

## THERMAL EXPANSION OF METHANOL + CYCLOHEXANE NEAR THE CRITICAL SOLUTION POINT †

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We report precise measurement of volume changes as function of temperature in the one phase region of methanol + cyclohexane near the critical solution point. We find a value for the critical exponent  $\alpha$  of  $0.11 \pm 0.07$  in the region  $11 \text{ mK} < T - T_c < 6.4 \text{ K}$ . This value agrees with the Ising value of  $1/8$ . For temperatures closer to  $T_c$  we observe a stronger divergence. In addition we observe unusual behavior over a small region of temperature centered at  $T - T_c = 15 \text{ mK}$ .

### 1. Introduction

Near the critical points of binary fluid mixtures both the specific heat at constant pressure and the thermal expansion at constant pressure increase in an anomalous fashion [1,2]. Both of these anomalies are described by the critical exponent  $\alpha$ . Since  $\alpha$  is small, the divergences are weak, so historically it has been difficult to obtain a reliable determination of  $\alpha$ . In this experiment we report a measurement of the thermal expansivity of a critical mixture of methanol and cyclohexane as a function of temperature near the critical point. Such a measurement should lead to a better determination of  $\alpha$ , the specific heat exponent. Similar measurements have been made recently by others, notably Greer and Hocken [3] and Morrison and Knobler [4]. Greer and Hocken measured the density as a function of temperature of the system nitroethane and 3-methylpentane in the region  $100 \text{ mK} < T - T_c < 5.0 \text{ K}$ . Although they observed an ano-

maly, their lack of precision prevented them from differentiating between a power law and a logarithmic divergence. Morrison and Knobler measured the thermal expansion of the critical mixture isobutyric acid and water in the region  $T - T_c < 500 \text{ mK}$ . Although they took data in the region  $T - T_c < 5 \text{ mK}$ , they did not include these in their analysis, since it showed an apparent divergence much larger than the remainder of the data. Also in some of their data they observe an anomalous "hump" in the region  $0.03 \text{ K} < T - T_c < 0.1 \text{ K}$ , when plotting volume versus  $T - T_c$ , and these data are not used in their determinations of  $\alpha$ .

In our experiment we were able to obtain data in the region  $2.0 \text{ mK} < T - T_c < 6.4 \text{ K}$ . This is a much larger temperature range than that utilized in the previous experiments. The precision of our measurements is better than Greer and Hocken's and is approximately the same as Morrison and Knobler's. As with Morrison and Knobler's experiment, our data very close to  $T_c$  diverges much more rapidly than expected, and so we have determined  $\alpha$  with and without this close-in data. In addition, we also observe an apparent hump in our data. Because of this hump we have chosen to analyze our data in a different fashion than Morrison and Knobler. Our method of analysis excludes the hump data but in addition eliminates any influence

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the hump may have upon the remainder of the data. Our method of analysis allows us to combine the data from our two runs, so that we obtain one best fit to all our data. Finally, by choosing the methanol–cyclohexane mixture to study we have minimized the effects of density gradients that appear in other systems.

## 2. Experimental apparatus and procedure

The fluids used on our experiment were Fisher “Spectranalyzed” methanol (99.95% pure) and cyclohexane (99.98% pure). The sample cell was filled in a dry box under a nitrogen atmosphere. The sample had a total mass of  $40.238 \pm 0.003$  g and a concentration by weight of  $29.03 \pm 0.02\%$  methanol. The often quoted value for the critical concentration is 29.03%. [5,6]. The critical temperature for the mixture was found to be  $45.043^\circ\text{C}$ . The precision of this determination was  $\pm 1.0$  mK, while the accuracy was  $\pm 10$  mK as determined by prior calibration of the monitor thermistor. Some typical values of  $T_c$  for the methanol–cyclohexane system found by other experiments are  $45.135^\circ\text{C}$  [5],  $45.29^\circ\text{C}$  [6],  $45.474^\circ\text{C}$  [7].

The sample cell consisted of two pyrex spheres joined by a length of precision bore tubing. The spheres had inner diameters of 4.5 cm. The lower bulb which held the fluid throughout the experiment has a volume of  $53.33\text{ cm}^3$  at  $29.6^\circ\text{C}$ . The tubing was obtained from Wilmad Glass Co., Inc. and was quoted as having a diameter of  $4000 \pm 1\ \mu$ . Subsequent measurement on our part revealed larger variations in the i.d. with a standard deviation of  $7\ \mu$ . These variations were of two kinds. Over short lengths of tubing there were random variations in diameter of approximately  $\pm 5\ \mu$ , while over length of several millimeters or more slow oscillators could be traced that could reach  $\pm 10\ \mu$  in magnitude. The length of the tubing was 8 cm. The upper sphere served throughout the experiment to keep the pressure essentially constant in the cell.

The sample cell was filled through a stem at the top of the upper sphere. The stoppered glass stem was sealed with a torch while the fluids were held at dry ice temperatures.

During the experiment the sample cell was rigidly clamped inside a well stirred oil bath. Two thin wires

were epoxied to the connecting tube to serve as fiducial marks; these enabled us to detect any accidental shift of the sample cell. A small window in the side of the bath allowed the lower bulb and connecting tube to be viewed. At operating temperature the critical fluid extended part way up the precision tube. The height of the meniscus at the top of the fluid column was measured as a function of temperature using a travelling telescope accurate to  $\pm 1\ \mu\text{m}$ .

The temperature of the bath was controlled to  $\pm 0.4$  mK. The controller was a DC bridge using a Fenwall thermistor as the sensing element. The temperature of the bath was monitored using an AC bridge with a YSI thermistor as the sensing element. Measurements of the thermal gradients in the bath showed a maximum gradient of 2 mK over the entire length of the bath. In the region of the fluid reservoir the gradients were less than 0.5 mK. The precision of the monitor system was 0.1 mK. The monitor system was calibrated shortly before use, using an NBS calibrated platinum resistance thermometer, so that the measurements made with the monitor system were accurate to 10 mK. Intercomparison of the monitor and control systems showed a discrepancy of approximately 5 mK over the 7 K temperature range of the experiment.

After the sample cell was filled and sealed, it was heated to well above  $T_c$ , shaken vigorously, and then mounted in the bath at a temperature 5 K above  $T_c$ . After several days of equilibration the critical point was located and data were taken in the one phase region from  $T - T_c = 3.8$  mK to  $T - T_c = 311.1$  mK. The critical point was then redetermined and data were taken in the one phase region from  $T - T_c = 2.3$  mK to  $T - T_c = 6.3818$  K. Preliminary experiments showed that we could determine the onset of the transition to  $\pm 1$  mK without actually passing into the two phase region. In these experiments the cell was brought close to  $T_c$ , and then the temperature was changed in 1 mK steps. At some point the fluid in the precision tubing would take on a granular appearance. If the temperature was held at that point, a meniscus would appear in the reservoir within 24 hours. If however the temperature was raised rapidly, the granularity would disappear and no meniscus would form. Furthermore, the vapor-liquid meniscus height versus temperature measurements made before and after this procedure agree to within the experimental errors. In both of the

actual data runs it was found that  $T_c = 45.043^\circ\text{C}$  as stated above.

In a preliminary experiment the meniscus height was measured as a function of time, after temperature changes. During these measurements a “rebound effect” was observed. If the temperature is raised, the fluid expands and the meniscus rises. The cell however also expands causing the meniscus to drop. What is observed is a rapid rise in height to a maximum value, followed by a gradual drop to a final equilibrium height. It was determined that final equilibrium was achieved after several hours for temperature changes of a few millidegrees, while temperature changes of several hundred millidegrees required a day. These observations were used throughout the experiment in deciding how soon to begin taking data after a temperature change.

The fiducial marks at the bottom and top of the precision tube were regularly checked to look for any unexpected change in the height of the telescope or cell. The measurements revealed only small changes, linearly dependent upon temperature, due to thermal expansion of the cell and bath.

Each of our data points for the position of the meniscus was the result of averaging at least three temperature measurements and typically 25 height measurements taken in groups over approximately a one hour period. The standard deviation of these averages was typically  $\pm 4 \mu\text{m}$ . These error bars were due in part to difficulty in measuring the meniscus height precisely and in part to temperature fluctuations. The meniscus shape was measured periodically during the experiment and no change in shape was detected.

Between the two data runs a sudden increase of  $126 \mu\text{m}$  was observed in the fluid level. A drop of fluid had remained in the upper reservoir after initial mixing and finally dropped into the tube during temperature cycling. The drop represented less than 0.004% of the total volume of the sample. No change in critical temperature was observed after the drop rejoined the bulk sample.

Previous work [8] has shown under what conditions gravity-induced density gradients appear and become significant. These gradients are functions of cell height, time, and density difference between the two components. We have attempted to minimize these factors in our experiment. Most of the fluid was in the lower bulb which had a height of only 4.5 cm.

All of the data was taken over a 30 day period. The first data run took 9 days after which the second run was begun with no shaking or mixing between the two runs. The data in the two runs are consistent indicating that either density gradients did not form or did not affect the data. Finally, methanol and cyclohexane are very closely matched in density with specific gravities of  $0.7914_4^{20}$  and  $0.7786_4^{20}$  respectively, further discouraging density gradient formation.

### 3. Data analysis

Table 1 contains the data recorded in our experiment. Before turning to the actual analysis of the data it is instructive to examine the data. We do so in figs. 1 and 2. These plots display several unusual features which were of pivotal importance in deciding how to best analyze the data.

Fig. 1 is a plot of anomalous height versus  $T - T_c$  near the critical point. The anomalous height is the height actually measured with the background contribution subtracted off. In our analysis we assume as usual that there are two effects present. One effect is the normal background change in fluid volume with temperature. The other effect is the anomalous portion due to the critical behavior [9]. The background was determined from our best fit to the data. The data show a slight hump centered at  $T - T_c = 15 \text{ mK}$ . This hump is similar to the one observed by Morrison and Knobler. If a smooth curve is drawn through the points of  $T - T_c > 15 \text{ mK}$  and is extrapolated to lower temperatures, then the data at low temperatures all fall to one side of the line. Conversely, if a smooth curve is drawn through the low temperature points and is extrapolated, then the points for  $T - T_c > 15 \text{ mK}$  all fall below this curve. The two sets of data appear displaced vertically relative to each other. This effect makes it difficult to fit the height data on both sides very well.

Several possibilities to explain the above behavior or hump in terms of experimental difficulties can be rejected immediately. A sudden and permanent shift in height of the cell or telescope would produce such behavior, however it would have been detected as a similar change in height of the fiducial marks, and it was not. Similarly a sudden change in the temperature measurement apparatus would have been detected

Table 1  
Data recorded in the experiment

Temperature (°C)	Meniscus height (cm)
Data run 1	
45.0468	2.2784
45.0446	2.2761
45.0488	2.2802
45.0542	2.2845
45.0513	2.2823
45.0579	2.2870
45.0617	2.2895
45.0704	2.2954
45.0760	2.2991
45.0849	2.3047
45.0931	2.3100
45.1062	2.3181
45.1265	2.3315
45.1496	2.3466
45.1708	2.3603
45.1955	2.3760
45.2278	2.3960
45.2827	2.4287
45.3541	2.4705
Data run 2	
45.0453	2.2887
45.0459	2.2986
45.0472	2.2909
45.0496	2.2936
45.0514	2.2950
45.0553	2.2981
45.0569	2.2992
45.0584	2.2997
45.0644	2.3042
45.0845	2.3175
45.0955	2.3243
45.1043	2.3301
45.1285	2.3460
45.1846	2.3811
45.2188	2.4016
45.2414	2.4149
45.2640	2.4291
45.3161	2.4613
45.3940	2.5071
45.4533	2.5425
45.5041	2.5736
45.5432	2.5957
45.5894	2.6228
45.6505	2.6592
45.7177	2.6986
45.8013	2.7473
45.9010	2.8054
46.0217	2.8770
46.1560	2.9552
46.3437	3.0646
46.5746	3.1979

Table 1 (continued)

46.8730	3.5407
47.4486	3.6842
47.8470	3.9031
48.3461	4.1794
48.9582	4.5183
49.6681	4.9094
50.3786	5.3004
50.8938	5.5822
51.4048	5.8609

instantly in a discrepancy between the control and monitor systems. A variation in the bore of the precision tubing could produce such an effect. However, measurement of the bore diameter revealed nothing unusual at this point. In fact the largest variation of the tubing found anywhere would account for only 1% of the observed effect. Finally, further measurements taken after the two primary data runs also suggest similar unusual behavior near  $T - T_c = 15$  mK.

Fig. 2 is a plot of the numerical derivative data,  $\Delta H/\Delta T$ , versus  $T - T_c$ ,  $\Delta H/\Delta T$  is the change in height per degree temperature change. In a later section we

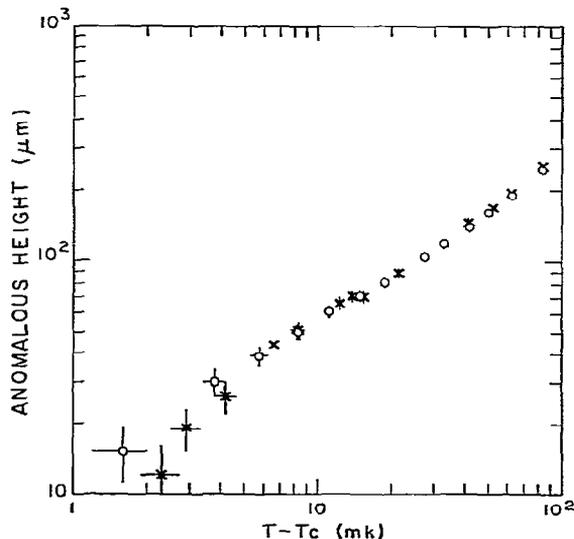


Fig. 1. Plot of anomalous height versus  $T - T_c$ , displaying hump at  $T - T_c = 15$  mK. The anomalous height is the height actually measured with the background changes (determined from the best fit) subtracted off. The height at  $T_c$  for data run 2 is estimated to be 2.2866 cm.

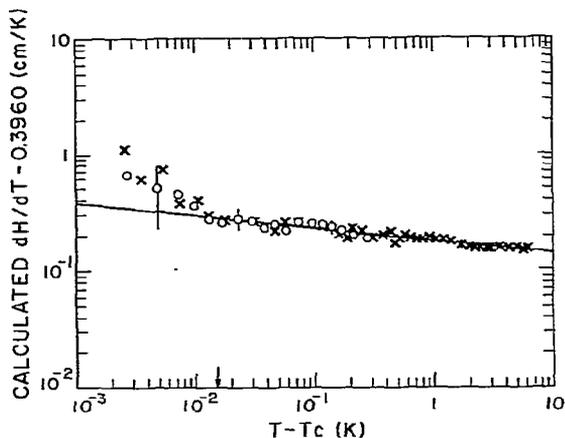


Fig. 2. Plot of calculated rate of change of height with temperature versus  $T - T_c$ . Four typical error bars have been indicated. One point at  $T - T_c = 15$  mK lies below the lower edge of the figure with a calculated  $dH/dT$  of 0.33 and is indicated by an arrow. The line through the data is the best fit for the data with  $T - T_c > 11$  mK yielding an exponent  $\alpha = 0.11 \pm 0.07$ .

explain how these derivatives were evaluated. On this plot the hump shows up as only one point at  $T - T_c = 15.4$  mK that is relatively low. However, in general the data on both sides of  $T - T_c = 15.4$  mK appear consistent. This suggests that the effect of the hump on the analysis can be minimized by working with the derivative data. Since the height behavior is the integral of the  $dH/dT$  behavior, the hump affects subsequent height measurements, propagating as a shift downward for all points at higher temperatures, while in the derivative data the effect is localized. The hump may affect more than this one point, but in our analysis we discard only this point, since it is the only one that obviously is effected.

Another interesting feature of fig. 2 is that the data for  $T - T_c < 11$  mK appear to diverge more rapidly than the remainder of the data. Morrison and Knobler have indicated that they saw similar behavior in their data for  $T - T_c < 5$  mK.

One final noticeable feature is the marked oscillation of the data between approximately  $T - T_c = 0.9$  K and  $T - T_c = 3.0$  K. This effect is traceable to an oscillation in the tube diameter. In the analysis section it will be shown to have little effect upon our results.

The behavior of the volume,  $V$ , of a critical mix-

ture as a function of temperature should have the form

$$V(T) = A'\epsilon^{1-\alpha} + B' + C'\epsilon + D'\epsilon^2 + \dots, \quad (1)$$

where  $\epsilon = (T - T_c)/T_c$ . The first term represent the critical anomaly, while the remainder of the terms represent the normal background contributions. Lange's Handbook of Chemistry [10] lists values of the background terms for various organic fluids. Inspection of these typical values indicates that with the precision of our apparatus we can ignore the terms of higher than second order in the background and that for the temperature range our measurements cover, it is sufficient to fit  $V(T) = A'\epsilon^{1-\alpha} + B' + C'\epsilon$ . Our measurements involve measuring  $H(T)$ , the relative height of the fluid-vapor meniscus in the precision bore tube.  $H(T)$  and  $V(T)$  are related in a simple manner by

$$V(T) = V_0 + \pi r^2 H(T), \quad (2)$$

where  $V_0$  is the volume of the lower bulb and  $r$  is the radius of the precision bore tube. From eqs. (1) and (2) we may write

$$dH(T)/dT \equiv \beta(T) = A\epsilon^{-\alpha} + C, \quad (3)$$

where  $A = (1 - \alpha)A'/T_c\pi r^2$  and the various temperature dependences of  $V_0$  and  $r$  have been assumed linear to first order and lumped into the coefficient  $C$  along with the background properties of the fluid.

We shall fit to  $dH(T)/dT$ , which is directly proportional to the thermal expansivity, rather than  $H(T)$  for three reasons. First, the jump in height of the meniscus due to an excess fluid drop which fell from the upper bulb between the two data runs makes it hard to combine the two runs when fitting to  $H(T)$ . The derivative data, however, are unaffected by this jump. Second, the unusual hump in the height data near  $T - T_c = 15$  mK leads to ambiguities in interpretation of the data as discussed above. Fitting to the derivative removes this ambiguity. Finally, the derivative fit requires one less parameter due to the differentiation and allows for a considerably simpler fitting routine.

Due to the inherently discrete nature of the data, we form a numerical derivative of the form

$$\beta'(T_M) = [H(T_2) - H(T_1)] / (T_2 - T_1), \quad (4)$$

where  $T_M = (T_1 + T_2)/2$ . Using eqs. (1) and (2) we can write

$$\beta'(T_M) = [4T_c \epsilon_M^{1-\alpha} / (T_2 - T_1)(1-\alpha)] \times [(\delta + 1)^{1-\alpha} - (1-\delta)^{1-\alpha}] + C, \quad (5)$$

where  $\delta = (T_2 - T_1) / 2\epsilon_M T_c$ . We may expand eq. (5) in the limit of small  $\delta$  to find

$$\beta'(T_M) \approx \beta(T_M) + \alpha(1+\alpha)\delta^2 A / 6\epsilon_M^\alpha \quad (6)$$

to second order in  $\delta$ . Using typical values of  $A$  obtained from fits, we found that the second term of eq. (6), which represents a correction term to the numerical derivative  $\beta'$ , was never more than 0.1% of  $\beta'$ . Since this correction term is significantly smaller than the experimental uncertainties for  $\beta'$  we assumed in our fits that  $\beta'(T_M) = \beta(T_M)$ .

The calculated  $\beta$  values were fit to eq. (3) using a weighted least squares fitting routine. The weighting factor for each point was determined solely by the relative uncertainty of the measurement. The errors on each  $\beta$  point came from three sources. The height measurements were precise to  $\pm 4 \mu\text{m}$ . The temperature measurements were precise to  $\pm 0.4 \text{ mK}$ . The bore of the presion tubing was uniform to  $\pm 7 \mu\text{m}$ . This last source of error predominated at large values of  $T - T_c$  but was unimportant at small  $T - T_c$  values. (All of our quoted errors represent one standard deviation.)

Each fit to a particular set of data consisted of choosing a value for  $\alpha$  and then having the program vary the other parameters to find the  $\chi^2$  minimum for that value of  $\alpha$ . The value of  $\alpha$  was then changed and a new minimum  $\chi^2$  value was found.  $\alpha$  was changed in this way a sufficient number of times so that a  $\chi^2$  versus  $\alpha$  plot could be made. From this plot the minimum value of  $\alpha$  and error bars on  $\alpha$  could be obtained. The average  $\chi^2$  per point is  $\chi^2/n$  for  $n$  points. The  $\alpha$  values for which the total  $\chi^2$  is  $\chi^2/n$  more than the minimum total  $\chi^2$  represents the one standard deviation limits on  $\alpha$ . This is Bevington's criterion [11].

The one very odd point at  $T - T_c = 15 \text{ mK}$  was not used in any of the fits. However, the nearby points were used. In most of the fits  $T_c$  was assumed to be  $45.043^\circ\text{C}$ . Fitting with  $T_c = 45.042^\circ\text{C}$  or  $T_c = 45.044^\circ\text{C}$  changed the value of  $\alpha$  by approximately 3%.

Fitting all 57 of the data points except the point at  $T - T_c = 15 \text{ mK}$  gave a value for  $\alpha$  of  $0.15 \pm 0.07$ , where this is a one standard deviation limit. However, as we have discussed above, the data for  $T - T_c < 11 \text{ mK}$  appear to diverge more strongly than the remain-

der of the data. By fitting only the 48 points for  $T - T_c > 11 \text{ mK}$  this observation is confirmed, with  $\alpha = 0.11 \pm 0.07$ . As seen in fig. 2 this fit is quite good over the region  $20 \text{ mK} < T - T_c < 6.4 \text{ K}$ . We feel that the value  $\alpha = 0.11 \pm 0.07$  is the better value, and that something as yet unexplained is affecting the behavior close to  $T_c$ .

As a further check of consistency the power law form was fit to all the data minus the seven points in the region  $1.0 \text{ K} > T - T_c > 2.7 \text{ K}$ . Fig. 2 shows that these data appear to oscillate slightly, and we wanted to check if this affected our results. The fitting routine gave a value of  $\alpha = 0.16 \pm 0.06$  for this set of 50 points.

Finally a logarithmic divergence of form  $dH/dT = G + H \ln(T - T_c)$  was fit to the data. In each case the logarithmic form was a much poorer fit.

Table 2 gives the results of the above analysis. The fits using several values of  $\alpha$  are given for the set of 57 points in order to show the sensitivity of the coefficients to the choice of  $\alpha$ .

Table 2  
Results of fits to various sets of data

$dH/dT = C + A\epsilon^{-\alpha}$				
$\alpha$	$C$	$A$	total $\chi^2$	$\chi^2/\text{point}$
all data (57 points)				
0.15	0.4437	0.05558	71.197	1.249
0.22	0.4871	0.02458	72.986	1.280
0.08	0.3265	0.15779	72.417	1.270
all data with $T - T_c > 11 \text{ mK}$ (48 points)				
0.11	0.3960	0.09557	65.180	1.358
all data except $2.7 \text{ K} > T - T_c > 1.0 \text{ K}$ (50 points)				
0.16	0.4573	0.04721	44.854	0.897
$dH/dT = G + H \ln \epsilon$				
	$G$	$H$	total $\chi^2$	$\chi^2/\text{point}$
all data (57 points)				
	0.4618	-0.02015	76.805	1.347
all data with $T - T_c > 11 \text{ mK}$ (48 points)				
	0.4627	-0.01998	68.450	1.426

Using our best fit we find  $dH/dT = 0.0956 \epsilon^{-0.11} + 0.3960$ . The various expansions of the bath and sample cell can be estimated and eliminated to give  $dH/dT = 0.0956 \epsilon^{-0.11} + 0.3985$ . At  $T_c$  the volume of fluid was  $53.8 \text{ cm}^3$ , equivalent to a height of 428 cm. Thus near  $T_c$  we can write  $(1/H) dH/dT = 2.23 \times 10^{-4} \epsilon^{-0.11} + 9.31 \times 10^{-4}$ , which is equivalent to  $(1/V) dV/dT$ . Inspection of Lange's Handbook of Chemistry [10] shows that the leading term in the expansion of organic fluids is typically  $1 \times 10^{-3}$  so that our background term appears reasonable. Comparison of the coefficient of our anomalous term with the coefficient found by Greer and Hocken [3] for the system nitroethane + 3-methylpentane shows our coefficient to be approximately five times larger. This confirms the prediction of Greer and Hocken [3] that the anomaly is large in methanol + cyclohexane.

#### 4. Conclusions

Our experiment shows that there is an anomalous or critical divergence in the thermal coefficient of expansion of a binary fluid mixture near the critical point. Furthermore, if certain irregularities in the data are ignored we find that the divergence is well described by a power law with exponent  $\alpha = 0.11 \pm 0.07$  in the range  $11 \text{ mK} < T - T_c < 6.4 \text{ K}$ . This value of  $\alpha$  is in good agreement with the predicted value of  $\alpha = 0.125$  found from approximations to the three dimensional Ising model [12]. If one assumes that the exponent inequality  $d\nu \geq 2\alpha$  is an equality then the recent renormalization calculation of  $\nu$  by Guillou and Zinn-Justin predicts  $\alpha = 0.11$  [13]. This value also agrees well with our results. A logarithmic form is a poorer fit to our data than the power law form. While the error bars on  $\alpha$  are large we feel that with better temperature control this method of determining  $\alpha$  could yield precise results. It is important to remember that our analysis assumes a simple analytical form for the background. The work of Greer [14] suggests that for our range of temperatures  $\epsilon < 0.2$ , extended scaling will not be important.

Two interesting irregularities in the data were ignored in the analysis. First is the mysterious hump in our data at  $T - T_c \simeq 15 \text{ mK}$  similar to that seen by Morrison and Knobler at  $T - T_c \simeq 90 \text{ mK}$ . We have discussed various experimental difficulties which might

lead to this behavior and none seemed satisfactory to account for it. It is our opinion that this hump is an actual property of the fluid system and warrants further study. Because of the apparent sharpness of this hump, as seen in fig. 2, good temperature control is necessary.

Recently Stephenson [14] has extended the arguments of Theeuwes and Bearman [15,16] to discuss local extrema in certain thermodynamic properties in the critical region at positions other than the critical point. In particular he shows that the thermal expansivity will have a locus of extrema in the  $\rho, T$  plane of a simple gas terminating at the critical point. Arguing from the reasonably verified critical equivalence of liquid-gas and binary liquid systems we may then expect a similar locus of extrema in the thermal expansivity in the concentration,  $T$  plane of a binary fluid system. Thus, if the concentration of the binary fluid system was not exactly the critical concentration we might expect a local extremum at some  $T > T_c$ ; which we indeed see. We further point out that this extremum would only be present when one component was in excess relative to the critical concentration rather than the other. This corroborates the observation of Morrison and Knobler who only saw the hump when iso-butyric acid was in excess. It would obviously be of great interest to try to map out this locus of extrema by measuring the thermal expansivity in several mixtures of varying concentration to test this hypothesis.

The second irregularity in the data is the apparent stronger divergence of the thermal expansivity for  $T - T_c < 11 \text{ mK}$ , as best illustrated in fig. 2. While the error bars on this data overlap with the best fit to the data for  $11 \text{ mK} < T - T_c < 6.4 \text{ K}$  and  $\alpha = 0.11$ , there appears to a systematic deviation of the data above the best fit line. This deviation was seen in both data runs. Morrison and Knobler notice a similar deviation of their data for  $T - T_c < 5 \text{ mK}$ . As yet, we can offer no experimental explanation of this deviation. If indeed this deviation or stronger power law divergence is real, it would suggest a deviation from the expected scaling behavior of  $\alpha \approx 0.125$  close to  $T_c$  which would be quite interesting. Finally, we point out that a similar nonscaling behavior of the thermal expansivity has been seen near the ferromagnetic phase transition in gadolinium by Dolejsi and Swenson [17].

In summary we have observed the divergence of the

thermal expansivity of the critical binary fluid system methanol and cyclohexane in the range  $2.4 \text{ mK} < T - T_c < 6.4 \text{ K}$ . The divergence is found to behave with a power law form with exponent  $\alpha = 0.11 \pm 0.07$  in good agreement with the expected value  $\alpha \approx 0.125$ . Irregularities in the data including a hump at  $T - T_c \approx 15 \text{ mK}$ , and a stronger divergence for  $T - T_c \leq 11 \text{ mK}$  may be significant and are deserving of a more careful study.

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