Coexistence curves at liquid-liquid critical points: Ising exponents and extended scaling

Sandra C. Greer

Institute for Basic Standards, National Bureau of Standards, Washington, D. C. 20234
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New measurements have been made of coexisting mass densities of isobutyric acid + water with a precision of 20 ppm and within 3.5°C of the critical temperature. The measurements were made using a single sample of composition very close to critical. It is found that the coexistence curve is more symmetric in terms of the difference in volume fraction ($\Delta\phi$) of coexisting phases than in terms of the difference in mass density. The difference $\Delta\phi$ is well fitted for $\epsilon = (T_c - T)/T_c < 0.006$ by the expression $\Delta\phi = B\epsilon^\beta$, where $B = 1.071 \pm 0.023$ and $\beta = 0.328 \pm 0.004$. (Uncertainties are given as 3 times the standard deviation.) A new analysis has been made of the recent data of Gopal *et al.* on the difference in volume fraction of coexisting densities of carbon disulfide + nitromethane. For this system, $\Delta\phi$ can be fitted for $\epsilon < 0.2$ by an extended scaling expression suggested by Wegner's work, $\Delta\phi = B\epsilon^\beta + B_1\epsilon^{\beta+\Delta_2} + B_2\epsilon^{\beta+2\Delta_2}$. The exponent Δ_2 is fixed at 0.5; the fit gives $\beta = 0.316 \pm 0.008$, $B = 1.63 \pm 0.09$, $B_1 = 0.77 \pm 0.31$, and $B_2 = -2.43 \pm 0.40$. This work suggests that liquid-liquid critical phenomena are consistent with the functional forms obtained from renormalization-group calculations and with asymptotic exponents which are like those presently calculated for the Ising model. The range of asymptotic behavior seems to be larger for a liquid-liquid critical point than for a liquid-gas critical point.

I. INTRODUCTION

Many binary-liquid mixtures are only partially miscible, and at constant pressure their regions of immiscibility have coexistence curves with critical points which are analogous to all other critical points.[1,2] We can begin to answer some questions currently important in the field of critical phenomena by examining the coexistence curves of such binary-liquid mixtures. These questions are the following: (1) What is the proper order parameter for a binary-liquid mixture? (2) What is the asymptotic critical exponent β for a binary liquid mixture? Is it the same as that for pure fluids? Is it the same as that for the Ising model? (3) Is a simple asymptotic scaling expression adequate to describe the data? If not, are current predictions for extensions to scaling consistent with the data? In what temperature range is the asymptotic regime reached? (4) Does the diameter of the coexistence curve show the anomaly predicted by current theories?

I will present here some progress toward answering these questions based on the analysis of new data on the coexistence curve of isobutyric acid + water and the analysis of data by Gopal *et al.*[3] on carbon disulfide + nitromethane.

The first question, that of the proper order parameter for a binary mixture, has been considered by Scott,[2] Stein and Allen,[4] and others.[5-7] An Ising representation[8,9] of a binary-liquid mixture would have an exact symmetry about the critical point in the proper order parameter. Therefore, we seek to find the order parameter in terms of which the coexistence curve is most symmetric. Possible choices are the mole fraction of one component

(x_1), the volume fraction of one component (ϕ_1), and the mass density (ρ). Experimental results[2-6] so far indicate that the volume fraction is a more symmetric representation than is the mole fraction. The results of the present work for isobutyric acid + water will show that the volume fraction is also to be preferred to the mass density. We can see why this might be. Since the order parameter in the lattice-gas representation of a pure fluid is the number density, we might expect that the best order parameter for a mixture will be the one closest to the number density of one component (ρ_N^1). Let us see how ρ and ϕ_1 are related to ρ_N^1. If V_1^0 and V_2^0 are the molar volumes of the pure components, V_m^0 is the ideal molar volume of the mixture, V^E is the excess volume of mixing, ρ_1^0 and ρ_2^0 are the mass densities of the pure components, $\phi_1 = V_1^0/(V_m^0 + V^E)$, and T is the temperature, then it can be shown that

$$\phi_1(T) = V_1^0(T)\rho_N^1(T) \tag{1}$$

while

$$\rho(T) = V_1^0(T)[\rho_1^0(T) - \rho_2^0(T)]\rho_N^1(T) + \rho_2^0(T). \tag{2}$$

We can see from Eqs. (1) and (2) that ϕ_1 is more directly related to ρ_N^1 than is ρ and thus ϕ_1 will probably be the better order parameter.

We also seek a determination of the critical exponent β, which characterizes the approach to zero of the difference in order parameter (p) between coexisting phases:

$$\Delta p = B\epsilon^\beta \tag{3}$$

when ϵ approaches zero.[9] [Here $\epsilon = (T_c - T)/T_c$ where T_c is the critical temperature.] Thus β is defined in the asymptotic regime as $T \to T_c$ and

attempts to determine β must include a considera-
tion of whether the asymptotic regime has been
attained in the experiment. Fits to the "simple
scaling" form [Eq. (3)] outside the asymptotic re-
gime may give an "apparent" β the value of which
has been altered by higher-order contributions.

The value of β for the Ising model is found by
series expansion to be $0.31 + 0.01$,[10] but more re-
cent calculations by renormalization-group tech-
niques give somewhat higher values: 0.3367[11] and
0.320 ± 0.015.[12] Past evaluations of β for pure
fluids[13-17] have shown an apparent β of 0.355 ± 0.007
in the range $10^{-4} < \epsilon < 10^{-1}$. Measurements on pure
fluids have since been made much closer to T_c by
new techniques.[18-20] Very recent accurate work[20]
gives β for pure fluids as $0.321-0.329$ in the range
$5 \times 10^{-6} < \epsilon < 5 \times 10^{-5}$, consistent with the values of
β for the Ising model. Coexistence curves of bi-
nary mixtures were surveyed in 1974 by Stein and
Allen,[4] who found an apparent β of 0.34 ± 0.01 for
nine mixtures in the range $2 \times 10^{-7} < \epsilon < 1.4 \times 10^{-2}$.
Since that study, there has been only one exten-
sive study of β for a binary liquid using the volume
fraction as the order parameter, namely, the work
of Gopal *et al.*[3] on carbon disulfide + nitromethane.
That work will be considered in detail below.[21] The
general conclusion on β for binary liquids to date
has been that the apparent β for simple scaling is
lower $(0.33-0.34)$ than it is for pure fluids $(0.34-0.35)$. The present analysis will show that the
asymptotic range for coexistence curves at some
liquid-liquid critical points is larger $(\epsilon < 10^{-2})$ than
it is at liquid-gas critical points[20] $(\epsilon < 10^{-4})$ and
that the β obtained in the asymptotic range for
these binaries is consistent with that given for the
Ising model and with that obtained in the asymptot-
ic range for pure fluids.[20] Thus both binary mix-
tures and pure fluids[20] seem to belong in the same
universality class[22] as the Ising model.

Since β is defined only in the asymptotic limit
near T_c, the proper description of a coexistence
curve beyond the asymptotic range should include
terms of higher order than the simple scaling
term of Eq. (3). The validity of simple scaling
has been tested for pure fluids by looking for any
dependence of β on the range of ϵ.[13-19] The older
data on pure fluids in the range $10^{-3} < \epsilon < 10^{-1}$
showed no such range dependence,[13-16] but newer,
more precise data[17,18] on pure fluids have shown
some range dependence. These recent range var-
iation tests suggest that corrections to simple
scaling are needed for pure fluids in the range
$10^{-3} < \epsilon < 10^{-1}$. Little range variation has been done
previously for binary mixtures. Balzarini[21] found no
range dependence for aniline + cyclohexane to $\epsilon = 0.01$.

Applying the techniques of renormalization-group
theory to the Ising model, Wegner[23] has calculated

the corrections to simple scaling. According to his
results,

$$\Delta p = \left| \epsilon \right|^\beta \sum_{n=0} \sum_{n_1=0} \sum_{n_2=0} \sum_{n_3=0} B_{n, n_1, n_2, n_3}$$

$$\times \left| \epsilon \right|^{n + n_1 (\Delta - 1) + n_2 \Delta_2 + n_3 \Delta_3}.$$

(4a)

Here $\Delta = \beta\delta$, δ is the critical exponent for the
change in chemical potential with composition[1],
and Δ_2 is a correction exponent which has been
calculated to be 0.50.[12] Terms with exponents
which are nearly the same can be collected to give

$$\Delta p = B \epsilon^\beta + B_1 \epsilon^{\beta + \Delta_2} + B_2 \epsilon^{\beta + 2\Delta_2} + B_3 \epsilon^{\beta + 3\Delta_2} + \cdots.$$

(4b)

There has been no published work on applying the
Wegner expansion to the coexistence curves of bi-
nary mixtures. Such corrections have been con-
sidered for the pure fluid Xe[17] and found not to be
useful. However, in this analysis of the coexis-
tence curve of Xe, it was assumed that $\Delta_2 = 0.64$
and that the Ising $\beta = 0.3125$; these are not the best
current estimates for these exponents and a dif-
ferent choice might change the conclusions
reached. The analysis to be given here of the
data[3] for carbon disulfide + nitromethane over a
broad range $(10^{-3} < \epsilon < 2 \times 10^{-1})$ will show these bi-
nary-mixture data to be consistent with a Wegner
expansion.

Theories have predicted[24-28] that the lack of Ising
particle-hole symmetry in real fluids will lead to
an anomaly in the diameter of the coexistence
curve. That is, if p_1 and p_2 are the values of the
order parameter in the coexisting phases,

$$\tfrac{1}{2}(p_1 + p_2) = P_c + C_1 \epsilon^{1-\alpha} + C_2 \epsilon + \cdots$$

(5)

This anomaly is difficult to observe because the
exponent $(1 - \alpha \approx 0.88)$ is so close to unity. There
have been only two observations of the anomaly
reported — one in a pure fluid[29] (SF_6) and one in a
binary liquid[3] (carbon disulfide + nitromethane).
The new measurements reported here on isobuty-
ric acid + water show no deviation from a rectilin-
ear diameter. This indicates that the coefficient
of the anomaly is small and that perhaps it is nec-
essary to have data over a much larger range and
closer to T_c in order to find the anomaly.

In summary, I report here new measurements
on the coexistence curve of isobutyric acid + water
and a new analysis of coexistence curve data on
carbon disulfide + nitromethane.[3] The results indi-
cate that the volume fraction is the preferred or-
der parameter for binary-liquid mixtures, that
the coexistence curves of such mixtures have Ising
asymptotic behavior, and that the behavior further
from the critical point is consistent with the cor-

rections to asymptotic behavior predicted by the renormalization-group theory. While both pure fluids[20] and binary-liquid mixtures seem to fall into the same universality class as the Ising model,[22] the liquid-liquid coexistence curves have a larger range of asymptotic Ising behavior than do liquid-gas coexistence curves.

II. ISOBUTYRIC ACID + WATER

A. Sample preparation

The isobutyric acid was provided by Graham Morrison of the University of California at Los Angeles; Morrison estimated the purity by titration and found the acid to be 99.5% pure, the main impurity being water. The isobutyric acid and distilled water were mixed together in a cylindrical Pyrex[30] cell, the inner diameter of which was 13 mm. The mixture was degassed twice by freezing it and then pumping off the residual gases, after which the cell was sealed at the vapor pressure of the mixture.

The sample consists of 4.918 g water and 3.005 g 99.5% isobutyric acid, so that the mole fraction x_1 of isobutyric acid is 0.110. The sample is 6.6 cm high and has 4 cm^3 of vapor above it. The transition temperature of this sample was found by visual observation two months after the sample preparation to be 25.988 °C; there is evidence that the transition temperature drifted slowly with time and this problem will be discussed below. Literature values of x_c vary from 0.111[31] to 0.115[32] and literature values for T_c vary from 26.086[33] to 26.385 °C.[34]

For binary-liquid mixtures, the critical temperature is known to be very sensitive to impurities and the system isobutyric acid + water is known to be particularly sensitive to ionic impurities.[35] The water used for this sample was not deionized and so could have introduced ionic impurities; also, ionic impurities could have been leached from the cell wall. However, there is evidence that, although small amounts of impurities affect T_c in fluids, they do not affect critical exponents.[15, 20, 36, 37]

B. Density measurement

Densities were determined using a magnetic densimeter,[38] which measures density by using a solenoid to levitate a small buoy containing magnetic material in the fluid of interest. The current required in the solenoid to support the buoy in the fluid at a given height is a measure of the fluid density:

$$\rho = \rho_B + CI^2 , \tag{6}$$

where ρ is the fluid density, I is the solenoid cur-

rent, ρ_B is the density of the buoy, and C is a calibration constant. In this densimeter, the buoy position is sensed by a differential transformer and the out-of-balance signal fed to a servo system which keeps the buoy at a fixed height. The solenoid current is determined from the voltage across a standard resistor in series with the solenoid. The voltage is measured by a digital voltmeter, 100 readings of which are averaged.

The buoy[39] used in these measurements is a quartz sphere 7 mm in diameter which has projections at the top and bottom, so that the overall height is 18 mm. The magnetic material, annealed Hy-Mu 80 (Carpenter Steel Co.), was cemented into the bottom of the buoy. The buoy was calibrated [Eq. (6)] by measuring the solenoid current required to suspend it in three liquids of known densities between 0.981 and 0.990 g/cm^3 (1 g/cm^3 = 10^3 kg/m^3) at 25 °C. The calibration data were fit by the following equation: $\rho = 0.96502(\pm 0.00042) + 0.02843(\pm 0.00057)V^2$, where ρ is in g/cm^3 and V is the voltage across a 1-Ω standard resistor in series with the solenoid. The standard deviation of this fit, which determines the accuracy of the density measurements, was 38 ppm of the density. The buoy is sensitive to density changes of about 20 ppm. The calibrated buoy was sealed inside the cell with the sample.

Since the buoy was suspended by the servo system at a fixed height in the apparatus,[38] the density in each of the coexisting liquid phases was measured by moving the sample relative to the buoy.

C. Temperature control and measurement

The temperature of the sample was controlled to ±0.001 °C by water which flowed from a controlled-temperature bath past the sample cell. The region of the cell was checked for temperature gradients and no differences greater than ±0.001 °C were found. The temperature was measured using a quartz crystal thermometer[40] which had recently been calibrated with respect to a platinum resistance thermometer on the International Practical Temperature Scale of 1968; the temperature measurement is believed to be accurate to ±0.002 °C.

D. Sources of systematic error

Errors can occur in the density measurement due to effects of temperature change on the buoy. The thermal expansion of the buoy affects the density ρ_B in Eq. (6). For this buoy, the correction to the measured density is about 1 ppm/°C, which is negligible. The permeability of the Hy-Mu in the buoy changes with temperature; this permeability

enters into the calibration constant C in Eq. (6). R. Mundy of NBS has measured the temperature dependence of the permeability of Hy-Mu and finds it to be $+0.01\%/°C$, which corresponds to a negligible density error (1 ppm/°C).

It has recently[39,41-43] become clear that systematic errors can arise from density gradients due to gravity in experiments near consolute points. The mixture isobutyric acid + water was chosen for this study because it is expected to have negligible gravity effects, since the densities of the pure components are nearly the same.[42] A search was made for such gradients. The sample was heated 11 °C above the transition temperature, shaken vigorously by hand to insure homogeneity, and placed in the densimeter. Then the temperature was lowered toward the transition temperature and the sample searched for density gradients at temperatures between 11 °C and a few millidegrees from the transition temperature. The sample was searched for density gradients by measuring the density as a function of height. No density gradients were ever observed in the one-phase region, even within millidegrees of the transition temperature. Furthermore, stirring the sample (by oscillating the buoy) never had any effect on the measured density. It was not possible to search for density gradients in the two-phase region because the buoy is too large compared to the heights of the separated phases. Jasnow et al.[44] calculated that gravity effects in isobutyric acid + water would be important only within 0.01 °C of the critical temperature. Since the measurements presented here in the separated phases are only as close as 0.014 °C to the critical temperature, I will assume that there were no significant density gradients present in the two-phase region either.

While the phenomenon of interest here is the coexistence curve at constant pressure, the experiment was performed at the vapor pressure of the mixture. This pressure change results in a shift of T_c. For isobutyric acid + water at 1 atm,[45] $dT_c/dp = -0.055$ °C/atm. If the vapor pressure is taken as that of water, then T_c is shifted by only -0.1 mK when the temperature is changed by 1 K and the error so introduced is well within the resolution of the measurements.

The change of composition of the vapor with temperature likewise has a negligible effect on the experiment. A change of vapor composition of 100% would change the average liquid density by only 2×10^{-7} g/cm^3.

E. Determination of T_c

It is very helpful in the data analysis to have an independent determination of the critical tempera-

ture. The words "transition temperature, T_t," and "critical temperature, T_c," have been used here with great care. T_t is the temperature at which a sample of a particular composition changes from one liquid phase to two liquid phases on cooling (or vice versa on heating). T_c is the maximum value of T_t if T_t is measured as a function of composition. Thus T_t equals T_c only if the sample is at the critical composition. Unfortunately, this sample is not quite at the critical composition, as will be explained, and, furthermore, it is very difficult even to obtain T_t in this system.

If the sample has precisely the critical composition and if both the diameter of the coexistence curve and the density in the one-phase region have no detectable anomalies (which, as we shall see, is the case), then $(\rho_1 + \rho_2)/2$ as a function of ϵ for $T < T_c$ and $\rho(\epsilon)$ for $T > T_c$ should meet at the critical point. Measurements were made of $\rho(\epsilon)$ for $T > T_c$ and some of these data are shown in Fig. 1. We see that for this sample the diameter of the coexistence curve and the curve of densities in the one-phase region do not meet (Fig. 1) and we conclude that the sample is not quite at the critical composition. Using the difference in density at the transition for the two lines ($\Delta\rho = 0.0006$ g/cm^3) and $d\rho/dx_1 = 0.1$ (as calculated for an ideal solution of isobutyric acid in water), we find that $x_{\text{sample}} = x_c - 0.005$, where x is the mole fraction of isobutyric acid. (This implies that $x_c = 0.115$.) Thus T_t is less than T_c, and T_c can only be obtained in-
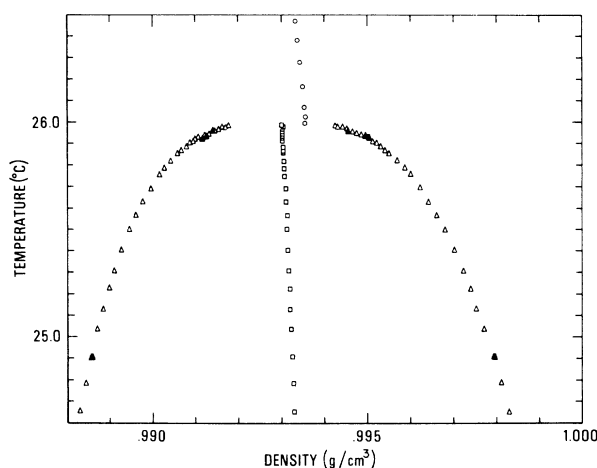

FIG. 1. Coexistence curve of isobutyric acid + water: coexisting densities ($\blacktriangle$, $\triangle$), diameter of the coexistence curve ($\square$), and the density in the one-phase region ($\bigcirc$). The coexisting densities are from run 1 (Appendix A) and the density data above T_c are from the set given in Appendix B. The ($\blacktriangle$) data were taken while heating the sample and the ($\triangle$) data while cooling; the heating data show slightly more scatter than, but no systematic differences from, the cooling data.

directly, for instance, as a parameter in the analysis of the data.

The upward movement of the liquid-liquid meniscus as the two-phase mixture was heated was another indication that $x_{sample} \neq x_c$. In fact, the shrinking of the upper liquid phase as the temperature was raised was a limit on how close to T_t measurements of the coexisting liquid densities could be made. At about $T_c - T = 0.01 \, °C$ the height of the upper phase became less than that of the buoy.

It is very difficult to measure T_t for this mixture. Inhomogeneities form easily near the liquid-vapor interface. The slow diffusion in this system[16] means that once an inhomogeneity is formed, it does not go away. On cooling, a meniscus can appear before it should and on heating, a meniscus can remain when it should be gone. Thus, it should be kept in mind that any measurement of T_t is probably an upper limit.

F. Coexistence curve of isobutyric acid + water

Two sets of data were taken — run 1 and run 2. All the data are listed in Appendix A. Run 1 was made within one month of the sample preparation and consists of 34 points taken while cooling the sample (see Fig. 1, open triangles). The sample was stirred after each temperature change. A few measurements were made while heating the sample (Fig. 1, solid triangles); these data were consistent with the cooling data, but showed more scatter, so they are not included in Appendix A or in the analysis. That the heating and cooling data agree indicates that the data represent the equilibrium states within the resolution of the measurements. Run 2, 26 points taken nine months after the sample preparation, consists of two different cooling sequences which agree with one another within error.

Run 1 and run 2 do not have the same T_c, as determined from the statistical analysis below. I attribute this change of T_c to a leaching of impurities from the cell walls. Fits were made to each run separately and to the combined set of 60 points (run 1 with run 2, allowing two critical temperatures). The fits were all essentially the same for both runs; so only the fits for the combined data set will be presented here.

The data analysis was done using a modified version of Bevington's nonlinear least-squares fitting program CURFIT[47] and all computer computations were made in double precision. The weighting of the data for the fits was made by the standard methods of propagation of errors[47] using a computer program for the numerical differentiation of the function being fitted. These same

techniques were used for all the data analysis described in this paper. Uncertainties will be given as three times the standard deviation (3σ).

The determination of the standard deviations (σ) for the density measurements included a correction for the fact that densities near to the buoy density were measured more precisely than were densities further from the buoy density. From the calibration equation given in the earlier discussion of the density measurements,

$$\frac{\partial \rho}{\partial V} = 2c(\rho - \rho_B)^{1/2} \tag{7}$$

and

$$\sigma_\rho = 2c(\rho - \rho_B)^{1/2}\sigma_V \tag{8}$$

where c is a constant and $\sigma_V = 0.0003$. These standard deviations were used in the numerical program to weight the data.

The difference in order parameter of coexisting phases of isobutyric acid + water has been fitted using two possible order parameters (density and volume fraction) and two different functional forms (simple scaling with only one term and simple scaling with an additional correction term).

The results of the fits to the difference in density of coexisting phases $(\Delta\rho = \rho_l - \rho_u$, where ρ_u and ρ_l are the densities of the upper and lower coexisting phases at each temperature) are given in Table I. The fit to the simple scaling form (function A, Table I) gives an apparent β of 0.309 ± 0.004 and leaves systematic residuals. When a correction term is added (function B, Table I), a significantly better fit is obtained, but the value of β (0.332 ± 0.011) is higher than we expect for the Ising model.

We can compare the $\Delta\rho$ fit to the fit of Δx, the difference in mole fraction of isobutyric acid, obtained by Stein and Allen[4] using the data of Woermann and Sarholz[31] on isobutyric acid + water. Stein and Allen find $\Delta x = (0.695 \pm 0.10)\epsilon^{0.335 \pm 0.029}$. If we assume an ideal mixture, then $\partial\rho/\partial x = -0.11$ for this system. Then function A in Table I gives

$$\Delta x = 0.48\epsilon^{0.309}, \tag{9}$$

At $T_c - T = 0.01 \, °C$, Eq. (9) gives $\Delta x = 0.020$, whereas the Stein and Allen expression gives $\Delta x = 0.022$ ± 0.009, so that the two forms agree within error.

We have defined the volume fraction as

$$\phi_1 = V_1^0 / V_{mix} \tag{10}$$

where V_1^0 is the volume of one pure component and V_{mix} is that of the mixture. Then at a given temperature

$$\rho = \phi_1(\rho_1^0 - \rho_2^0) + \rho_2^0, \tag{11}$$

where ρ_1^0 and ρ_2^0 are the densities of the pure com-

TABLE I. Results of fits to the differences in coexisting densities ($\Delta\rho$) and volume fractions ($\Delta\phi$) for isobutyric acid+water. Uncertainties are given at the 99% confidence level (3σ). T_{c1} refers to the critical temperature for run 1 and T_{c2} to that for run 2. $\bar{\sigma}$ is the average standard deviation of $\Delta\rho$ or of $\Delta\phi$. ϵ is $(T_c - T)/T_c$.

T_{c1}	T_{c2}	B	β	B_1	$\bar{\sigma}$	χ_ν^2
		Density fits				
		A. $\Delta\rho = B\epsilon^\beta$				
25.994	25.969	0.053	0.309	$\cdots$	3.2×10^{-5}	2.8
±0.003	±0.003	±0.001	±0.004			
		B. $\Delta\rho = B\epsilon^\beta + B_1\epsilon^{\beta+\Delta_2}$,	$\Delta_2 = 0.50$			
25.999	25.973	0.063	0.333	−0.048	3.1×10^{-5}	1.6
±0.003	±0.003	±0.005	±0.010	±0.023		
		Volume fraction fits				
		C. $\Delta\phi = B\epsilon^\beta$				
25.999	25.974	1.071	0.328	$\cdots$	5.5×10^{-4}	1.4
±0.002	±0.002	±0.023	±0.004			
		D. $\Delta\phi = B\epsilon^\beta + B_1\epsilon^{\beta+\Delta_2}$,	$\Delta_2 = 0.50$			
25.999	25.973	1.04	0.324	0.17	5.5×10^{-4}	1.4
±0.003	±0.003	±0.15	±0.018	±0.76		

ponents at that temperature, ρ is the density of the mixture, and the subscript 1 refers to isobutyric acid. It is not possible to convert each measured ρ value to a ϕ_1 value because the ρ measurements are not sufficiently accurate. However, accurate values of ρ_1^0 and ρ_2^0 are available and can be used to obtain $\Delta\phi_1$ from $\Delta\rho$:

$$\Delta\phi_1 = \Delta\rho/(\rho_1^0 - \rho_2^0). \qquad (12)$$

The density of water, $\rho_2^0(T)$, was taken from the work of Kell[48] and the density of isobutyric acid, $\rho_1^0(T)$, was obtained from a fit to unpublished data by Morrison and Knobler.[49] The values of $\Delta\phi$ so obtained are given in the data list in Appendix A. Using Eq. (12), $\sigma_{\Delta\phi}$ was taken to be $\sim 18\sigma_{\Delta\rho}$. One datum—the last point (22.404 °C) in run 2—always deviated significantly from the curves fitted to the $\Delta\phi$ data and is omitted in the fits reported here.

The results of the fits to the difference in volume fraction are given in Table I, functions C and D. A simple scaling form (function C) gives a good fit with $\beta = 0.328 \pm 0.004$. A function including a correction to scaling (function D) shows no improvement in the fit and indicates that the second term is not necessary. The value of β for the simple scaling form is quite consistent with theoretical values for the Ising model.

From this analysis, the volume fraction seems to be a better choice for an order parameter than the density because a better fit is obtained with the simpler one-term function. For the volume fraction as order parameter, the value $\beta = 0.328 \pm 0.004$ is sufficiently close to that recently obtained very near the critical point in pure fluids[20] and to that obtained theoretically for Ising models[10-12] to conclude that binary-liquid mixtures

probably also have the asymptotic critical exponents of the Ising model. It is interesting that a β so like that of the Ising model is obtained in a region of reduced temperature which is much larger for this binary mixture ($\epsilon < 6 \times 10^{-3}$) than it is for pure fluids ($\epsilon < 10^{-4}$).[20]

G. Diameter of the coexistence curve of isobutyric acid + water

The diameter of the coexistence curve, $(\rho_u + \rho_l)/2$, was fitted to a straight line:

$$(\rho_u + \rho_l)/2 = \rho_c + C_2\epsilon. \qquad (13)$$

After the removal of five rather randomly distributed points (22.404, 25.906, 25.925, 25.937, and 25.961 °C) which were outliers, the remaining 55 points fit Eq. (13) very well, with quite random residuals. The outliers could result from the fact that some errors (for example, a temperature gradient) might be partially cancelled in the difference $\Delta\rho$, but not in the sum $(\rho_u + \rho_l)$. For this fit, $\rho_c = 0.993\,00 \pm 0.000\,01$, $C_2 = 0.066 \pm 0.005$, $\chi_\nu^2 = 1.97$, and $\bar{\sigma} = 1.19 \times 10^{-5}$. T_{c1}, the critical temperature for run 1, and T_{c2}, the critical temperature for run 2, were fixed at 25.998 and 25.971, respectively. There is, therefore, no indication of the anomaly in the diameter which has been predicted.[23-27] No analysis was made of the diameter in the variable volume fraction, $(\phi_1^u + \phi_1^l)/2$, because, as discussed above, the quantities ϕ_1^u and ϕ_1^l cannot be calculated with sufficient accuracy.

A coefficient C_1 [Eq. (5)] of the anomalous term of unity would give a contribution at the level of the noise in these data at $\epsilon = 5 \times 10^{-5}$. Thus C_1 for isobutyric acid + water must be less unity, since no evidence of an anomaly was seen in the diameter.

H. Thermal expansion above T_c for isobutyric acid + water

As the liquid-liquid critical point is approached along the critical isochore in the one-phase region, the volume or density is expected to show an anomaly[3,39,50,51]:

$$\rho \sim \epsilon^{1-\alpha} . \tag{14}$$

Klein and Woermann[52] reported the observation of such an anomaly in isobutyric acid + water. Their measurements had a resolution of 1 ppm of the density.

Measurements of $\rho(T)$ were made three months after the sample preparation from 0.001 to 12 °C above T_c with a precision of about 20 ppm in density. These data are given in Appendix B. Using the same weighting procedure described above for the coexistence curve fits, I can fit $\rho(\epsilon')$ [where $\epsilon' = (T - T_t)/T_t$] above T_t (25.988 °C) with no systematic deviations by a polynomial:

$$\rho = \rho_0 + A_1 \epsilon' + A_2 \epsilon'^2 \tag{15}$$

with $\chi_\nu^2 = 0.74$, $\rho_0 = 0.99357 \pm 0.00001$, $A_1 = -1.648 \pm 0.002$, and $A_2 = -0.449 \pm 0.065$. Thus my data do not require an anomalous term.

New data with a resolution of 0.1 ppm in ρ have recently been obtained on this system by Morrison and Knobler,[49] who will soon publish a complete study of these three sets of thermal-expansion data on isobutyric acid + water. No further discussion of these data will be given here.

III. ANALYSIS OF THE COEXISTENCE CURVE OF CARBON DISULFIDE + NITROMETHANE

Gopal and his colleagues[3] have measured the coexistence curve of carbon disulfide + nitromethane in the range $10^{-6} < \epsilon < 0.2$ by visually observing the transition temperatures of 70 samples of different compositions. They converted the mole fractions of the samples to volume fractions. In their analysis of the data, Gopal et al. find that the data fit a simple scaling relation $\Delta\phi = B\epsilon^\beta$, over the entire range in ϵ, with $\beta = 0.315 \pm 0.004$ and $B = 1.64 \pm 0.01$. They also observe an anomalous diameter of the coexistence curve.[23-27]

I also have analyzed these data on the coexistence curve of carbon disulfide + nitromethane, using $\sigma_{\Delta\phi} = 0.002$ and σ_T as one in the least significant place given in the data list (0.001-0.1 °C). I have been unable to duplicate the fits which Gopal et al. report. The fits which I obtain for a simple scaling function using the entire data set show large systematic deviations with $\beta \sim 0.29$ and $T_c = 61.977$ °C, which is less than that observed experimentally (61.983 °C).

In my further analysis of these data, I have omitted the data which might be affected by gravity[41-43] ($T_c - T < 0.02$ °C) and two points which were outliers. The 50 points which remain were then fitted to various functions as shown in Table II and in Figs. 2 and 3. T_c was kept fixed at the experimental value. Table II shows that the data

TABLE II. Results of fits to differences in volume fractions of coexisting phases of carbon disulfide + nitromethane.[a] ϵ is $(T_c - T)/T_c$. T_c is fixed at 61.983 °C.[a] Uncertainties are given at the 99% confidence level (3σ). $\bar{\sigma}$, the average standard deviation of $\Delta\phi$, is 1.1×10^{-3}.

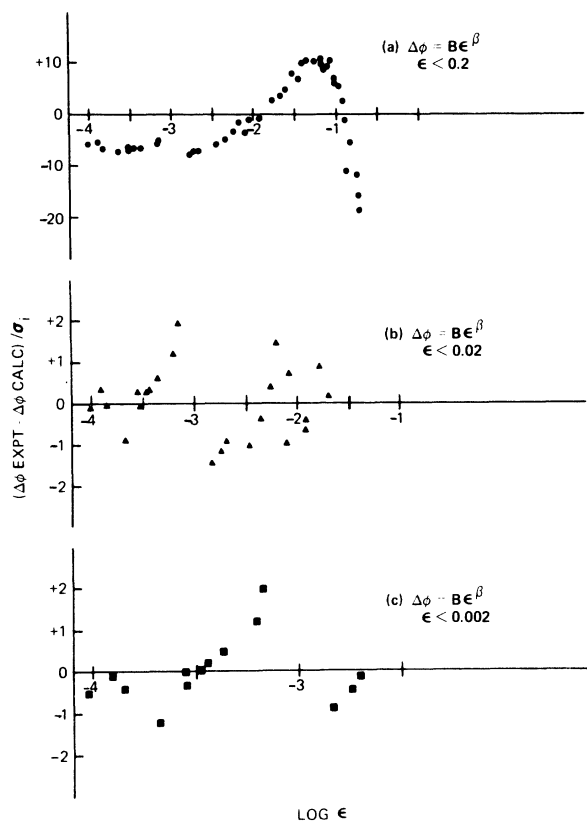| ϵ range	β	B	B_1	B_2	B_3	χ_ν^2	No. points
A. $\Delta\phi = B\epsilon^\beta$							
$6 \times 10^{-5} - 0.002$	0.316 ±0.010	1.66 ±0.13	· · ·	· · ·	· · ·	0.79	14
$6 \times 10^{-5} - 0.02$	0.322 ±0.004	1.73 ±0.03	· · ·	· · ·	· · ·	0.83	24
$6 \times 10^{-5} - 0.2$	0.294 ±0.011	1.53 ±0.05	· · ·	· · ·	· · ·	68	50
B. $\Delta\phi = B\epsilon^\beta + B_1\epsilon^{\beta+\Delta_2}$, $\Delta_2 = 0.50$							
$6 \times 10^{-5} - 0.2$	0.352 ±0.009	2.14 ±0.10	-1.20 ±0.19	· · ·	· · ·	6.5	50
C. $\Delta\phi = B\epsilon^\beta + B_1\epsilon^{\beta+\Delta_2} + B_2\epsilon^{\beta+2\Delta_2}$, $\Delta_2 = 0.50$							
$6 \times 10^{-5} - 0.2$	0.316 ±0.008	1.63 ±0.09	0.77 ±0.31	-2.43 ±0.40	· · ·	0.89	50
D. $\Delta\phi = B\epsilon^\beta + B_1\epsilon^{\beta+\Delta_2} + B_2\epsilon^{\beta+2\Delta_2} + B_3\epsilon^{\beta+3\Delta_2}$, $\Delta_2 = 0.50$							
$6 \times 10^{-5} - 0.2$	0.306 ±0.014	1.49 ±0.17	1.59 ±0.89	-4.9 ±2.5	2.7 ±2.8	0.76	50

[a] Reference 3.

FIG. 2. Residuals from simple scaling fits over various ranges in ϵ [$\epsilon = (T_c - T)/T_c$] for the coexistence curve of carbon disulfide + nitromethane (Ref. 3): (a) $\epsilon < 0.2$; (b) $\epsilon < 0.02$; (c) $\epsilon < 0.002$. See Table II, function A, for the parameters in these fits. σ_i is the estimated standard deviation for each point. Fits (b) and (c) in this figure show a slight systematic deviation at $\epsilon \sim 10^{-3}$ which may be due to experimental artifacts.
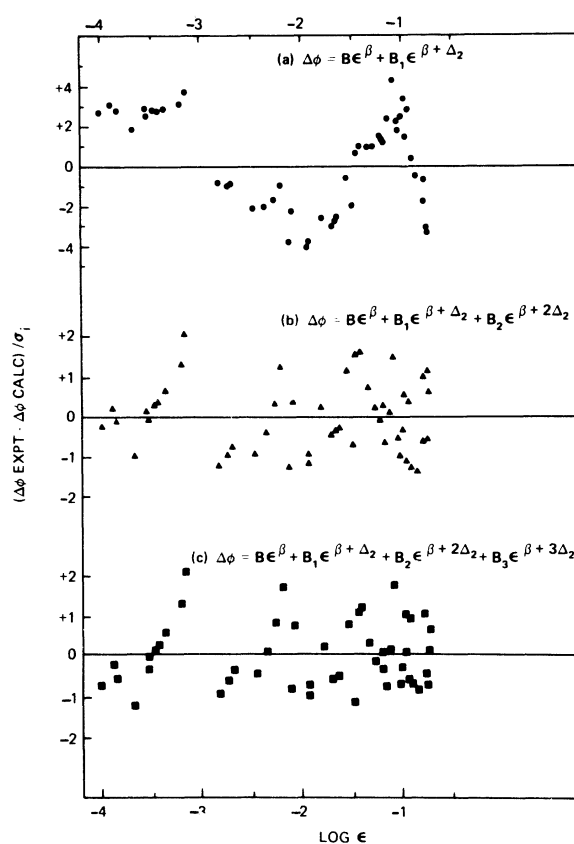

FIG. 3. Residuals from fits to functions with correction terms for the coexistence curve of carbon disulfide + nitromethane (Ref. 3). ϵ is $(T_c - T)/T_c$. σ_i is the estimated standard deviation for each point. See Table II, functions B–D, for the parameters in these fits.

over the entire range $6 \times 10^{-5} < \epsilon < 0.2$ still cannot be fit by a one-term function (A) or even by two terms (function B — simple scaling with one correction term). Function C, simple scaling with two correction terms (five free parameters plus T_c and Δ_2), gives a very good fit to the data. Function C also gives a value of β which is consistent with the Ising value.[10-12]

Function D includes yet another correction term, so that it allows six free parameters (plus T_c and Δ_2). The χ_ν^2 is not very much reduced by the addition of this term. Indeed, an F test[47] indicates that the probability of χ_ν^2 being so changed by chance is greater than 50%. Thus the inclusion of the fourth term is not justified by these data, and function C gives the best fit to the data.

Since the coefficients of such an expansion are highly correlated, one wonders about the effects of truncating the series. Since the Wegner expansion is an asymptotic expansion,[23] one wonders

whether we may have exceeded its range of validity. These two points can be checked to some extent by comparing the three term fit (C, Table II) to one term fits in reduced ranges of ϵ (A, Table II). When the range is reduced to $\epsilon < 0.02$, the simple scaling form suffices. The χ_ν^2 thus obtained is not significantly different from that for a fit of the entire data set with function C. Most importantly, the values of β and B for the asymptotic one-term fits agree quite well with the values obtained for the leading term in the Wegner expansion, which gives us more confidence in the values for β and B. The asymptotic regime for CS_2 + nitromethane ($\epsilon < 0.02$) is not very different from that obtained above for isobutyric acid + water ($\epsilon < 0.006$).

By this analysis, the differences in volume fraction of coexisting phases of carbon disulfide + nitromethane can be fit over the range $6 \times 10^{-5} < \epsilon < 0.2$, where $\Delta\phi$ at $\epsilon = 0.2$ is measured to 0.1%, by an expansion of simple scaling with two cor-

rection terms[23] and with an asymptotic β value close to that of the Ising model.

IV. CONCLUSIONS

Let us summarize the main conclusions from the above work. (1) The volume fraction is a better choice than is the mass density for the order parameter of a binary-liquid mixture. (2) The asymptotic exponent β for liquid-liquid critical points is close to that obtained in the most recent calculations for the Ising model[11,12] and close to that obtained very near liquid-gas critical points.[20] (3) The asymptotic range for β seems to extend to a larger range of reduced temperature for these liquid-liquid critical points than it does for liquid-gas critical points.[13,20,53] The data over an extended range are consistent with Wegner's corrections to asymptotic scaling.[23]

The result that the asymptotic range for liquid-liquid critical points may be larger than for gas-liquid critical points deserves further consideration. Rowlinson[54] has commented that binary mixtures may be more like the Ising model than are

pure fluids because the occupation of sites by two components is more like the occupation of sites by two spin orientations than is the occupation by a particle and a vacancy; i.e., the two components have a more symmetrical relationship than do a particle and a hole.

The result that binary fluids, like pure fluids,[20] are asymptotically like the Ising model supports the hypothesis that all these systems belong to the same universality class.[22]

APPENDIX A

Coexistence curve data for isobutyric acid+ water. T is the temperature and ρ_u and ρ_l are the densities of the upper and lower phases. $\Delta\phi$ is the difference in volume fraction between the coexisting phases.

T (°C)	ρ_u (g/cm³)	ρ_l (g/cm³)	$\sigma_T(10^{-3}$ °C)	$\Delta\phi$	T(°C)	ρ_u(g/cm³)	ρ_l(g/cm³)	$\sigma_T(10^{-3}$ °C)	$\Delta\phi$
A. Run 1 ($\sigma_T = 0.001$ °C)					A. Run 1 ($\sigma_T = 0.001$ °C)				
25.983	0.991 75	0.994 22		0.0439	25.564	0.989 62	0.996 61		0.1254
25.978	0.991 70	0.994 36		0.0474	25.500	0.989 45	0.996 79		0.1317
25.973	0.991 59	0.994 42		0.0505	25.405	0.989 27	0.997 02		0.1392
25.968	0.991 53	0.994 51		0.0530	25.307	0.989 11	0.997 23		0.1463
25.961	0.991 37	0.994 53		0.0563	25.226	0.989 00	0.997 39		0.1512
25.961	0.991 45	0.994 58		0.0557	25.130	0.988 85	0.997 53		0.1569
25.955	0.991 41	0.994 66		0.0580	25.035	0.988 72	0.997 71		0.1629
25.949	0.991 31	0.994 74		0.0611	24.909	0.988 59	0.997 93		0.1696
25.941	0.991 19	0.994 86		0.0653	24.908	0.988 57	0.997 95		0.1704
25.937	0.991 24	0.994 91		0.0653	24.783	0.988 45	0.998 12		0.1763
25.930	0.991 06	0.994 98		0.0697	24.652	0.988 30	0.998 30		0.1827
25.925	0.991 15	0.995 02		0.0689					
25.920	0.991 00	0.995 04		0.0719	B. Run 2				
25.909	0.990 94	0.995 13		0.0748	25.960	0.991 91	0.994 13	1.0	0.0395
25.902	0.990 86	0.995 20		0.0773	25.948	0.991 66	0.994 38	1.0	0.0484
25.884	0.990 77	0.995 31		0.0809	25.945	0.991 53	0.994 43	2.0	0.0517
25.867	0.990 66	0.995 40		0.0844	25.936	0.991 40	0.994 59	2.0	0.0568
25.852	0.990 57	0.995 50		0.0879	25.933	0.991 41	0.994 61	1.0	0.0571
25.819	0.990 42	0.995 67		0.0938	25.926	0.991 27	0.994 71	1.0	0.0612
25.785	0.990 26	0.995 86		0.1000	25.917	0.991 17	0.994 81	1.0	0.0650
25.755	0.990 16	0.995 98		0.1040	25.915	0.991 17	0.994 83	1.0	0.0653
25.692	0.989 95	0.996 21		0.1120	25.906	0.991 02	0.994 89	1.0	0.0689
25.629	0.989 77	0.996 41		0.1188	25.893	0.990 97	0.995 05	1.0	0.0726

APPENDIX A *(Continued)*

T(°C)	ρ_u (g/cm³)	ρ_l (g/cm³)	$\sigma_T(10^{-3}$ °C)	$\Delta\phi$	T (°C)	ρ_u(g/cm³)	ρ_l(g/cm³)	$\sigma_T(10^{-3}$ °C)	$\Delta\phi$
	B. Run 2					B. Run 2			
25.892	0.990 94	0.995 04	2.0	0.0730	25.318	0.989 20	0.997 14	2.0	0.1430
25.885	0.990 89	0.995 16	2.0	0.0761	25.211	0.988 98	0.997 29	2.0	0.1500
25.866	0.990 81	0.995 22	1.0	0.0785	25.128	0.988 88	0.997 53	1.0	0.1563
25.770	0.990 31	0.995 76	1.0	0.0973	25.024	0.988 73	0.997 66	2.0	0.1618
25.699	0.990 02	0.996 11	1.0	0.1089	24.939	0.988 62	0.997 77	1.0	0.1660
25.583	0.989 69	0.996 43	2.0	0.1209	24.557	0.988 27	0.998 34	2.0	0.1844
25.509	0.989 50	0.996 67	1.0	0.1287	24.177	0.987 98	0.998 78	1.0	0.1200
25.398	0.989 29	0.996 93	1.0	0.1372	22.404	0.987 21	1.000 54	1.0	0.2625

APPENDIX B

Density (ρ) as a function of temperature (T) in the one-phase region above the transition temperature in isobutyric acid+ water. The mole fraction of isobutyric acid is 0.110. $\sigma_T = 0.001$ °C.

T (°C)	ρ (g/cm³)	T (°C)	ρ (g/cm³)
37.793	0.986 36	26.614	0.993 21
36.851	0.986 99	26.567	0.993 24
35.747	0.987 73	26.520	0.993 27
34.631	0.988 44	26.471	0.993 31
33.514	0.989 10	26.421	0.993 33
32.406	0.989 81	26.373	0.993 36
31.297	0.990 50	26.327	0.993 39
30.189	0.991 17	26.281	0.993 41
29.216	0.991 73	26.218	0.993 44
28.534	0.992 13	26.168	0.993 47
28.252	0.992 31	26.121	0.993 50
27.423	0.992 77	26.071	0.993 52
26.870	0.993 08	26.025	0.993 54
26.839	0.993 11	26.010	0.993 56
26.807	0.993 12	25.993	0.993 57
26.759	0.993 13	25.991	0.993 54
26.711	0.993 17	25.989	0.993 52
26.662	0.993 20		

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