Pramāṇa, Vol. 1, No. 6, 1973, pp. 260–68. Printed in India. © 1973

Coexistence curve and rectilinear diameter in the critical liquid system carbon disulphide+nitromethane

E S R GOPAL, R RAMACHANDRA and
P CHANDRA SEKHAR
Department of Physics, Indian Institute of Science, Bangalore 560012

MS received 3 September 1973; in final form 15 November 1973

Abstract. The phase boundary of the binary liquid system $CS_2+CH_3NO_2$ is studied over nearly six decades in reduced temperature $3\times10^{-6}<\varepsilon=(T_C-T)/T_C<2\times10^{-1}$ and over the composition range 8-98 mole % of CS_2. The critical parameters are $T_C=335{\cdot}13_2$K and $x_C=57{\cdot}3_4$ mole % of CS_2. A single critical exponent $\beta=0{\cdot}315\pm0{\cdot}004$ fits the observations over the entire range with no indication of β increasing to the classical value of $\frac{1}{2}$ far away from T_C. The diameter of the coexistence curve shows a rectilinear behaviour only far away from T_C. Near T_C, the deviation ΔX from the rectilinear law seems to fit a curve of the form $\Delta X=f\varepsilon^{7/8}\exp(-g\varepsilon h)$, the derivative of which has a singularity like that of specific heat. An ambiguity in the analysis of the data in terms of mole fractions and volume fractions is pointed out. It is also suggested that the curvature of the diameter may be much weaker in a liquid-gas system and hence might have escaped detection.

Keywords. Critical point phenomena; rectilinear diameter; critical exponents; phase boundary; $CS_2+CH_3NO_2$ liquid system.

1. Introduction

The similarity and the scaling among various critical phenomena are now fairly well established. Many features of binary mixtures have been studied in this context. Recently the suggestions of a possible curvature in the diameter of the coexistence curve of critical fluid systems (Widom and Rowlinson 1970, Hemmer and Stell 1971, Mermin 1971, Green *et al* 1971, Mermin and Rehr 1971, Widom and Stillinger 1973) have aroused considerable interest. The model calculations suggest that as $\varepsilon=(T_C-T)/T_C\to0$, the slope of the diameter should diverge approximately like the specific heat of the system. Experimental observations on liquid gas systems near the critical point (Levelt-Sengers *et al* 1971, Zollweg and Mulholland 1972, Cornfeld and Carr 1972) do not show specific evidence for such a singularity. The theoretical situation is also under some discussion (Biswas 1973). However, some earlier experiments on binary systems (Jones and Betts 1928, Cox and Herington 1956, Haselden *et al* 1957, Chandra Sekhar *et al* 1972, Wold *et al* 1973) show some indications of a deviation from rectilinearity. Therefore, a study of the coexistence curve and the diameter of the binary liquid system over nearly six decades in the reduced temperature ε namely $3\times10^{-6}\lesssim\varepsilon\lesssim2\times10^{-1}$, has been undertaken. The results show that there is probably a singularity in the slope of the diameter near the critical temperature T_C.

A second point of interest, motivating the study of the coexistence curve over a large range in temperature, lies in the possible variation of the critical index β, which

characterises the behaviour of the order parameter as a function of temperature; suggestions have been made that β may *increase* from the Ising model value of $\sim 1/3$ (Fisher 1967, Stanley 1971) to a classical value of $\frac{1}{2}$ (Landau and Lifshitz 1968, Stanley 1971) either very near or far away from T_c. Experiments on magnetic systems (Howard *et al* 1965, Gorodetsky *et al* 1966, Wertheim 1967, Srinivasan 1968, Giterman and Malyshenko 1968, Chieux and Sienko 1970, Muller and Berlinger 1971), liquid gas (Michels 1958) and liquid He^3 Systems (Sherman 1965) indeed show both types of deviations. In the present case, it is found that the value of β *decreases* to about 0·28 far away from T_c but there is no definite indication of its going to $\sim \frac{1}{2}$ near T_c.

A brief preliminary account of the work (Ramachandra *et al* 1973) has been reported.

2. Experimental arrangement

The system $CS_2+CH_3NO_2$ was chosen in continuation of a series of studies, some of which involved CS_2 as one of the components (Viswanathan *et al* 1970; Lele *et al* 1971; Govindarajan *et al* 1972). Chemicals of the analytical grade purity were used in all the observations and vapour phase chromatography revealed no measurable impurities. A special thermostat, with a temperature stability and resolution of 10^{-3} °C, was used for the studies. The liquid mixture was taken in compositions ranging from 0·08 mole fraction to 0·98 mole fraction of CS_2, in $\sim$10 ml sample bulbs. The maximum height of the liquid sample was $\lesssim 1$ cm to reduce gravity effects, although in a liquid-liquid system the compressibility effects are very much less serious than in a critical liquid-gas system (Blagoi *et al* 1971). The samples were first heated to the one phase region in the thermostat. They were then cooled slowly and the temperature at which each sample separated into two phases was noted. The phase separation temperature vs the composition x gives the coexistence curve. Equilibrium times of several hours were allowed in the critical region. The upper critical solution temperature (UCST), or the highest phase separation temperature was $\sim$62·0°C, which agrees well with earlier observations (Timmermans and Roland 1932, Joukovsky 1934, Poppe 1935, Francis 1956).

Six samples, with compositions $X=0{\cdot}596_1$, $0{\cdot}571_2$, $0{\cdot}573_4$, $0{\cdot}573_8$, $0{\cdot}574_8$, $0{\cdot}579_0$ mole fraction of CS_2, had the same highest phase separation temperature $t_c = 61{\cdot}98_3$ C. For the sample with $X=0{\cdot}573_4$, the meniscus formed at the middle of the bulb and remained stationary on slight cooling. For $X=0{\cdot}573_8$ the meniscus was a little above the middle whereas for the other samples, it formed either above or below the middle of the bulb and moved down or up on further cooling, a phenomenon well studied in liquid-gas and binary liquid systems (Mason *et al* 1940, Quantie 1954). On this basis the critical composition X_c was chosen as $0{\cdot}573_4 \pm 0{\cdot}0004$ mole fraction of CS_2.

3. Analysis of the critical index

The coexistence curve of a binary liquid system is given by the equation

$$|X'-X''| = B_x \varepsilon^{\beta} \qquad (1)$$

where X' and X'' are the mole fraction compositions of the two phases coexisting in equilibrium at temperature T. $|X'-X''|$ is the order parameter for the system and β is the corresponding critical index.

The coexistence curve was drawn from 70 different observations and for each experimental composition X' the composition X'' of the coexisting phase was read off

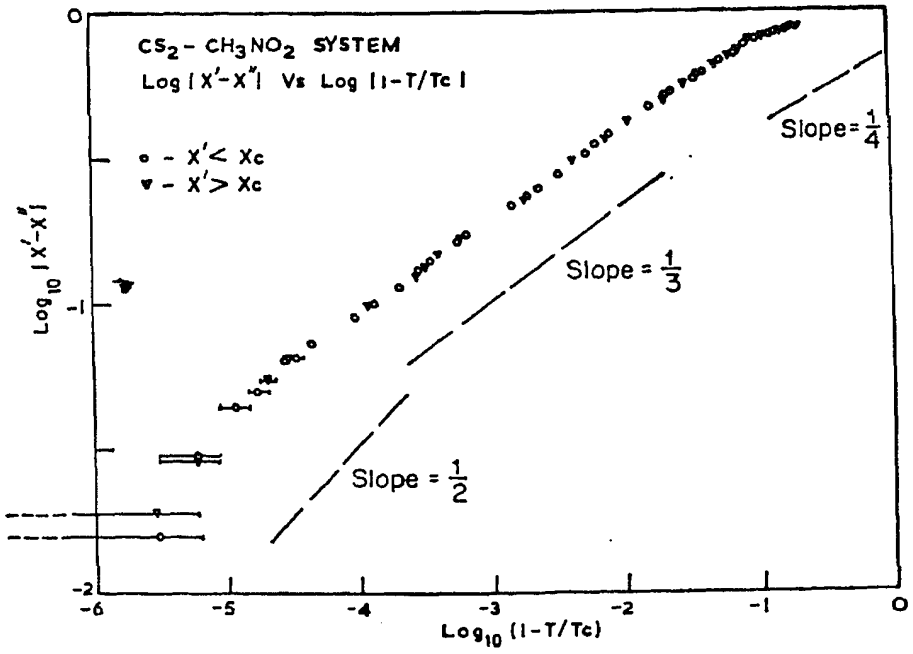

Figure 1. Temperature variation of the order parameter. Log-log plot of $|X'-X''|$ against $(T_c-T)/T_c$ for the carbon disulphide+nitromethane system.

from the curve. A least squares fit, for the log-log plot (figure 1) of equation (1), with T_c as adjustable gave $T_c=335{\cdot}13_2$ K, $B_x=1{\cdot}67\pm0{\cdot}01$, and $\beta=0{\cdot}315\pm0{\cdot}004$. The value of T_c is within the experimental uncertainty of the observed highest phase separation temperature. Over six decades in ε, a single value of β fits the data quite well. The value of β is in general agreement with that obtained in other experiments (Scott 1972) and model calculations (Stanley 1971).

Although generally mole fractions of mixtures are considered to be analogous to densities of pure systems for critical phenomena (e.g. Swift 1968), some authors (Rice and Chang 1972) suggest that volume fractions should be used; but as far as the co-existence curve is concerned, the value of β remains the same whether volume fractions or mole fractions are used. Indeed if

$$|X'-X''| = B_x\varepsilon^\beta$$

and

$$1/\phi = (1-K)+K/X$$

where ϕ is the volume fraction corresponding to X and $K = \rho_A M_B/\rho_B M_A$, the ρ's being densities and the M's molecular weights of the components, then

$$|\phi'-\phi''| = B_\phi\varepsilon^\beta + \ldots \qquad (2)$$

with no change in β. In fact an analysis of the present data according to eq (2) gives $B_\phi=1{\cdot}64\pm0{\cdot}01$, and $\beta=0{\cdot}315\pm0{\cdot}004$ (figure 2). This point has been noted by earlier workers (Heller 1967, Wims *et al* 1969).

Far away from T_c, the classical value of $\beta=\frac{1}{2}$ is not approached. In fact in the region $10^{-2} < \varepsilon < 2\times10^{-1}$ the effective value of β *decreases* to about 0·28. Alternatively the data may be interpreted as fitting an equation $|X'-X''|=B_x\varepsilon^\beta-B'_x\varepsilon^{\beta+1}$ with $B'_x\sim1$ which goes over to equation (1) as $\varepsilon\to0$.

The evidence for $\beta\to\frac{1}{2}$ as $T\to T_c$ is inconclusive. If at all this were to happen, it must be for $\varepsilon\gtrsim10^{-6}$ in these systems, a region accessible to experiments only with difficulty.

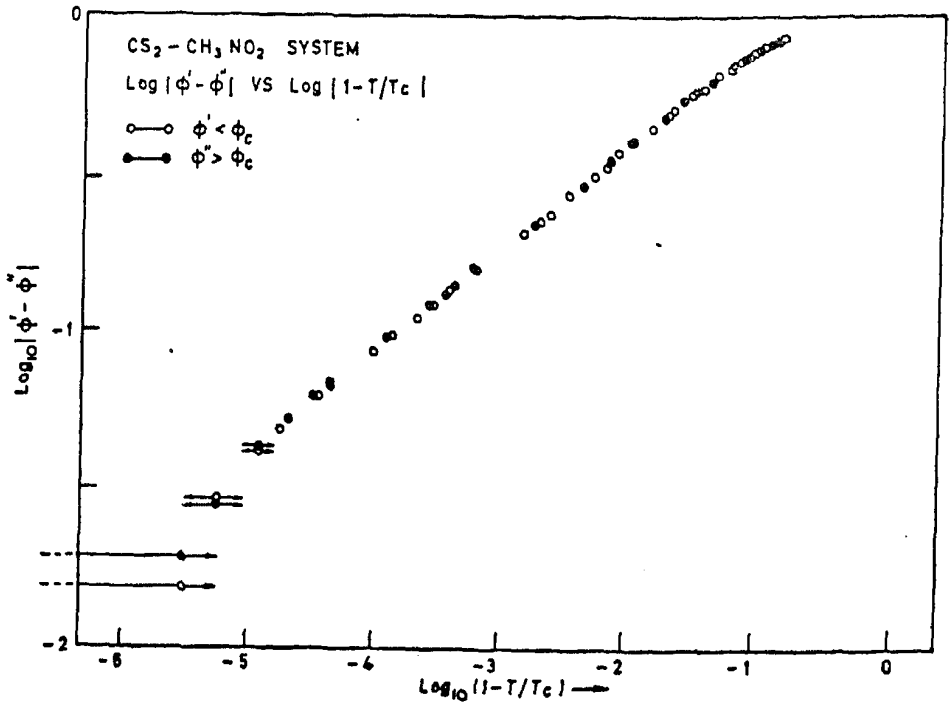

Figure 2. Temperature variation of the order parameter. Log-log plot of $|\phi' - \phi''|$ against $(T_c - T)/T_c$ for the carbon disulphide+nitromethane system.

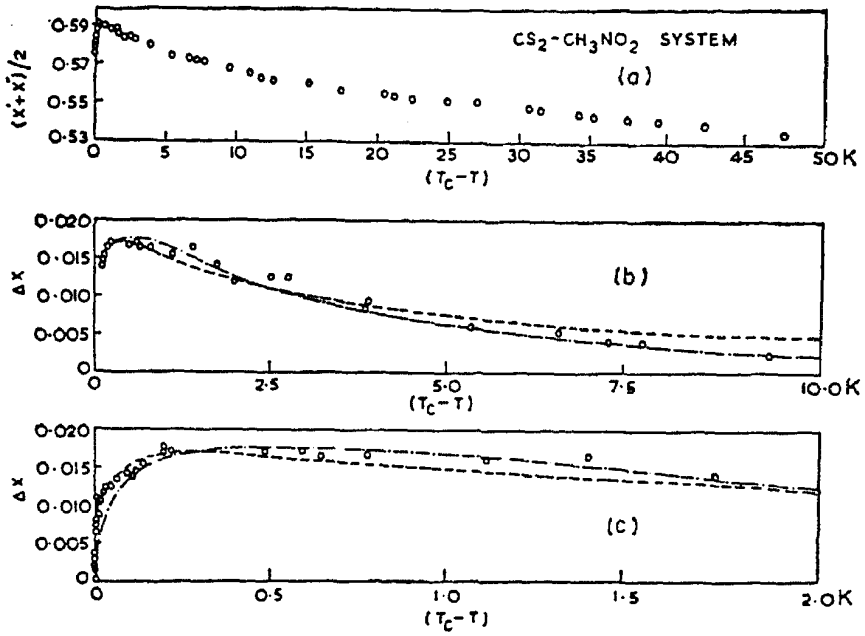

Figure 3. (a) Behaviour of the diameter $(X'+X'')/2$, showing rectilinear behaviour away from T_c and extrapolating to X_c as $T \to T_c$. (b) and (c) Deviation from the rectilinear behaviour slightly away from T_c and very close to T_c. Dashed line corresponds to $h=0{\cdot}19$ and the dot-dash line to $h=0{\cdot}3$ of eq (4). Other parameters are given in the text.

4. Behaviour of the diameter

The plot of $(X'+X'')/2$ against $t=(T_c-T)$, to test the law of the rectilinear diameter, shown in figure 3a, reveals the following features. Far away from T_c, the rectilinear behaviour is found with $(X'+X'')/2$ extrapolating to X_c. This part of the curve is described by the equation

$$(X'+X'')/2 = X_c + b_x t \tag{3}$$

with $b_x = -0{\cdot}00085$ mole fraction of CS_2/°C. As T_c is approached, the mean composition $(X'+X'')/2$ deviates from the straight line and then falls back to X_c. Thus the

rectilinear diameter law seems to be obeyed only far away from T_c. The deviation $\Delta X=\frac{1}{2}(X'+X'')-X_c-b_x t$ from the line (3) is also plotted in figures 3 b and 3 c revealing a slightly peaked curve falling off to zero as $t\to 0$ and as $t\to\infty$.

As mentioned in the introduction, several workers have suggested that $\partial(\Delta X)/\partial t$ must have a singular curvature and have therefore looked for a diameter plot of the form $\Delta X\sim t^{1-\alpha}$ with $\alpha\approx 1/8$. Such a behaviour has not been clearly found. The conditions that $\Delta X\to 0$ as $t\to 0$ and $t\to\infty$ and that $\partial(\Delta X)/\partial t\sim t^{-1/8}$ as $t\to 0$ suggest a trial function

$$\Delta X=Ft^f \exp(-Gt^h) \tag{4}$$

A four parameter least squares fit to eq (4) gives $F=5{\cdot}0$, $f=0{\cdot}87$, $G=5{\cdot}8$ and $h=0{\cdot}19$ which agrees well with the data close to T_c (dashed lines in figures 3b and 3c). The parameters $F=0{\cdot}46$, $f=0{\cdot}87$, $G=3{\cdot}34$ and $h=0{\cdot}3$ seem to fit the data better away from T_c (dot dash line in figures 3 b and 3 c).

Equation 4 gives a power law singularity with $\alpha=0{\cdot}13$ for $\partial(\Delta X)/\partial t$.. Some experiments on specific heats are analysed either by a power law with $\alpha\approx 1/8$ singularity or by a logarithmic singularity of the form $C_v=A\ln|t|+B$. A logarithmic divergence of the curvature requires a function

$$\Delta X\sim(t/t_0)\ln(t/t_0)\exp[-a(t/t_0)^b] \tag{5}$$

Equation (5) gives a change in sign of ΔX at some value of $|T-T_c|$. The evidence for this is as yet uncertain. Clearly more detailed investigations are necessary to clarify this situation.

Another point* requires some discussion. In the case of a liquid gas system, it can be easily shown (Buckingham 1972) that if the diameter in the densities $(\rho_L+\rho_G)/2$ shows an anomalous behaviour of the form $t^{1-\alpha}$, the diameter in the specific volume $(V_L+V_G)/2$, where $V=1/\rho$, should show a dominant term of the form $t^{2\beta}$. The situation in the case of a binary mixture is similar. The volume fraction ϕ is related to the mole fraction X by the relation $1/\phi=(1-K)+KX^{-1}$ where $K=\rho_A M_B/\rho_B M_A$, the ρ's being the densities and the M's the molecular weights of the components. If the diameter is given in terms of mole fractions by

$$(X'+X'')/2=X_c+b_x t+Ft^f\exp(-Gt^h) \tag{6}$$

then

$$(\phi'+\phi'')/2=\frac{1}{K}\left(\frac{X'+X''}{2}\right)+\frac{1-K}{K^2}\left(\frac{X'+X''}{2}\right)^2+\frac{(1-K)^2}{K^3}\left(\frac{X'+X''}{2}\right)^3+\ldots$$
$$-\frac{B_x}{T_c^{2\beta}}\frac{1-K}{4K^2}t^{2\beta}+\frac{B_x^2}{T_c^{2\beta}}\frac{3(1-K)^2}{16K^3}\left(\frac{X'+X''}{2}\right)t^{2\beta} \tag{7}$$

In the derivative $(\partial/\partial t)(\phi'+\phi'')$ the divergent terms are the ones coming from the first term and the $t^{2\beta}$ term on the right, proportional to $t^{-\alpha}$ and $t^{2\beta-1}$ respectively. Therefore as $t\to 0$, the singularity must be dominated by the $t^{2\beta}$ term. Conversely if the diameter $(\phi'+\phi'')/2$ in terms of the volume fractions has a singular part of the form $t^{1-\alpha}$, the diameter $(X'+X'')/2$ in terms of the mole fractions must have asymptotically the dominant term as $t^{2\beta}$.

As mentioned in the introduction, the theoretical discussions of the liquid-gas systems have suggested a $t^{1-\alpha}$ anomaly in the diameter $(\rho_L+\rho_G)/2$ in terms of the densities. In a binary mixture some authors (Rice and Chang 1972) have taken the volume

*The authors are grateful to the referee of the preliminary account for drawing their attention to this point.

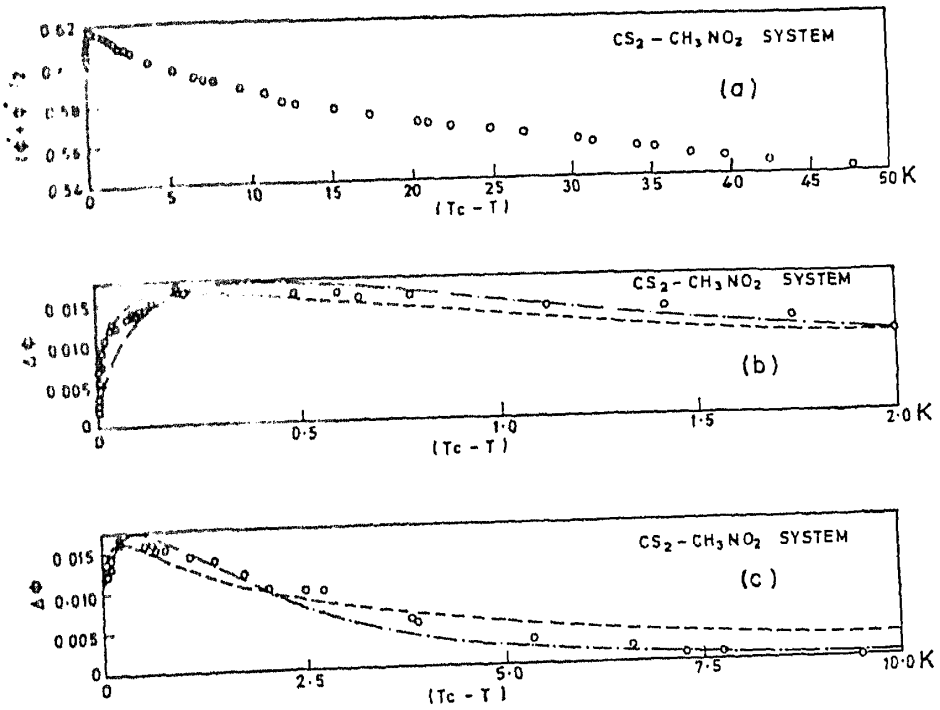

Figure 4. (a) Behaviour of the diameter $(\phi' + \phi'')/2$, showing rectilinear behaviour away from T_c and extrapolating to ϕ_c as $T \to T_c$. (b) and (c) Deviation from the rectilinear behaviour slightly away from T_c and very close to T_c. Dashed line corresponds to h' 0·21 and the dot-dash line to $h' = 0{\cdot}41$. Other parameters are given in the text.

fraction ϕ as the exact analogue of the density ρ of a one component system, while some others (Swift 1968, Jasnow and Goldburg 1972) have used the mole fraction X as the analogue of ρ. Because of the differences in the exponents of the anomaly when analysed in terms of $(X' + X'')/2$ and $(\phi' + \phi'')/2$, one might have expected at first the possibility of resolving this ambiguity on the basis of the experimental observations. Unfortunately, because K is nearly unity and T_c is large, the ambiguity is not resolved by the present observations. Indeed with $K = 0{\cdot}89$ and the other parameters as given earlier, eq (7) gives the derivative

$$\frac{\partial}{\partial t}\left(\frac{\phi' + \phi''}{2}\right) \approx 5{\cdot}6\, t^{-0{\cdot}13} \exp\left(-5{\cdot}8\, t^{0{\cdot}19}\right) + 0{\cdot}0017\, t^{2\beta-1}$$

Even though $t^{2\beta-1}$ diverges faster than $t^{-\alpha}$, the coefficients make the former term negligible even at the present experimental resolution of $t = 10^{-3}$ K; at $t = 10^{-3}$ K, the second term is 0·019 while the first term is 2·9. It is only at $t \sim 10^{-6}$ K giving $\varepsilon \sim 10^{-9}$, that the $t^{2\beta-1}$ term begins to be appreciable, and this value of ε is two to three orders finer than the best resolution so far obtained in experiments on critical point phenomena.

Hence in the present level of experiments, there is no difference in the observed anomaly whether the analysis is done in terms of mole fractions or volume fractions. In figure 4, the analysis in terms of volume fractions is given, using a trial function similar to eq (4). The values $F' = 3{\cdot}5$, $f' = 0{\cdot}86$, $G' = 5{\cdot}6$, $h' = 0{\cdot}21$ and $b_4 = -0{\cdot}0014$ volume fraction of CS_2/°C give a good fit close to T_c (dashed line in figures 4 b and 4 c), whereas the set $F' = 0{\cdot}32$, $f' = 0{\cdot}86$, $G' = 3{\cdot}1$, $h' = 0{\cdot}41$ gives a good fit away from T_c (dot-dash line in figures 4 b and 4 c). If the volume fraction analysis is taken as the primary $t^{1-\alpha}$ anomaly, a simple inversion in terms of the mole fractions shows that the $t^{2\beta}$ term in $(X' + X'')/2$ begins to be felt only at $\varepsilon \lesssim 10^{-9}$.

Because of the fact that K is nearly unity and T_c is large, the analysis of both $(X'+X'')/2$ and $(\phi'+\phi'')/2$ seems to show a $t^{1-\alpha}$ anomaly, although one of them must show a $t^{2\beta}$ anomaly at a resolution three orders of magnitude better. Experiments on binary systems with low T_c and proper value of K are necessary to resolve this ambiguity.

5. Discussion

The most striking unexpected result of the present investigation over six decades in ε is the observation of a small curvature in the diameter. The deviation Δx, though small, is systematic and seems to agree in a general way with some of the theoretical predictions. Apart from confirming this on other systems, it is necessary to rule out the possibility of the effect being the result of impurities in the system or of imperfections in the experimental arrangement.

As mentioned earlier, the chemicals CS_2 and CH_3NO_2 used were of analytical reagent grade and vapour phase chromatography could reveal no measurable impurity. Moreover a similar curvature was reported in the data on cyclohexane+acetic anhydride (Chandra Sekhar *et al* 1972), although at that time the full significance of the observations was not realized. Further, Jones and Betts (1928) had earlier reported an anomalous behaviour of the diameter in the system CS_2 and $(CH_3CO)_2O$, but the matter was not pursued further since there was no apparent reason to suspect a failure of the rectilinear diameter law. Other workers (Cox and Herington 1956, Haselden *et al* 1957 and Wold *et al* 1973) have found similar features in binary and ternary systems. It is also not clear how any imperfection of the experimental technique can give such a curious deviation from the rectilinear diameter. Therefore one must conclude that there is a small but measurable curvature of the diameter.

In this connection, it is worth pointing out that the curvature is zero for a ferromagnet because of symmetry. In a liquid-gas system, the asymmetry can arise from the different liquid and gas states of aggregation, the molecules being identical. In a

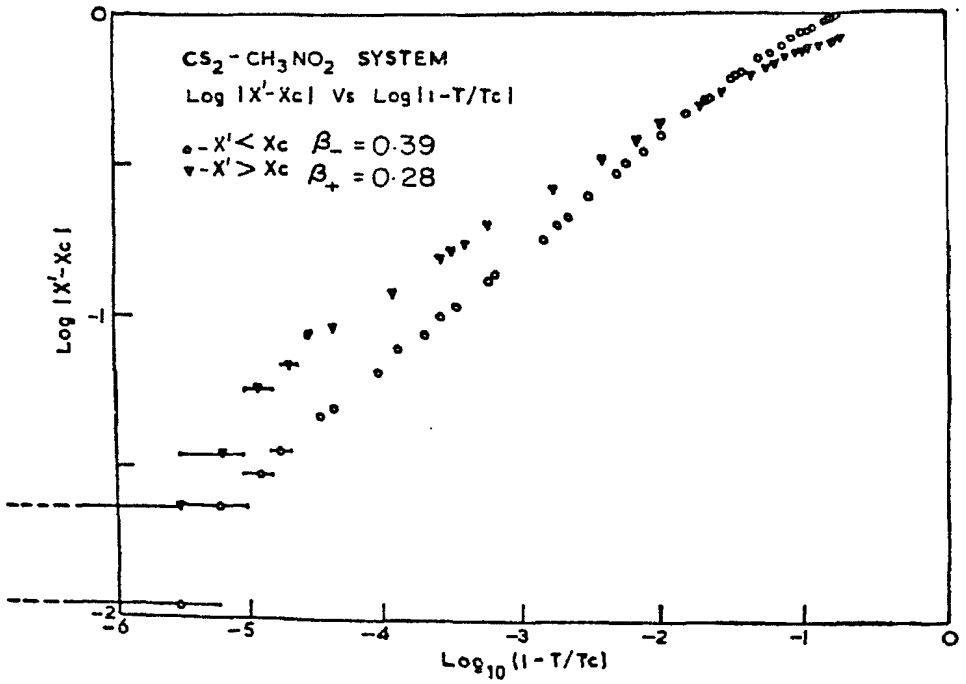

Figure 5. Behaviour of $|X'-X_c|$ against $(T_c-T)/T_c$ on a log-log scale, showing different slopes for $X'<X_c$ and $X'>X_c$.

liquid-liquid system, besides aggregation, differences in intermolecular forces are present and perhaps they may enhance the curvature of the diameter. Thus it is possible that the anomaly is much weaker in a liquid-gas system and might have escaped detection. The data analysed by Zollweg and Mulholland (1972) show an anomaly much smaller than the present one. A theoretical study by Biswas (1973) suggests no failure of the law of rectilinear diameter. Clearly further work on other systems is required.

Finally, one notes that the presence of a curvature in the diameter destroys one of the symmetries about X_c. Figure 5 shows plots of $(X_+ - X_c)$ and $(X_c - X_-)$ against ε, where X_+ and X_- are compositions greater than and less than X_c respectively. It is seen that different values of β (β_+ and β_-) describe these two branches of the coexistence curve. Unfortunately in earlier experiments it has been usual to assume that $\beta_+ = \beta_-$ and use this as a criterion to locate X_c. We, from this laboratory, (Viswanathan *et al* 1970, Lele *et al* 1971, Govindarajan *et al* 1972) have been guilty of falling into the trap. But with an accurate experimentally available value of X_c, as in the present case, such a procedure is not valid. Even in this case, a mistaken choice of $X_c = 0{\cdot}587_5$ would make $\beta_+ \simeq \beta_-$. This composition has a phase separation temperature 2×10^{-3} °C lower than T_c and the meniscus formation is also not from the middle of the bulb.

There have been recent suggestions of asymmetric scaling laws and their consequences. In view of the fundamental importance of the presence of a symmetry in the phase boundary, it is urgently necessary to confirm the presence of a curvature in the diameter in other systems and by other experimental techniques.

Acknowledgements

The authors thank S V Subramanyam, K Govindarajan, M V Lele, N Nagarajan and J Ramakrishnan for considerable assistance during the early stages of the work, the authorities of National College, Bangalore for granting study leave to R Ramachandra, the Council of Scientific and Industrial Research for the award of a senior research fellowship to P Chandra Sekhar and the Department of Atomic Energy and PL-480 programme for financial support to the programme. The suggestions of the referees are also gratefully acknowledged.

References

Biswas A C 1973 *Pramana* **1** 109
Blagoi Yu P, Sokhan V I and Pavlichenko L A 1971 *Sov. Phys. JETP* **33** 1183
Buckingham M J 1972 in *Phase transitions and critical phenomena*, Vol. 2 eds Domb C and Green M S (Academic Press, London and New York) p 17
Chandra Sekhar P, Subramanyam S V and Gopal E S R 1972 *Proc. Nucl. Phys. Solid State Phys. Symp.* **14C** 199
Chieux P and Sienko M J 1970 *J. Chem. Phys.* **53** 566
Cornfeld A B and Carr H Y 1972 *Phys. Rev. Lett.* **29** 28
Cox J D and Herington E F G 1956 *Trans. Faraday. Soc.* **52** 926
Fisher M E 1967 *Rep. Progr. Phys.* **30** 615
Francis A W 1956 *J. Phys. Chem.* **60** 20
Giterman M Sh and Malyshenko S P 1968 *Sov. Phys. JETP* **26** 1176
Gorodetsky G, Shtrikman S and Treves D 1966 *Solid State Commun.* **4** 147
Govindarajan K, Subramanyam S V and Gopal E S R 1972 *J. Chem. Phys.* **56** 4255
Green M S, Cooper M J and Levelt Sengers J M H 1971 *Phys. Rev. Lett.* **26** 492

Haselden G G, Holland F A, King M B and Strickland Constable R F 1957 *Proc. Roy. Soc. Sec. A* **240** 1
Heller P 1967 *Rep. Progr. Phys.* **30** 731
Hemmer P C and Stell G 1970 *Phys. Rev. Lett.* **24** 1284
Howard D G, Dunlap B D and Dash J G 1965 *Phys. Rev. Lett.* **15** 628
Jasnow D and Goldburg W I 1972 *Phys. Rev.* **6A** 2492
Jones D C and Betts H F 1928 *J. Chem. Soc.* 1177
Joukovsky N I 1934 *Bull. Soc. Chim. Belg.* **43** 397
Landau L D and Lifshitz E M 1968 *Statistical physics*, 2nd edn (Oxford: Pergamon Press) chap 14
Lele M V, Subramanyam S V and Gopal E S R 1971 *Chem. Phys. Lett.* **11** 542
Levelt Sengers J M H Straub J and Vicentini Missoni M 1971 *J. Chem. Phys.* **54** 5034
Mason S G, Naldrett S N and Maass O 1940 *Can. J. Res.* **B18** 103
Mermin N D 1971 *Phys. Rev. Lett.* **26** 169
Mermin N D and Rehr J J 1971 *Phys. Rev. Lett.* **26** 1155
Michels A, Levelt J M and DeGraaf W 1958 *Physica, Utrecht* **24** 659
Muller K A and Berlinger W 1971 *Phys. Rev. Lett.* **26** 13
Poppe G 1935 *Bull. Soc. Chim. Belg.* **44** 640
Quantie C 1954 *Proc. Roy. Soc. Sec. A* **234** 90
Ramachandra R, Nagarajan N, Ramakrishnan J and Gopal E S R 1973 *Proc. Nucl. Phys. Solid State Phys. Symp.* **15C** 331
Rice O K and Chang D R 1972 *Phys. Rev.* **5A** 1419
Scott R L 1972 *Ber. Bunsenges Phys. Chem.* **76** 296
Sherman R H 1965 *Phys. Rev. Lett.* **15** 141
Srinivasan C 1968 *Proc. Nucl. Phys. Solid State Phys. Symp.* **10B** 382
Stanley H E 1971 *Introduction to phase transitions and critical phenomena* (Clarendon Press, Oxford) chap 9
Swift J 1968 *Phys. Rev.* **173** 257
Timmermans J and Roland H 1932 *J. Chim. Phys.* **29** 529
Viswanathan B, Gambhir R D and Gopal E S R 1970 *J. Chem. Phys.* **53** 4405
Wertheim G K 1967 *J. Appl. Phys.* **38** 971
Widom B and Rowlinson J S 1970 *J. Chem. Phys.* **52** 1670
Widom B and Stillinger F H 1973 *J. Chem. Phys.* **58** 616
Wims A M, McIntyre D and Hynne F 1969 *J. Chem. Phys.* **50** 616
Wold L E, Pruitt G L and Morrison G 1973 *J. Phys. Chem.* **77** 1572
Zollweg J A and Mulholland G W 1972 *J. Chem. Phys.* **57** 1021