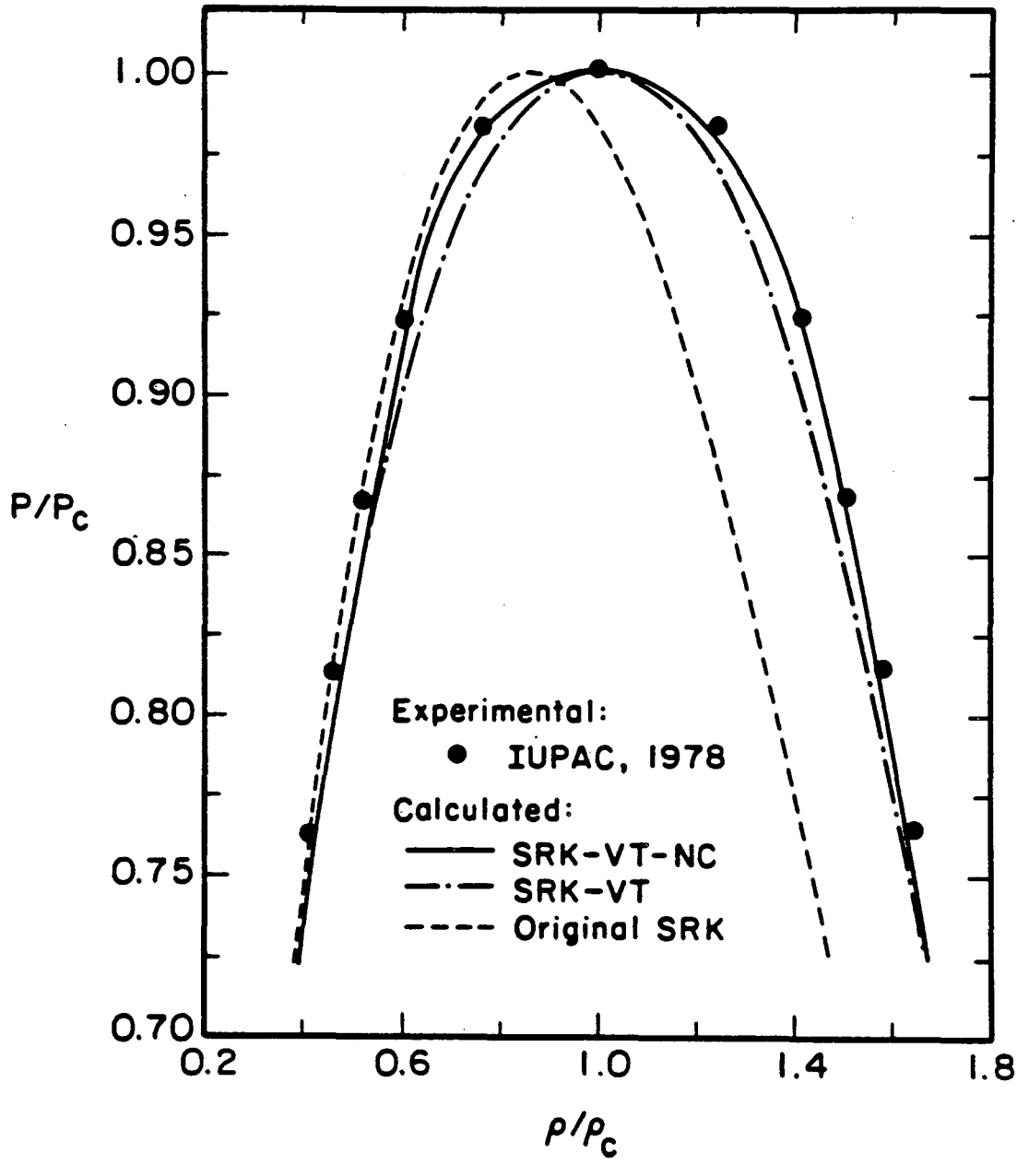

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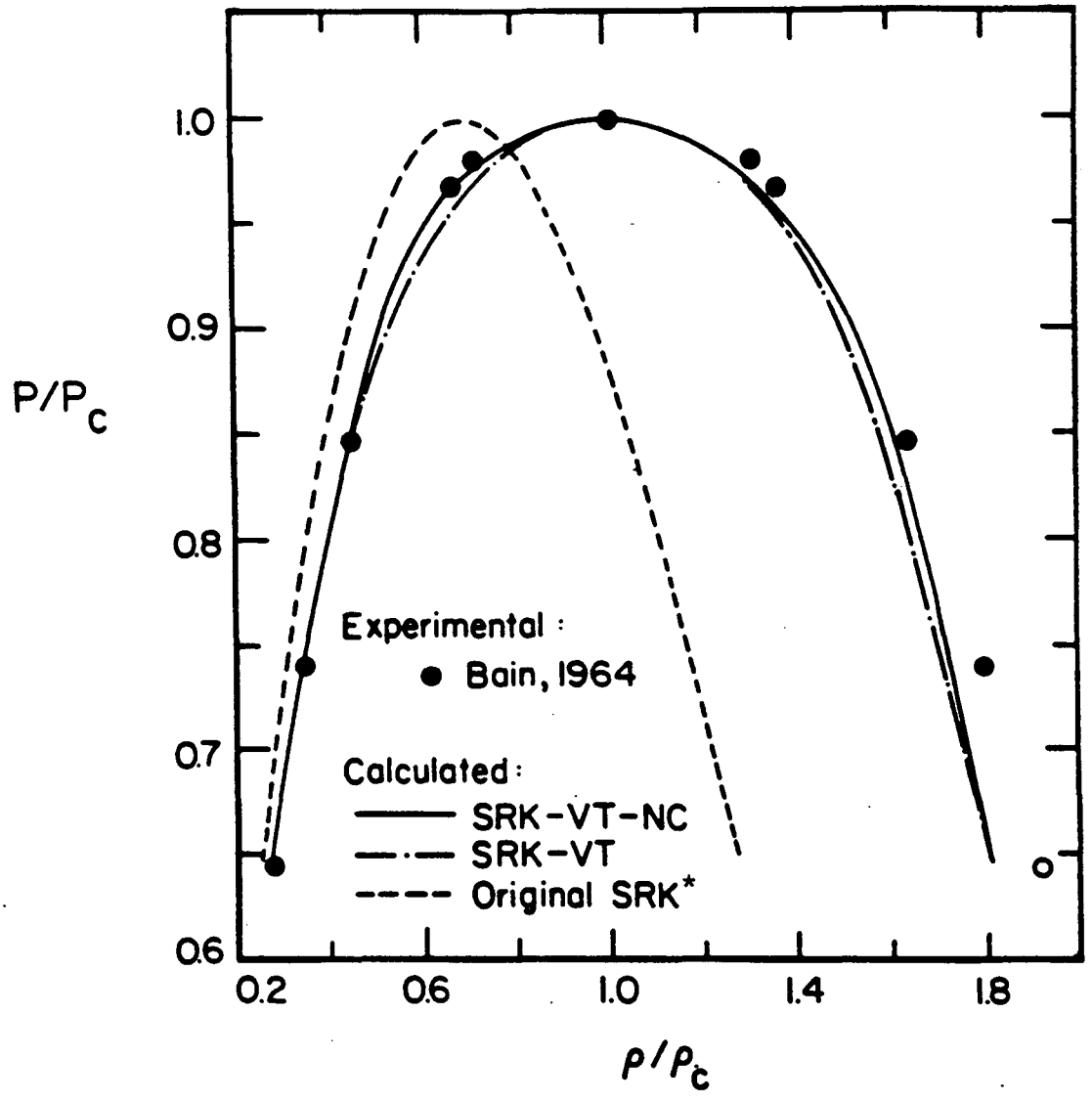

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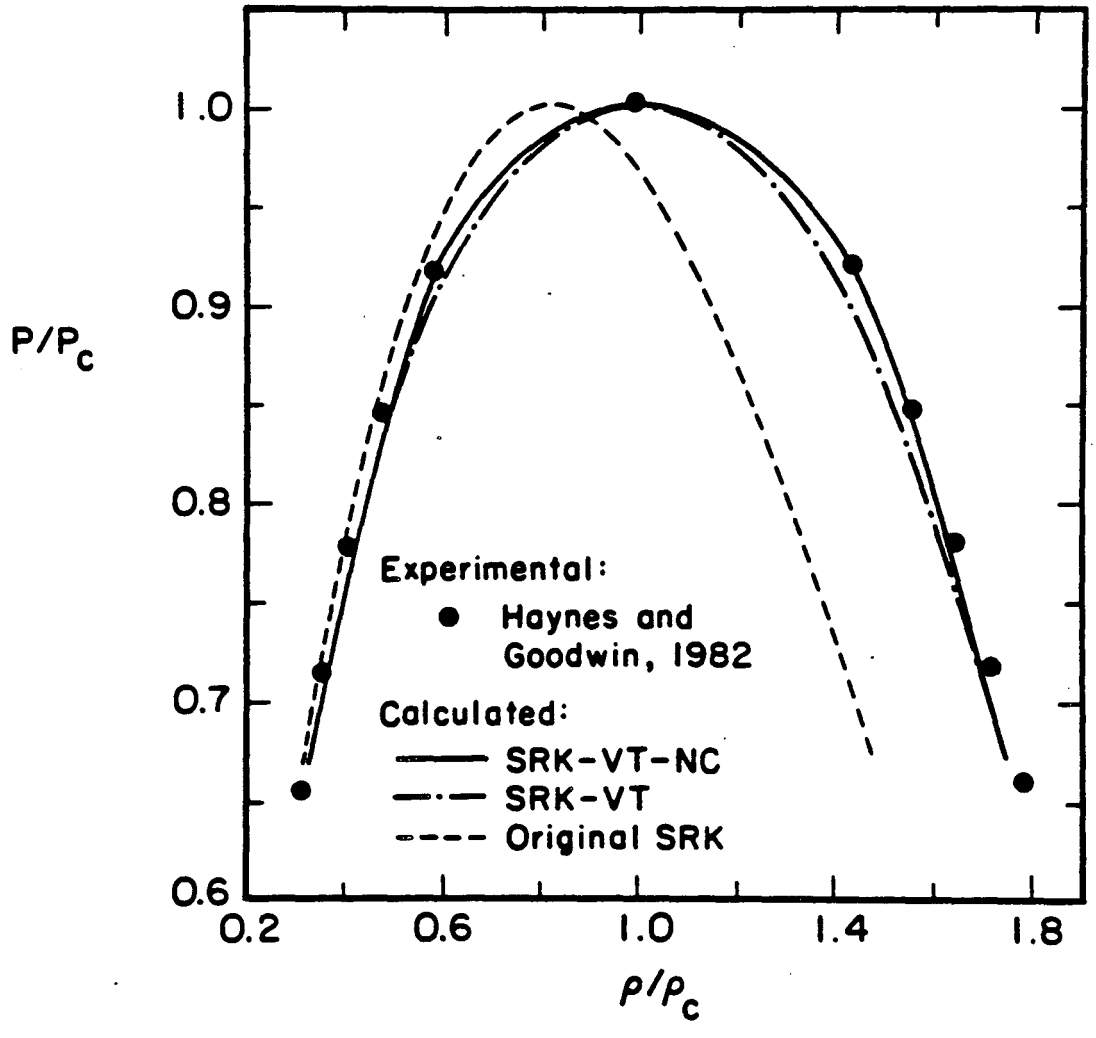

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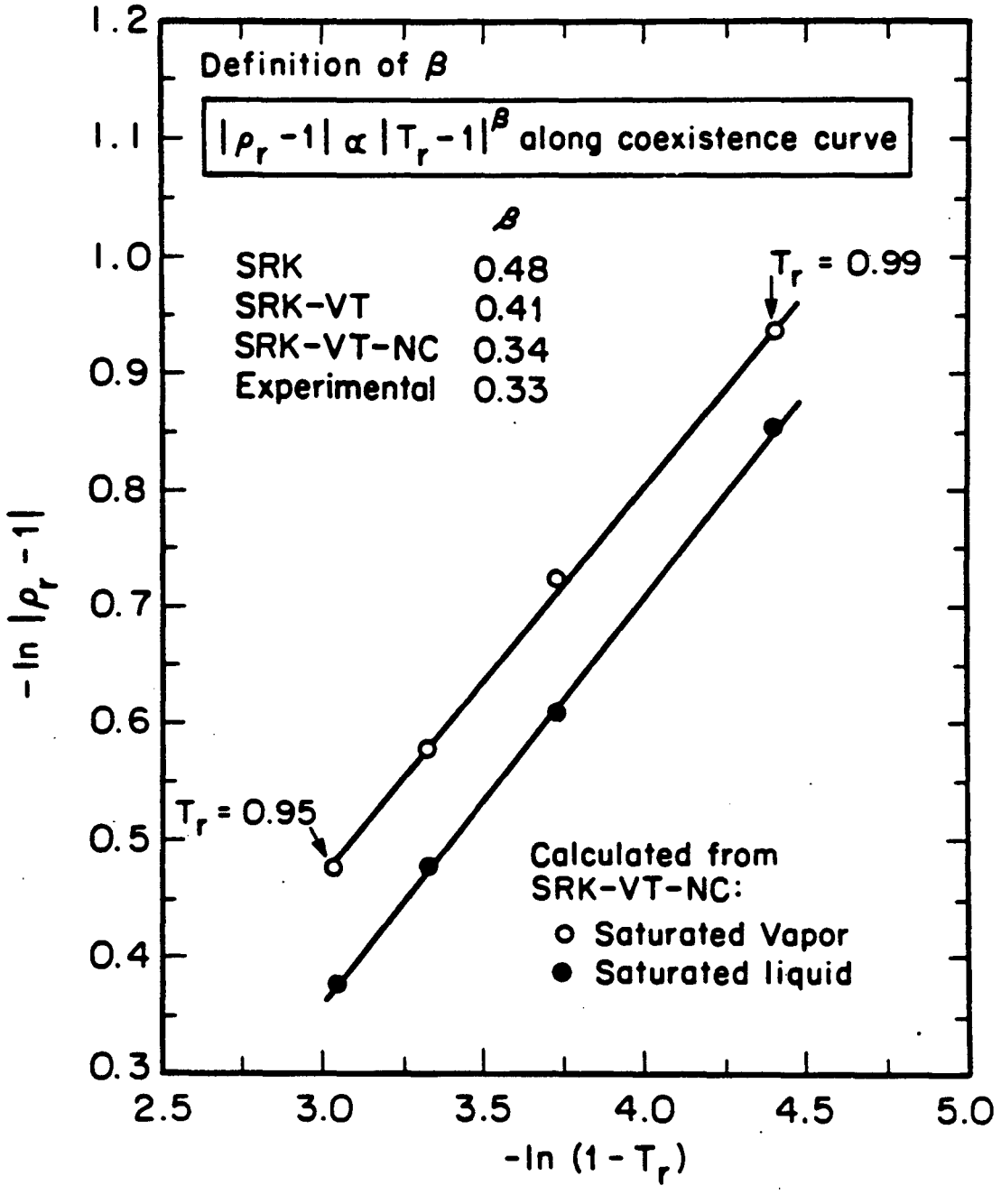

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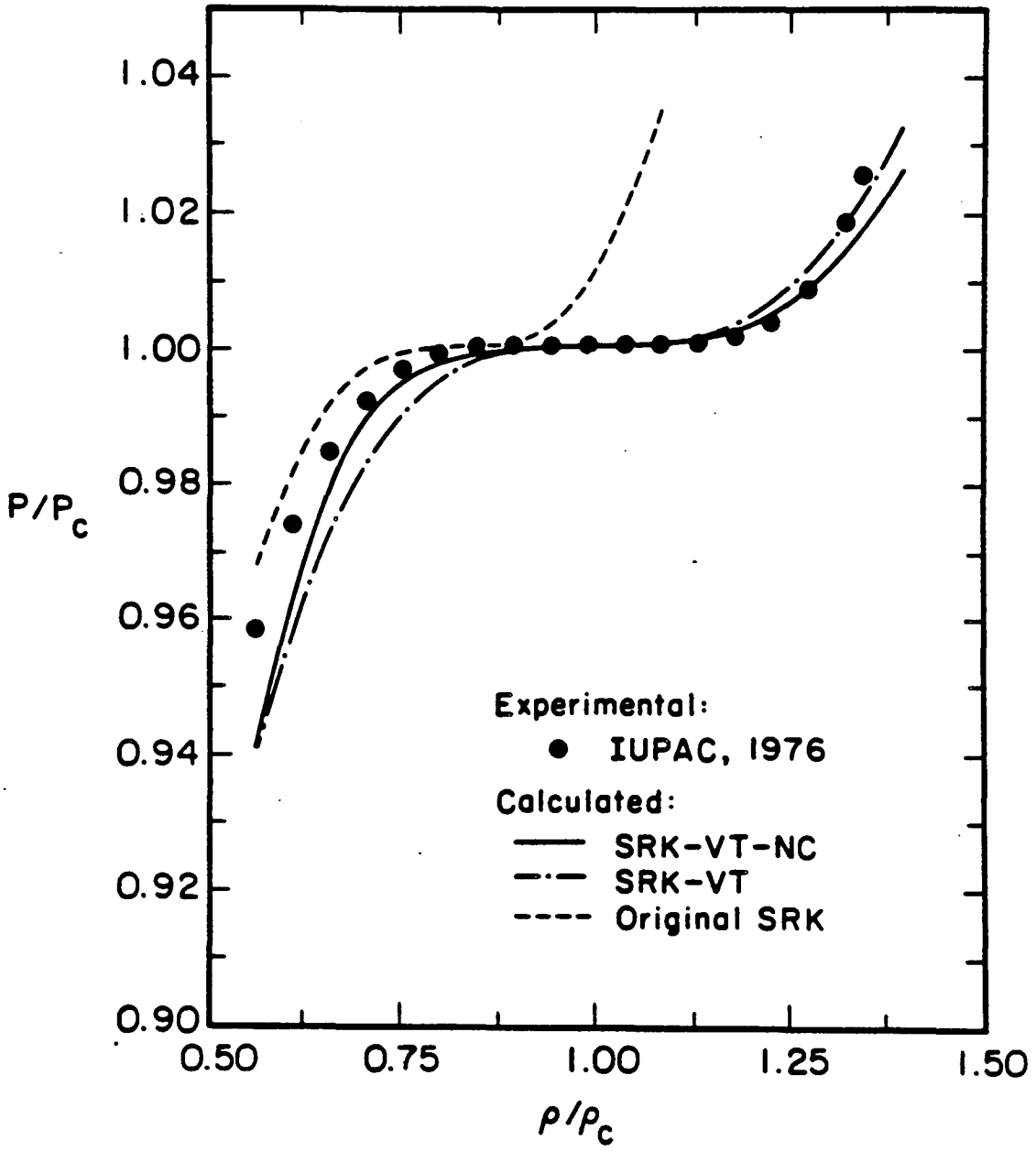

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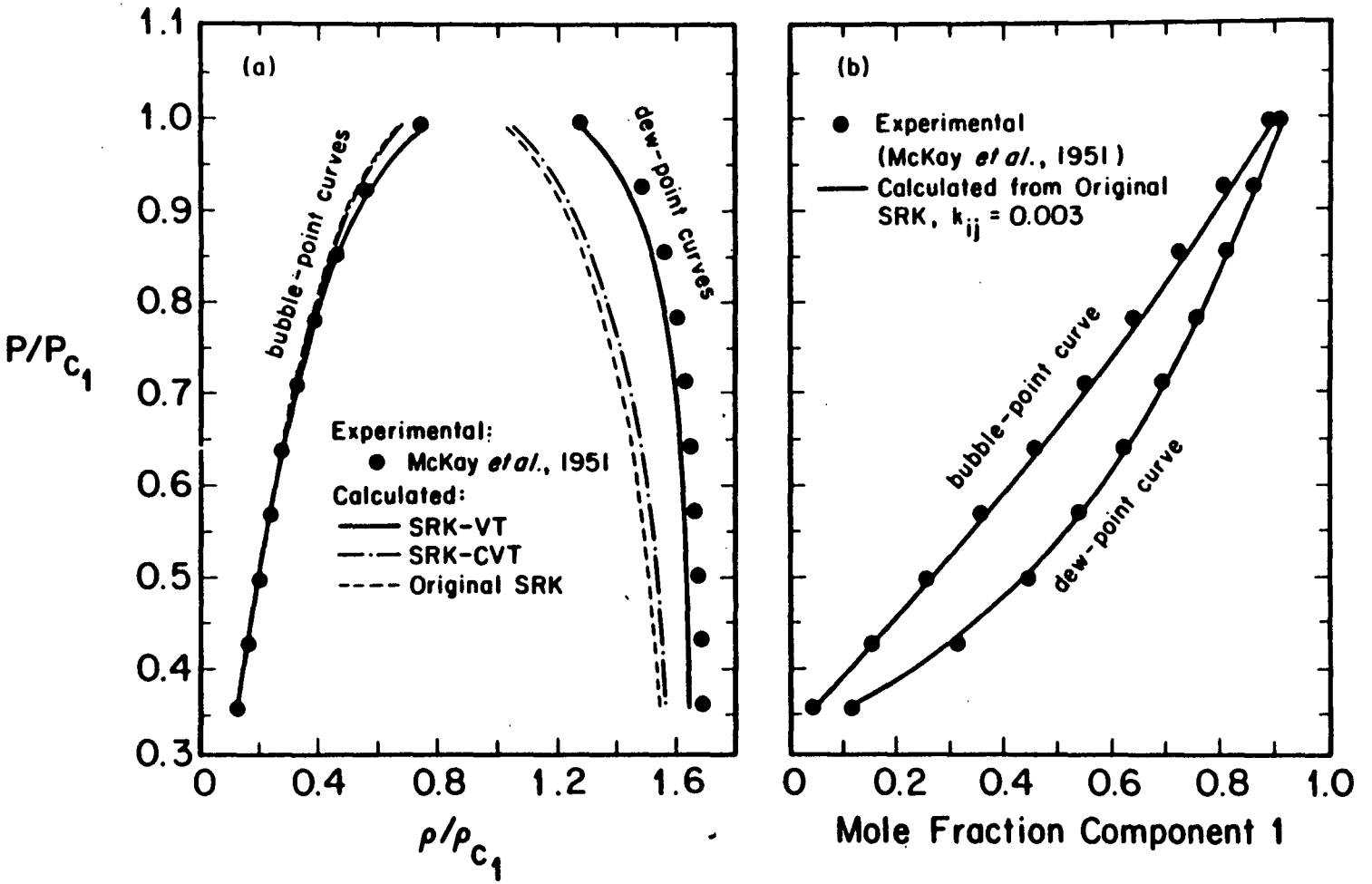

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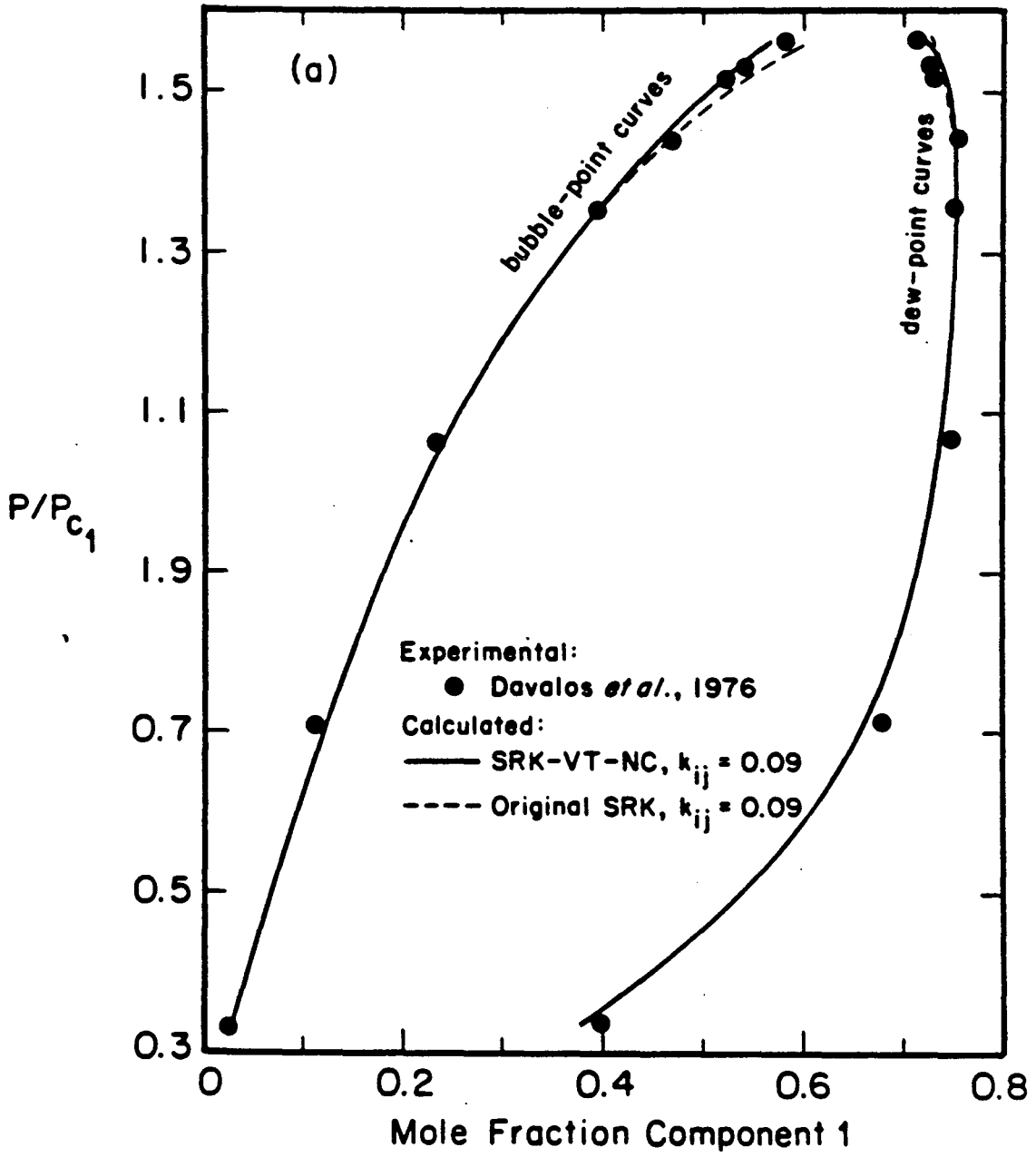

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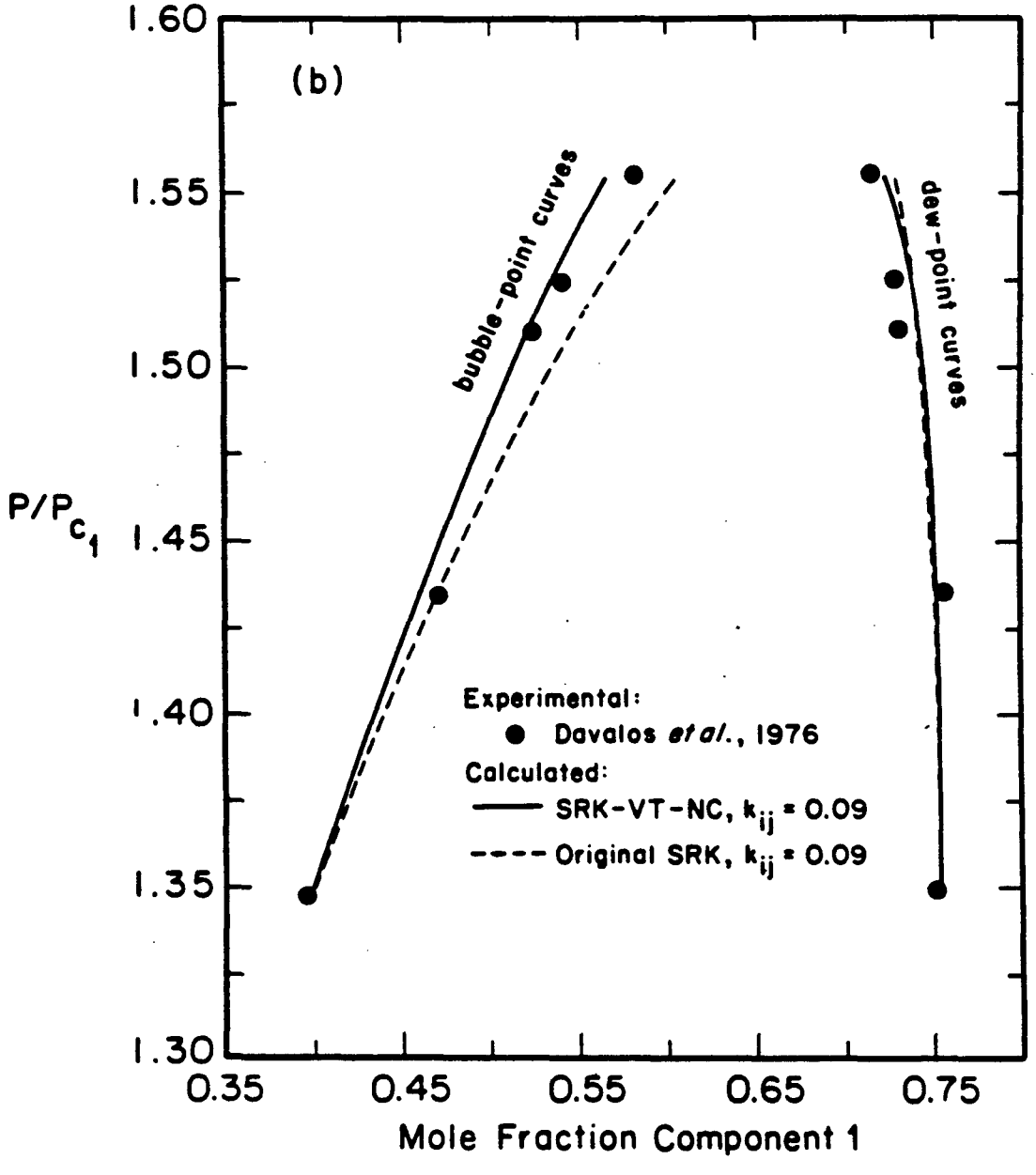

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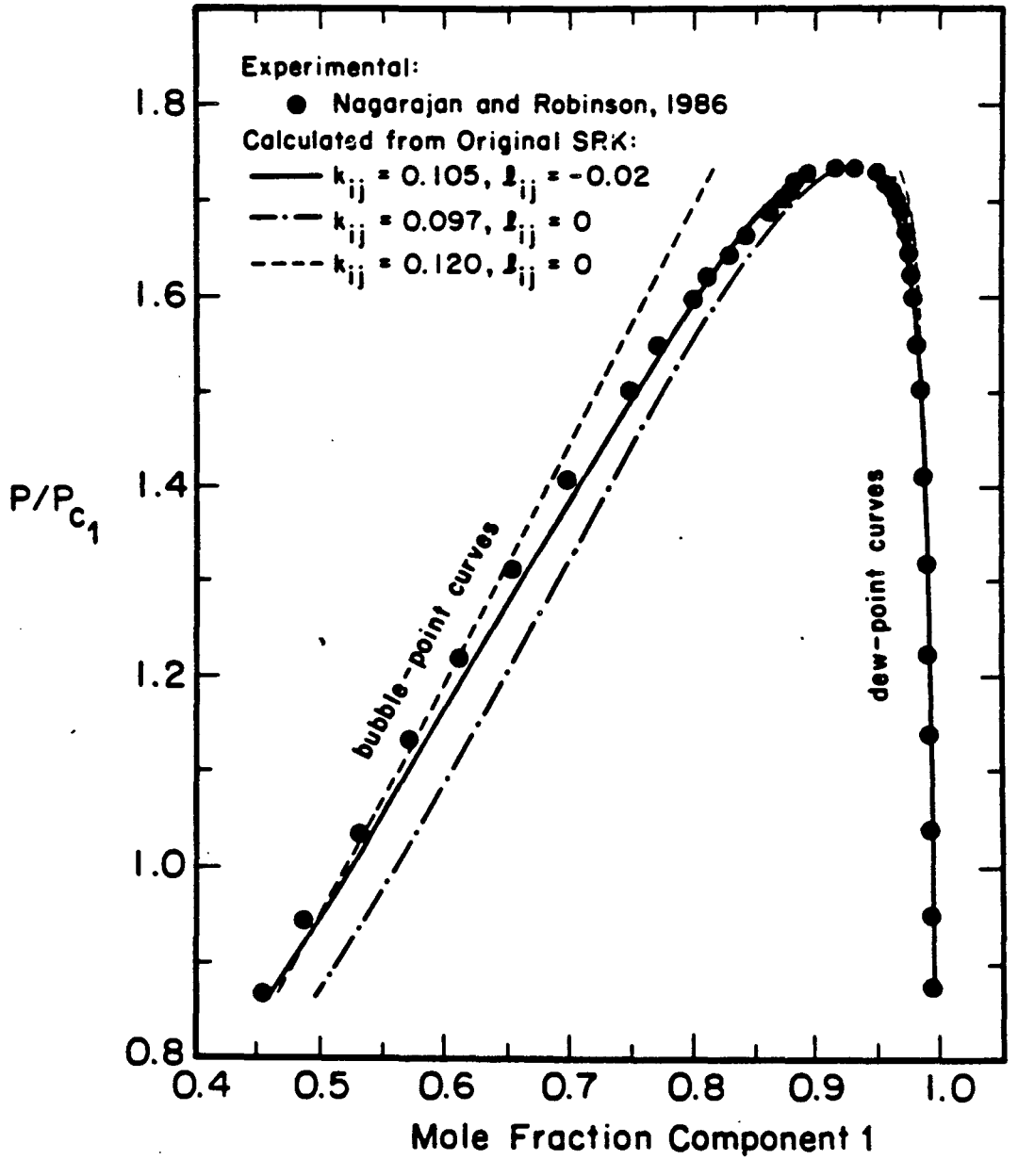

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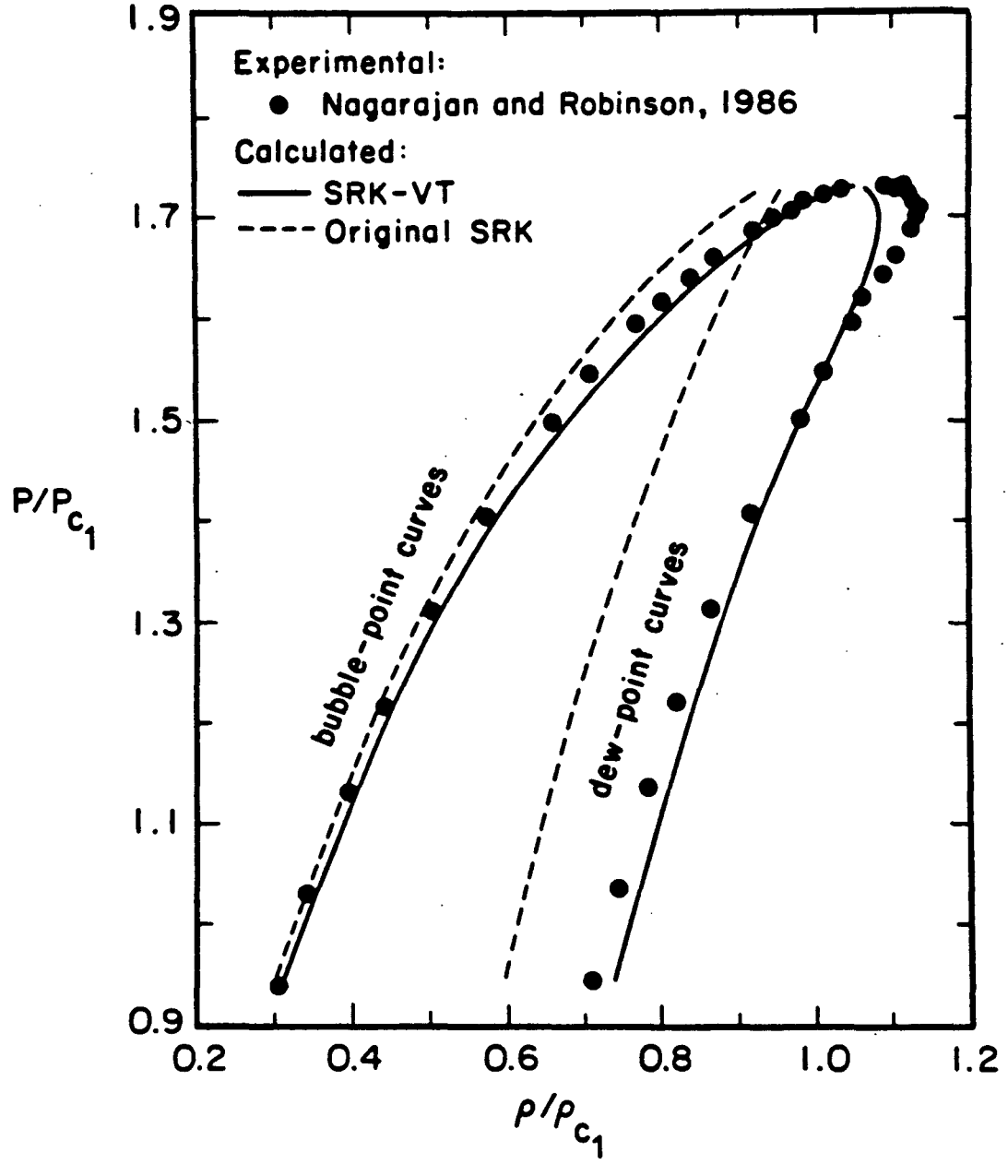

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