

Critical heat capacity in a 3-methylpentane + nitroethane mixture near its consolute point

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A computerized high-resolution ac calorimetric technique has been used to measure the heat capacity C_{px} of a critical 3-methylpentane + nitroethane binary-liquid mixture. An analysis of these results yields universal parameters in good agreement with those expected for the $d=3, n=1$ (three-dimensional Ising) universality class. The critical exponent $\alpha=\alpha'$ lies in the range 0.11–0.12, the ratio A'/A of the amplitudes of the leading singularity in C_{px} above and below T_c is 1.79 ± 0.06 . The ratio of the corrections-to-scaling amplitudes D'/D is ~ 1 . The quantity $A_v\xi_0^3/k_B$, which relates the critical amplitude of the heat capacity to that of the correlation length, is also in agreement with the renormalization-group value for the three-dimensional Ising model as expected from two-scale-factor universality.

I. INTRODUCTION

According to the concept of universality, the behavior of the equilibrium properties of systems near a critical point can be divided into a small number of static universality classes. In the case of fluid systems, both one-component pure fluids near their liquid-gas critical point and binary liquids near their consolute (critical-mixing) point should belong to the same universality class as the three-dimensional (3D) Ising model.¹ There are now detailed renormalization-group calculations which support the universality principle and provide quite good numerical values for universal quantities asymptotically close to the critical point.² Thus experimental results can be compared with well-defined theoretical predictions, and a variety of experiments supporting critical universality for many properties of fluid systems have already been reported.³

We are concerned here with the critical divergence in the heat capacity of binary liquids since the behavior of this property has not yet been extensively tested. For a binary liquid near its consolute point there should be a weak divergence in C_{px} , the heat capacity at constant pressure and concentration $x=x_c$.^{1,4} This quantity is analogous to the constant-volume heat capacity of a pure fluid along the critical isochore. Since binary liquids possess an extra thermodynamic degree of freedom, there is a line of second-order critical-mixing points with the critical temperature T_c varying with the pressure. The work described here was carried out at a pressure of 1 atm.

The most detailed study made previously on the critical heat capacity of a binary mixture is for the system triethylamine + heavy water (TEA + D₂O).⁵ Very good agreement was observed between renormalization-group (RG) theory and experiment for data close to T_c , but there was substantial asymmetry in the higher-order terms that become important far from T_c . Furthermore, TEA + D₂O is a complex system in which acid-base hydrolysis and hydrogen bonding play a role, the consolute point is a lower critical-mixing temperature (i.e., phase separation occurs

above T_c), and the phase diagram is very asymmetric. In the present investigation, we have chosen the more typical and more ideal system 3-methylpentane + nitroethane (3-MP + NE). This system has been very well studied; the critical point is an upper consolute point with a convenient critical temperature, the phase diagram is symmetric,⁶ and the critical behavior of the correlation length ξ is well known.⁷

The results reported here are in good agreement with the behavior expected for a 3D Ising model. Thus this work strengthens the case for universality in the critical behavior of binary liquids. In addition, the heat-capacity data are very valuable in testing current dynamical theories for the critical sound absorption in this 3-MP + NE system.^{8,9}

II. EXPERIMENTAL

The ac calorimeter used for these measurements was an automated version of the apparatus described previously for the study of liquid crystals.¹⁰ Several important changes have been made in the construction and operation of this system, and the essential features of these changes will be described below. Complete details are given elsewhere.¹¹

The design of the sample cell has been simplified and improved. The body of the cell was pressed from thin silver sheet to form a cylindrical cup (1 cm i.d. \times 0.12 cm deep) with a flange. Both the cell body and a circular lid cut from silver foil were thoroughly cleaned and dried. Then, working under an argon atmosphere, a thin uniform coating of indium was deposited on the flange and the edge of the lid, the cell was filled with a well-mixed critical solution at a temperature above T_c , and the cell was sealed by applying pressure with a handpress to form a cold-welded indium seal. The resulting filled cells were leak tight under both vacuum and pressure. Furthermore, this type of cell proved to be suitably inert with respect to chemical reactions with the solution. There was no evidence of sample degradation over a period of several

months, which is much longer than the 7-day duration of the heat-capacity run reported in Sec. III.

In addition to the 3-MP + NE solution, the cell also contained four short lengths of nickel wire. These tiny rods provided very good stirring when activated by a magnetic stirrer bar mounted beneath the calorimeter. Such stirring is essential for obtaining reliable measurements in the two-phase region. After the cell had been filled and sealed, an 80- Ω coil of Chomel heater wire was attached to the base of the cup with General Electric 7031 varnish, and a small bead thermistor was cemented to the center of the lid. The final weight of the filled cell was ~ 600 mg, of which ~ 80 mg was the weight of the binary-liquid solution. As a result, the heat-capacity contribution due to the binary liquid was always greater than one-half the total observed heat capacity.

The basic theory of the method given in Ref. 10 is still valid. Under the conditions of our operation, the heat capacity is well described by the simple expression

$$C_p = Q_0 / \omega \Delta T_{ac} \quad (1)$$

where Q_0 is the rms value of the ac power input from the heater, ω and ΔT_{ac} are the frequency and the zero-to-peak amplitude of the resulting temperature oscillations. The system was operated at a constant frequency $\omega = 0.196$, which corresponds to a 32-sec period for the temperature oscillations. The cell temperature was monitored by direct readings of the thermistor resistance with a Keithley Model 192 Programmable Digital Multimeter every 0.5 sec during eight periods of oscillation. The operation of the heater and the multimeter were synchronized with a Tecmar timer-counter board so that there were exactly 128 evenly spaced thermistor readings during each heater period. A multiplexer allowed the Keithley to also measure the heater current and voltage and the resistance of a Leeds and Northrup 8164B platinum resistance thermometer for each data point. The various outputs of the Keithley meter were sent via an IEEE (Institute of Electrical and Electronic Engineers) interface to the memory of a North Star microcomputer for processing and eventually storage of the average temperature and the heat capacity on a floppy disk.

The calorimeter was operated in a slow scanning mode in which the temperature of the regulated thermostat bath was varied linearly with time at an adjustable rate. Very slow scan rates were used near T_c : 12 mK h^{-1} for $\Delta T = |T - T_c| < 0.5 \text{ K}$, 120 mK h^{-1} for $0.5 \text{ K} < \Delta T < 1 \text{ K}$, and 360 mK h^{-1} for $1 \text{ K} < \Delta T < 3 \text{ K}$. This protocol had been established as sufficiently slow to ensure thermodynamic equilibrium throughout the run. No hysteresis was observed between data taken on warming or cooling through the transition region. Furthermore, no change in the heat-capacity value occurred when the temperature was held constant at a value $\sim 0.5 \text{ K}$ below T_c for a period of 2 h.

The stored thermistor readings were analyzed after first correcting for the temperature drift that occurred during the taking of a data point. This was done by fitting a quadratic curve to the thermistor readings corresponding to the zero crossings of the heater input. The resulting

curve, representing the slow drift in the average temperature of the sample due to the finite scanning rate, was subtracted from all the thermistor readings. Note that near T_c this drift only amounted to $\sim 0.85 \text{ mK}$ during the 256-sec duration of thermistor readings taken for a data point. The amplitude ΔT_{ac} of the oscillating sample temperature was then determined from Fourier sine and cosine sums over the corrected set of thermistor readings. Typical values of the amplitude were $\pm 5 \text{ mK}$ zero to peak.

Approximately 20 g of the critical mixture was prepared by weight using pure 3-methylpentane and nitroethane obtained from Aldrich Chemical. The manufacturer's stated purity was better than 99.9% for 3-MP and better than 99.5% for NE, and these materials were used without any further purification. The binary-liquid sample contained in a sealed weighing bottle was heated about 15 K above T_c and vigorously shaken to ensure good mixing prior to filling the calorimeter cell. The mole fraction of nitroethane x was 0.502 ± 0.001 , in good agreement with the best estimate of the critical concentration as $x_c = 0.500$.⁶

Although the heat capacities reported from many ac calorimetric investigations are given in relative or arbitrary units, we have endeavored to use the ac technique here as an absolute method. The desired heat capacity per mole of critical mixture \tilde{C}_{px} was obtained from

$$\tilde{C}_{px} = \frac{\overline{M}_W}{m} [C_p(\ell) - C_p(e)] \quad (2)$$

where ℓ denotes the filled cell, e denotes the empty cell, m is the mass of the binary mixture contained in the filled cell, and the "average" molecular weight \overline{M}_W is the mass of one mole of mixture [$\overline{M}_W = 0.498M_W(3\text{-MP}) + 0.502M_W(\text{NE}) = 80.62 \text{ g}$ for our mixture]. The heat capacity of the empty cell was determined as follows. After completion of all the measurements on the filled cell, a small hole was made in the lid of a cell and most of liquid was withdrawn with a syringe. The cell was then rinsed with acetone and placed in a drying oven at 70°C for 2 h to completely evaporate any residual liquid. The empty cell was weighed and its heat capacity was measured over the same temperature range as that used for studying the filled cell.

Absolute temperature values were obtained from a calibration of the thermistor against the platinum resistance thermometer mounted in an aluminum block attached to the sample holder. These thermistor temperatures are estimated to be accurate to within $\pm 30 \text{ mK}$, but a determination of T_c on an absolute basis is not important for the analysis of the variation of C_{px} with the temperature difference $T - T_c$. The precision in the \tilde{C}_{px} values near T_c is quite good, but the uncertainty in the absolute accuracy of \tilde{C}_{px} is estimated to be 5–10% which is typical of that achieved previously with the ac method.^{12,13}

III. RESULTS

The heat capacity of a cell filled with a constantly stirred critical mixture of 3-methylpentane and nitroethane was measured over the temperature range 292–310 K. A very large number of data points (2108)

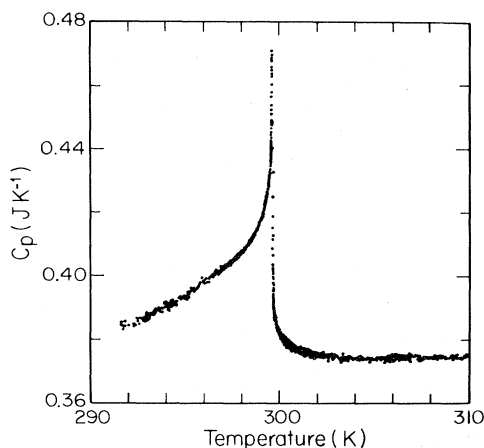


FIG. 1. Raw data for the heat capacity of a filled cell containing 0.079 g of the critical 3-MP + NE mixture.

was collected on both slow warming and cooling scans over a period of 7 d. No hysteresis effects were observed, and all of these raw data points are shown in Fig. 1 without distinguishing between warming and cooling runs.

After completion of these measurements of C_p ($\not\approx$), the binary mixture was removed and a second set of measurements were made on the heat capacity of the empty cell. The latter quantity varied in a smooth and regular manner with temperature. Indeed, these empty cell data could be very well described by the empirical polynomial

$$C_p(e) = 0.188 + 3.6 \times 10^{-4}(T - 290) + 9.9 \times 10^{-6}(T - 290)^2, \quad (3)$$

which was obtained by a least-squares fit to 361 data points over the 290–310-K range.

By using Eqs. (2) and (3), one can convert the raw data points shown in Fig. 1 into molar heat capacities \tilde{C}_{px} . However, it is not attractive to carry out a least-squares fitting procedure with as many points as are in this direct data set. Instead, a merged data set was created by properly averaging n_i adjacent direct data points, where n_i varied from 1 to 15 depending on the distance from T_c . This process also has the advantage of providing additional statistical averaging which reduces the random scatter for the merged data points. The resulting set of 291 points is shown in Fig. 2 in the form of the dimensionless quantity \tilde{C}_{px}/R .

It is clear from Fig. 2 that the random scatter in the merged data points is quite small except at temperatures below 295 K, where it becomes about twice that observed above this temperature. The cause of this increased scatter was a difficulty in achieving really good regulation in the temperature of the Lauda NBS circulating thermostat bath below 295 K. Fortunately, this is not a serious problem since the fits to be carried out in Sec. IV will not include data at temperatures outside the range $-3 \text{ K} < (T - T_c) < 3 \text{ K}$.

The maximum value of C_{px} was observed at 299.613 K, but this does not correspond to T_c due to a systematic distortion of the ac heat-capacity values very close to T_c .

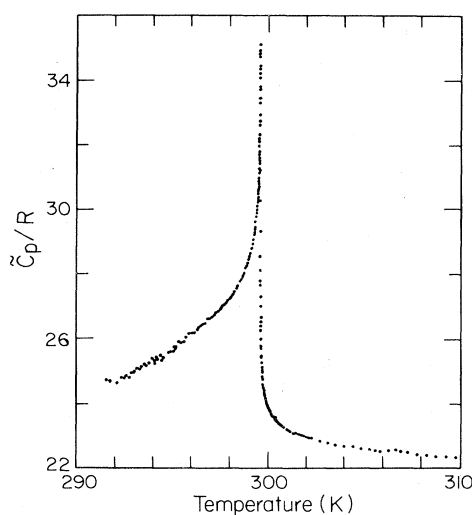


FIG. 2. Molar heat capacity \tilde{C}_{px} of a 3-MP + NE critical mixture (see text for a discussion of the data reduction).

Equation (1) will provide an appropriate average heat capacity over the range $2\Delta T_{ac}$ of the temperature oscillation as long as C_{px} can be considered to be effectively linear over that range. A simple convolution calculation based on $\Delta T_{ac} \approx 5 \text{ mK}$ and an assumed Ising variation for C_{px} indicates that significant differences between C_p (true) and C_p (observed) will occur in the range $299.609 \text{ K} < T < 299.629 \text{ K}$ and that T_c should be close to 299.619 K. Such a value for T_c is consistent with the literature value of 299.600 K.⁶

The absolute accuracy of our \tilde{C}_{px} values can be tested by comparison with a heat-capacity value calculated from the thermodynamic expression $C_p = TV\alpha_p/(\partial T/\partial p)_S$. By combining available data on the density and thermal expansion coefficient with a value for $(\partial T/\partial p)_S$ at $(T - T_c) = 45 \text{ mK}$, Clerke *et al.*⁸ have obtained a specific heat of $(2.48 \pm 0.10) \text{ J K}^{-1} \text{ g}^{-1}$. This corresponds to a molar heat capacity \tilde{C}_{px} of $(200.0 \pm 8.1) \text{ J K}^{-1} \text{ mol}^{-1}$ at $\Delta T = +45 \text{ mK}$. The present experiment yields $\tilde{C}_{px} = 212.5 \text{ J K}^{-1} \text{ mol}^{-1}$ at that ΔT value when T_c is chosen to be 299.621 K (see Sec. IV A). The difference of 6.25% between these heat-capacity values is greater than the error bounds cited in Ref. 8 but well within the 5–10% uncertainty in absolute values that are typical for ac calorimetric results. Indeed, it would not be surprising if the ac heat-capacity values reported here were systematically high by a temperature-independent multiplicative factor of 1.06. Systematic errors of this type can arise due to nonuniform heat-flux densities across the heater.¹³ Such an error will have no effect on the shape of the \tilde{C}_{px} curve or the resulting critical exponents and critical amplitude ratios. However, a consideration of two-scale-factor universality (see Sec. IV C) suggests that our \tilde{C}_{px} values are indeed 6% high.

Finally, we should note the importance of stirring. An exploratory run made on an unstirred sample yielded a sharp and almost symmetrical heat-capacity peak. The C_p variation above T_c was essentially the same as that shown

in Fig. 1 for a stirred sample. However, the C_p values below T_c were appreciably smaller than those reported here and there was a definite hysteresis between warming and cooling measurements. Clearly thermodynamic equilibrium was not achieved on the time scale of our experiment due to the very slow diffusion of the components between the coexisting phases in the absence of stirring.

IV. ANALYSIS AND DISCUSSION

A. Fitting procedure

The theoretical form for the variation in the heat capacity C_{px} near T_c for a binary mixture with $x = x_c$ can be represented by¹⁴

$$\tilde{C}_{px}/R = At^{-\alpha}(1 + Dt^{\Delta_1}) + B + Et \quad (4)$$

in the homogeneous one-phase region ($T > T_c$), and

$$\tilde{C}_{px}/R = A'|t|^{-\alpha}(1 + D'|t|^{\Delta_1}) + B' + E't \quad (5)$$

in the two-phase region, ($T < T_c$). The reduced temperature t is defined by $t \equiv (T - T_c)/T_c$. Since we have chosen to express the heat capacity in the dimensionless form \tilde{C}_{px}/R , all the amplitude parameters (A , B , D , and E) will also be dimensionless. The terms $At^{-\alpha}$ and $A'|t|^{-\alpha}$ represent the dominant contributions to the singularity in the heat capacity at T_c , while the terms Dt^{Δ_1} and $D'|t|^{\Delta_1}$ are corrections-to-scaling terms which become important only for large values of t . The terms B and B' contain contributions from both the singular and the regular parts of the free energy. The terms Et and $E't$ arise completely from the regular part of the free energy and represent the normal linear variation expected over a short range of temperature in the absence of any phase transition. Scaling laws, supported by RG calculations, lead to several constraints on these fitting parameters: $\alpha = \alpha'$, $\Delta_1 = \Delta_1'$,

and $B = B'$.¹⁴ One would also expect that $E = E'$ since the linear term arises from regular (noncritical) contributions.

The Marquardt algorithm has been used to carry out least-squares fits of the data with Eqs. (4) and (5). The quality of a fit is characterized by the reduced χ^2 value

$$\chi_v^2 = \frac{1}{\nu} \sum_{i=1}^n \sigma_i^{-2} [(\tilde{C}_p/R)_i^{\text{obs}} - (\tilde{C}_p/R)_i^{\text{calc}}]^2, \quad (6)$$

where $\nu = n - p$ is the number of degrees of freedom (n being the number of data points and p the number of adjustable parameters). Our data are consistent with a constant standard deviation $\sigma_i = 0.06$ (i.e., equal weights) for $|t| > 3.3 \times 10^{-5}$, which represents the smallest t values used in the fitting procedure. Data points closer to T_c have been excluded from the fit due to systematic errors associated with the finite size of ΔT_{ac} (see Sec. III).

A few preliminary fits were made as separate fits with Eq. (4) to data above T_c and Eq. (5) to data below T_c . These fits were undertaken primary to define a range for the value of the critical temperature T_c to be used in simultaneous fits to data above and below T_c . Owing to convolution problems near T_c , we could only obtain from the experimental data an estimate that T_c should be close to 299.619 K but could not determine a precisely defined value. For these initial "single-sided" fits, the maximum reduced temperature $|t|_{\text{max}}$ was taken to be 3×10^{-3} and the corrections-to-scaling terms were neglected. The parameters E and E' were both fixed at 19.5, which corresponds to choosing a linear temperature dependence for C_{px} in the critical mixture that is the average of that observed for C_p in pure 3-MP and pure NE. For fits 1 and 2 in Table I, α was fixed at the Ising value and only T_c , A (or A') and B (or B') were allowed to vary. Although the T_c values obtained from these separate fits differed by 8 mK, the B and B' values were almost identical, as expected from scaling. In fits 3 and 4, T_c was fixed at 299.621

TABLE I. Parameter values obtained from least-squares fits of the 3-MP + NE heat-capacity data with Eqs. (4) and (5). Fits 1–4 involved separate fits to data above T_c and data below T_c ; all other fits involved simultaneous fits to data above and below T_c with the use of the scaling constraints $\alpha = \alpha'$ and $B = B'$. Parentheses indicate that the parameter was held fixed at the indicated value.

Fit	$ t _{\text{max}}$	T_c	α, α'	A	A'	B, B'	D	D'	$E = E'$	ν	χ_v^2
1	3×10^{-3}	299.625	(0.11)	2.96		17.72	(0)		(19.5)	71	0.72
2	3×10^{-3}	299.617	(0.11)		5.60	17.42		(0)	(19.5)	74	0.73
3	3×10^{-3}	(299.621)	0.1233	2.60		17.92	(0)		(19.5)	71	1.73
4	3×10^{-3}	(299.621)	0.1168		5.42	17.21		(0)	(19.5)	74	1.68
5	1×10^{-3}	(299.619)	0.1045	3.85	6.46	16.06	(0)	(0)	(0)	115	1.88
6	1×10^{-3}	(299.620)	0.1117	3.33	5.81	16.79	(0)	(0)	(0)	115	1.70
7	1×10^{-3}	(299.621)	0.1188	2.90	5.25	17.42	(0)	(0)	(0)	115	1.61
8	1×10^{-3}	(299.622)	0.1259	2.53	4.76	17.99	(0)	(0)	(0)	115	1.75
9	1×10^{-3}	(299.623)	0.1310	2.20	4.32	18.50	(0)	(0)	(0)	115	1.90
10	1×10^{-2}	(299.619)	0.1050	3.90	6.48	15.80	0.708	0.478	30.95	197	1.58
11	1×10^{-2}	(299.620)	0.1142	3.24	5.63	16.80	0.529	0.546	32.72	197	1.42
12	1×10^{-2}	(299.621)	0.1192	2.93	5.23	17.27	0.388	0.583	33.86	197	1.32
13	1×10^{-2}	(299.622)	0.1254	2.59	4.79	17.81	0.311	0.479	31.01	197	1.46
14	1×10^{-2}	(299.623)	0.1301	2.33	4.43	18.25	0.176	0.599	29.54	197	1.59
15	1×10^{-2}	299.619	(0.110)	3.41	5.91	16.65	0.460	0.342	30.26	197	1.48
16	1×10^{-2}	(299.621)	0.1210	2.68	4.99	17.86	(0)	(0)	$\begin{cases} E = 32.06 \\ E' = 3.00 \end{cases}$	197	1.46

K (the midpoint of the range obtained from fits 1 and 2) for data above and below T_c but α and α' were allowed to be free parameters. The results in Table I show that scaling is quite well obeyed (i.e., $\alpha \cong \alpha'$, $B \cong B'$ in fits 3 and 4).

All subsequent fits were carried out as simultaneous fits to data above and below T_c . In these fits we imposed the scaling constraints $\alpha = \alpha'$ and $B = B'$. We also used the same T_c value in both Eqs. (4) and (5), but this value was varied over the range 299.619–299.623 K. It will be seen later that the corrections-to-scaling terms are small and strongly coupled to the linear Et terms. Thus it was impractical to determine the exponent Δ_1 empirically, and we have fixed this exponent at its theoretical value of 0.5.¹⁴ For fits 5–9, the value of $|t|_{\max}$ was 10^{-3} and both the linear terms and corrections-to-scaling terms can be neglected. Table I shows that there is a broad minimum in χ^2_{ν} when T_c is varied by 1-mK steps, with the best fit occurring for $T_c = 299.621$ K. Note that there is a clear correlation among the values of the fitting parameters. As T_c is increased, there is a monotonic increase in α and B and an associated decrease in both A and A' .

The fits to data very close to T_c (fits 5–9) are stable on expanding the range to $|t|_{\max} = 10^{-2}$. For fits 10–15, the higher-order terms in Eqs. (4) and (5) are included since neither the linear nor the corrections-to-scaling terms can be neglected at the much larger t values involved here. We have assumed that $E = E'$, and the value of E is now taken to be a freely adjustable parameter. No constraints were imposed on D or D' . The value of T_c was again varied by 1-mK steps over a range of values. As seen from fits 10–14, the χ^2_{ν} minimum is still broad and the best fit occurs for $T_c = 299.621$ K as before. Furthermore, the values of the parameter α , A , A' , and B in fits 10–14 are very close to those obtained in fits 5–9. The least-squares values of $E = E'$ found in fits 10–14 are physically reasonable: $E/T_c \cong 0.10 \text{ K}^{-1}$ for the critical mixture is comparable to the linear slope of \tilde{C}_p/R for the pure components (0.05 K^{-1} for nitroethane and 0.08 K^{-1} for 3-methylpentane).

Two additional fits were carried out on the extended data sets with $|t|_{\max} = 10^{-2}$. In fit 15, the critical ex-

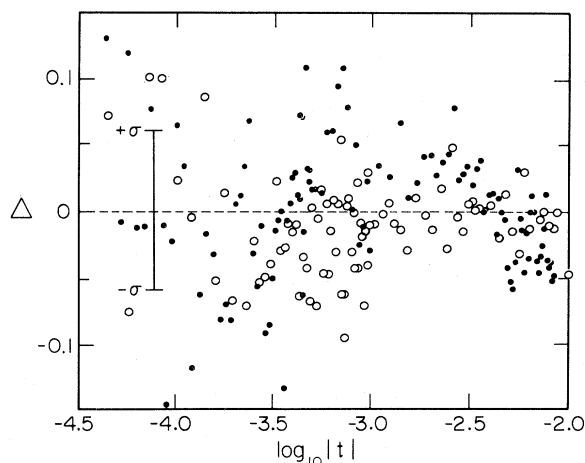


FIG. 3. Deviations between the observed heat-capacity values and the heat capacities calculated with Eqs. (4) and (5) and the parameters of fit 12 in Table I: $\Delta = \tilde{C}_p(\text{obs})/R - \tilde{C}_p(\text{calc})/R$.

ponent α was fixed at the theoretical Ising value of 0.110. As expected, the parameters for this fit lie between those obtained in fits 10 and 11. The ratio of the χ^2_{ν} values for fit 15 and fit 12 (the “best” fit) is only 1.12. If one uses the F test at a probability level of 10%, the limiting value of $F(197,197)$ is 1.14. Thus the better quality of fit 12 compared to fit 15 is not statistically significant at the 90% confidence level.

The final fit demonstrates the effect of neglecting the corrections-to-scaling terms and simultaneously allowing an abrupt change at T_c in the regular linear term by relaxing the constraint $E = E'$. Comparison of fits 12 and 16 shows that one can obtain a fairly reasonable fit to the extended data set when $D = D' = 0$ and $E \neq E'$, but fit 16 involves systematic changes in both A and A' from the values obtained in fit 7 where $|t| < 10^{-3}$. We consider fit 16 to be rather artificial in view of these changes in A

TABLE II. A comparison of the parameter values for two almost equivalent fits to 3-MP + NE with those for triethylamine + heavy water (Ref. 5) and the 3D Ising model.

Parameter	Three-dimensional Ising	3-MP+NE		TEA + D ₂ O
		fit 12	fit 15	
T_c (K)		299.621	299.619	287.7439
$\alpha = \alpha'$	0.110 ± 0.008	0.119 ± 0.010	(0.110)	0.107 ± 0.002
A		2.93	3.41	6.457
A'/A	1.95 ± 0.13	1.79 ± 0.06	1.73	1.75 ± 0.03
$B = B'$		17.27	16.65	5.12
$\Delta_1 = \Delta_1'$	0.5	(0.5)	(0.5)	(0.5)
D		0.388	0.460	−0.247
D'/D	~1	1.5	0.74	−1.90
E				−31.46
E'		33.86	30.26	−232.93
χ^2_{ν}		1.32	1.48	1.53

and A' , the unattractively large difference between E and E' , and the unwarranted neglect of corrections to scaling. However, fit 16 is useful in demonstrating that the universal quantities α and A'/A are not very sensitive to substantial changes in the way the higher-order terms are handled.

The quality of the agreement between the observed heat-capacity points and the best theoretical fit [Eqs. (4) and (5) with the parameters obtained in fit 12] is shown in Fig. 3, which gives the deviations

$$\Delta = \tilde{C}_p(\text{obs})/R - \tilde{C}_p(\text{calc})/R$$

in both the one- and two-phase regions. The deviations obtained with fit 15 were very similar.

B. Comparison with Ising universality class

In this section we wish to compare the critical behavior in the heat capacity observed in 3-MP + NE with that reported previously⁵ for triethylamine (TEA) + D₂O and with those universal features that can be calculated theoretically for the 3D Ising model. The values of the appropriate parameters are given in Table II. For 3-MP + NE, we cite parameter values for both fit 12 (the best least-squares fit) and fit 15 (an almost comparable fit with α fixed at the theoretical Ising value). The parameters for TEA + D₂O correspond to those given in Table III of Ref. 5 modified to match the form of the theoretical equations given here. The TEA + D₂O mixture exhibits a lower consolute point; thus the homogeneous phase occurs below T_c and the two-phase region is above T_c . Unprimed parameters are used for the single phase, and primed parameters are used for the two-phase region, just as in the case of an upper consolute point system like 3-MP + NE.

The theoretical value of the critical exponent α has been obtained from both RG calculations¹⁵ ($\alpha=0.110\pm0.008$) and from high-temperature series ($\alpha=0.125\pm0.02$ is given by Camp *et al.*¹⁶ but a more recent reanalysis¹⁷ yields $\alpha=0.110$). According to the best least-squares fit (fit 12), the α value for 3-MP + NE is given by $\alpha=0.119\pm0.010$, where the error bounds are 95% confidence limits based on the F test. The fairly large magnitude of these error bounds reflects the absence of reliable experimental data very close to T_c . This difficulty (and the related uncertainty in the value of T_c) is, of course, due to the systematic distortion near T_c caused by the finite ΔT_{ac} amplitude. The deconvolution estimate that $T_c \cong 299.619$ K (see Sec. II) is consistent with the value of T_c obtained in fit 15 where α is fixed at 0.110. Thus we believe that the experimental value of α lies in the range 0.11 to 0.12 and is unlikely to be as large as 0.13 (which would imply a T_c value greater than that expected from the position of the observed maximum in C_{px}). Such a conclusion about the experimental α value is clearly consistent with theory, but our 3-MP + NE data do not provide as stringent a test as the TEA + D₂O data of Ref. 5.

The ratio A'/A of the critical heat-capacity amplitude in the ordered phase to that in the disordered phase is a universal quantity; i.e., A'/A should have the same value for all members of a given universality class. For the 3D

Ising model, theoretical estimates have been obtained for A'/A from high- and low-temperature series calculations and from RG calculations involving expansions in $\epsilon=4-d$, where d is the dimensionality of the system. The most recent series result for A'/A is 1.96,¹⁸ whereas RG theory yields 1.82 to first order in ϵ and 2.08 to second order.^{19,20} The best experimental A'/A value for 3-MP + NE is 1.79 ± 0.06 , a value which is in good agreement with the ratio reported for TEA + D₂O. Both of these binary liquids appear to have A'/A ratios that are somewhat smaller than the theoretical estimates. However, the accuracy of both the experimental and the theoretical ratio needs to be improved before one can judge the possibility of any systematic disagreement.

The ratio of the corrections-to-scaling amplitudes D'/D is also a universal quantity. Theoretical evaluations of this ratio for a 3D Ising model indicate that D'/D is a positive quantity of the order of unity.²¹ All of our 3-MP + NE fits are consistent with this theoretical conclusion. In this regard, the 3-MP + NE data are in better agreement with Ising universality than the TEA + D₂O data, which yield a negative value for D'/D .

Finally, there is a striking difference in the behavior of the linear background terms for 3-MP + NE and TEA + D₂O. The present data are fully consistent with the imposed equality $E=E'$, and the resulting value of E is positive which is physically plausible. Furthermore, the background slope in the critical 3-MP + NE mixture is comparable to the linear slopes observed in the pure components. For TEA + D₂O, the slopes are negative and there is a drastic change in the magnitude of the slope on going into the two-phase region. Bloeman *et al.*⁵ speculate that this effect is related to strong concentration dependent terms in a system where the coexistence curve is very asymmetric. This seems plausible since such odd behavior for E and E' is not required to describe the background terms in 3-MP + NE, where the coexistence curve is symmetrical over a wide range of temperature.

C. Two-scale-factor universality

According to the hypothesis of two-scale-factor universality,²² the length scale for static correlations in the order parameter is universally related to the thermodynamic scales. It follows that there is a universal quantity

$$X = A_v \xi_0^3 / k_B \quad (7)$$

which connects the amplitudes of the leading singularities in the heat capacity and the correlation length $\xi = \xi_0 t^{-\nu}$. For the 3D Ising model, the theoretical value of X given by RG calculations^{20,23} is $(1.97\pm0.02)\times 10^{-2}$ and that obtained from series expansions²² is $(1.65\pm0.01)\times 10^{-2}$.

The quantity A_v appearing in this definition of X is the amplitude of the singular heat capacity per unit volume when the leading singularity is represented in the form $(A/\alpha)t^{-\alpha}$. Thus $A_v = \rho_c \alpha AR / \bar{M}_w$, where $\rho_c = 0.792$ g cm⁻³ is the critical density²⁴ and A is the dimensionless amplitude appearing in Eq. (4). In order to calculate an experimental value for X , it is necessary to combine C_{px} and ξ fits that are compatible in the sense that the critical exponents α and ν satisfy the hyperscaling relation

TABLE III. Evaluation of the two-scale-factor universality quantity X for 3-MP + NE and TEA + D₂O (Ref. 5).

Quantity	3-MP + NE	TEA + D ₂ O
α	0.110	0.107
$A_v(10^5 \text{ J K}^{-1} \text{ m}^{-3})$	0.30±0.01	2.15±0.1
ν	0.630	0.63
$\xi_0(10^{-10} \text{ m})$	2.13±0.05	1.08±0.1
100 X	2.12±0.2	1.96±0.4
100 $X(\text{corr})$	2.00±0.2	

$3\nu=2-\alpha$. Measurements of the intensities of scattered light⁷ yield a critical correlation length exponent ν in the range 0.625 to 0.630. These values would imply $\alpha=2-3\nu$ values in the range 0.125–0.110, which are consistent with our C_{px} fits.

Table III gives the result of a determination of X using amplitudes that correspond to the choice of the best theoretical critical exponents $\alpha=0.11$ and $\nu=0.63$. The A_v value is derived from C_{px} fit 15, and the ξ_0 value was taken from Eq. (4.18) in Ref. 7. The resulting X value is fairly insensitive to this choice. (If we use A_v and ξ_0 values corresponding to the choices $\alpha=0.119$ and $\nu=0.627$, the X value is found to be 2.16×10^{-2} .)

Before comparing the experimental and theoretical X values, it is necessary to consider the possibility of a systematic error in the absolute heat capacities measured with the ac method. Comparisons with theory in Sec. IV B were unaffected by such concerns since only amplitude ratios were involved. However, the evaluation of X requires the absolute value of A_v . The error limit cited in Table III reflects only uncertainties in determining the fitting parameters due to random scatter in the data. As described in Sec. III, our \tilde{C}_{px} value at $\Delta T=45$ mK is 6% larger than the value determined by Clerke *et al.*⁸ If we

assume that all our C_{px} values are systematically high by a constant multiplicative factor of 1.06, then the true A_v value should be 0.94 times the value given in Table III and the “corrected” value $X(\text{corr})=0.020$ is obtained. This experimental $X(\text{corr})$ value is in excellent agreement with the RG theoretical value of X , but even the uncorrected X value agrees with the RG theory within the cited error limit. Thus, our result confirms the RG value and is not consistent with the lower value given by series calculations.

V. SUMMARY

Heat-capacity data near the consolute point in a critical mixture of 3-methylpentane and nitroethane have been analyzed in terms of the appropriate theoretical expressions [(Eqs. (4) and (5)]. These data are fully consistent with scaling predictions. The values of the fitting parameters that should be universal quantities—the critical exponent α , the amplitude ratio A'/A , and the corrections-to-scaling amplitude ratio D'/D —agree well with 3D Ising values obtained from RG calculations. By combining information on the critical amplitudes of the heat capacity and the correlation length, we have produced support for the validity of two-scale-factor universality in the 3-MP + NE system. Thus the present results confirm and strengthen the conclusion that the critical behavior of binary-liquid systems belongs to the $d=3$, $n=1$ (3D Ising) universality class.

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- ¹J. V. Sengers and J. M. H. Levelt Sengers, in *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley, New York, 1978), p. 103.
- ²M. E. Fisher, *Rev. Mod. Phys.* **46**, 597 (1974); K. G. Wilson and J. Kogut, *Phys. Rep.* **12c**, 75 (1974).
- ³J. V. Sengers, in *Phase Transitions Cargese 1980*, edited by M. Levy, J. C. Le Guillou, and J. Zinn Justin (Plenum, New York, 1982), p. 95.
- ⁴R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A* **2**, 1047 (1970).
- ⁵E. Bloemen, J. Thoen, and W. Van Dael, *J. Chem. Phys.* **73**, 4628 (1980).
- ⁶A. M. Wims, D. McIntyre, and F. Hynne, *J. Chem. Phys.* **50**, 616 (1969).
- ⁷R. F. Chang, H. Burstyn, and J. V. Sengers, *Phys. Rev. A* **19**, 866 (1979).
- ⁸E. A. Clerke, J. V. Sengers, R. A. Ferrell, and J. K. Bhattacharjee, *Phys. Rev. A* **27**, 2140 (1983).
- ⁹C. W. Garland and G. Sanchez, *J. Chem. Phys.* (in press).
- ¹⁰G. B. Kasting, K. J. Lushington, and C. W. Garland, *Phys. Rev. B* **22**, 321 (1980).
- ¹¹G. Sanchez, Ph.D. thesis, Massachusetts Institute of Technology, 1983 (unpublished).
- ¹²J. Thoen, H. Marynissen, and W. Van Dael, *Phys. Rev. A* **26**, 2886 (1982).
- ¹³K. J. Lushington and C. W. Garland, *J. Chem. Phys.* **72**, 5752 (1980) and references therein.
- ¹⁴F. J. Wegner, *Phys. Rev. B* **5**, 4529 (1972); M. Barmatz, P. C. Hohenberg, and A. Kornbit, *ibid.* **12**, 1947 (1975).
- ¹⁵G. A. Baker, Jr., B. G. Nickel, and D. I. Meiron, *Phys. Rev. B* **17**, 1365 (1978).
- ¹⁶W. J. Camp, D. M. Saul, J. P. Van Dyke, and W. Wortis, *Phys. Rev. B* **14**, 3990 (1976).
- ¹⁷J. Zinn-Justin, *J. Phys. (Paris)* **40**, 969 (1979).
- ¹⁸A. Aharony and P. C. Hohenberg, *Phys. Rev. B* **13**, 3081 (1976).
- ¹⁹E. Brézin, J. C. Le Guillou, and J. Zinn-Justin, *Phys. Rev. D* **8**, 2418 (1973).
- ²⁰C. Bervillier, *Phys. Rev. B* **14**, 4964 (1976); C. Bervillier and C. Godreche, *ibid.* **21**, 5427 (1980).
- ²¹M. C. Chang and A. Houghton, *Phys. Rev. B* **21**, 1881 (1980); *Phys. Rev. Lett.* **44**, 785 (1980); A. Aharony and G. Ahlers, *ibid.* **44**, 782 (1980); A. Bourgou and D. Beysens, *ibid.* **47**, 257 (1981).
- ²²D. Stauffer, M. Ferer, and M. Wortis, *Phys. Rev. Lett.* **29**, 345 (1972).
- ²³P. C. Hohenberg, A. Aharony, B. I. Halperin, and E. D. Siggia, *Phys. Rev. B* **13**, 2986 (1976).
- ²⁴S. C. Greer and R. Hocken, *J. Chem. Phys.* **63**, 5067 (1973).