Critical Exponent β and Rectilinear Diameter of the Binary-Liquid System Carbon Disulfide + Nitromethane*

E. S. R. Gopal, R. Ramachandra, P. Chandra Sekhar, K. Govindarajan,† and S. V. Subramanyam
Department of Physics, Indian Institute of Science, Bangalore-560012, India

(Received 19 July 1973; revised manuscript received 24 October 1973)

The system $CS_2 + CH_3NO_2$ shows $\beta = 0.315 \pm 0.004$ over $10^{-6} < \epsilon = |T - T_c|/T_c < 2 \times 10^{-1}$ with no indication of a classical value $\frac{1}{2}$ even far away from T_c. The diameter shows a curvature and is of the form $\varphi_c + b\epsilon + f\epsilon^{7/8}\exp(-g\epsilon^h)$.

Theoretical suggestions[1] have been made that the diameter of the coexistence curve of a fluid system exhibits a singular curvature near the critical point. There have also been suggestions[2] of a possible deviation of the exponent β from the Ising-model value for small or large values of $\epsilon = (T_c - T)/T_c$. This note summarizes a study of the coexistence curve of the binary liquid system carbon disulfide + nitromethane over nearly six decades in ϵ.

The experiments were performed in a thermostat having a temperature stability and resolution of 1 mdeg. Analytical grade samples of CS_2 and CH_3NO_2 were used, with vapor-phase chromatography showing no measurable impurities. The liquid mixtures, with compositions ranging from 0.08 mole fraction to 0.98 mole fraction of CS_2, were taken in ~10-ml sample holders of maximum height 10 mm. The visual observation technique was used to find the phase separation temperatures,[3] as the samples were slowly cooled from the one-phase region. Equilibration times of several hours were given in the critical region. In addition the samples were repeatedly shaken to hasten the attainment of equilibrium. The compositions of the samples were obtained in mole fractions X of CS_2, correct to ± 0.0002, by weighing the liquids. These were converted into volume fractions φ, using the relation $\varphi^{-1} = (1 - K) + KX^{-1}$, where $K = \rho_A M_B/\rho_B M_A$, ρ is the density, and M the molecular weight. Since the volumes of mixing in most binary liquid mixtures are quite small, the neglect of the volume of mixing in the above conversion gives an additional error of only ± 0.0001 in φ.

Six samples, $\varphi = 0.597_5$, 0.599_3, 0.601_4, 0.601_8, 0.602_9, and 0.607_3 volume fraction of CS_2, had the same highest phase separation temperature, 61.98_3°C. For the sample $\varphi = 0.601_4$, the meniscus appeared at the middle of the bulk and remained stationary on slight cooling. For $\varphi = 0.601_8$ the meniscus was a little above the middle. For the other samples it appeared either above or below the middle of the bulb and moved down or up on further cooling. This phenomenon, well studied in liquid-gas and binary liquid systems,[4] was used as the basis for choosing the critical composition φ_c as $0.601_4 \pm 0.0004$.

The coexistence curve was drawn with seventy data points. For each experimental composition φ', the other possible composition φ'' having the same phase separation temperature T was read off from the curve. This method of determining φ'' produced a rather large error of 0.001. The sample height was kept small, $\lesssim 10$ mm, to avoid direct gravity effects, which are in any case weak since the compressibility of a binary system does not have the strong γ singularity. A careful study by Blagoi and co-workers[5] shows that for $t = T_c - T \gtrsim 1$ mdeg the composition and density gradients due to gravity are negligible. Rice[6] has also estimated that even in an unstirred binary liquid sample, appreciable composition gradients can not be established in the scales of ordinary experiments.

A least-squares fit to the data, with T_c adjust-

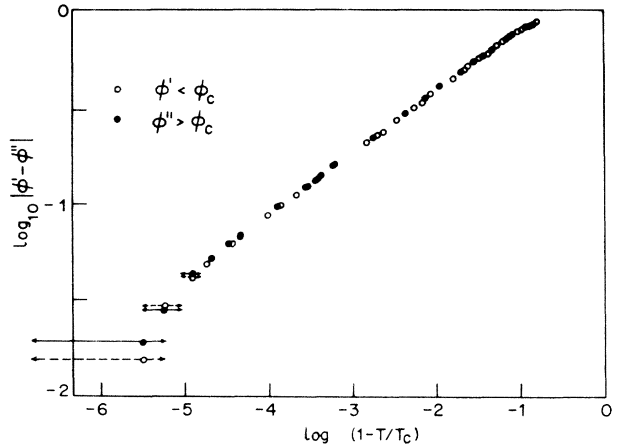

FIG. 1. Log-log plot of $|\varphi' - \varphi''|$ versus $1 - T/T_c$.

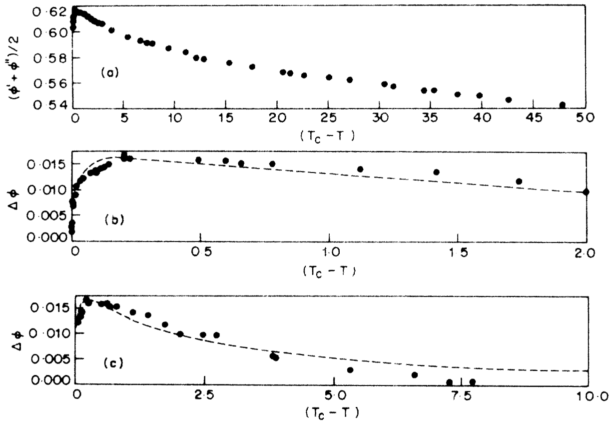

FIG. 2. (a) Behavior of the diameter; (b), (c) deviation from a rectilinear diameter.

able, gave the shape of the coexistence curve $|\varphi' - \varphi''| = B_\varphi \epsilon^\beta$ with $T_c = 335.13_2$°K, $B_\varphi = 1.64 \pm 0.01$, $\beta = 0.315 \pm 0.004$ (Fig. 1). The value of T_c agrees with the experimentally observed highest phase separation temperature and also with earlier experiments on the same system.[7] The value of β also agrees with that obtained in other experiments and calculations.[8] However in the region $10^{-2} < \epsilon < 2 \times 10^{-1}$, the effective β *decreases* to about 0.28. Alternatively the data may be fitted by an equation $|\varphi' - \varphi''| = B_\varphi \epsilon^\beta - B' \epsilon^{\beta+1}$ with $B' \sim 1$. The evidence for β increasing to $\frac{1}{2}$ very near T_c is inconclusive, but certainly a classical value is not approached far away from T_c.

The rectilinear diameter law given by $(\varphi' + \varphi'')/2 = \varphi_c + bt$ is found to be obeyed far away from T_c with $b = -0.0014$ (volume fraction of CS_2)/°C [Fig. 2(a)]. There is a small *deviation*[9] from this law near T_c and Figs. 2(b) and 2(c) show the deviation $\Delta\varphi = (\varphi' + \varphi'')/2 - (\varphi_c + bt)$. Also plotted is a curve $\Delta\varphi = Ft^f \exp(-Gt^h)$ with $F = 3.5$, $f = 0.86$, $G = 5.6$, and $h = 0.21$ as determined by a four-parameter least-squares fit. This gives an $\sim \frac{1}{8}$-power-law singularity for $\partial(\Delta\varphi)/\partial t$ near T_c, in agreement with the suggestions that the slope of the diameter should be asymptotically as singular as the specific heat.[10] Some earlier experiments[11] on binary liquid mixtures do show indications of a curvature in the diameter while experiments on liquid-gas systems[12] do not seem to be unambigous. The effect may be difficult to observe in liquid-gas systems where the molecules are identical and any asymmetry is due to a difference in the state of aggregation only. Perhaps in a binary liquid system the curvature is enhanced by the additional differences in the intermolecular interaction. In a ferromagnet symmetry requires zero curvature.

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*Work supported by the Department of Atomic Energy, the Council of Scientific and Industrial Research, and Public Law 480 funds.

†Now at Nuclear Physics Division, Bhabha Atomic Research Centre, Department of Atomic Energy, Bombay-400085, India.

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[9] The authors thank G. Stell for suggesting that the rectilinear diameter of a binary liquid system should be analyzed in terms of volume fractions instead of mole fractions.

[10] If the rectilinear diameter in terms of volume fractions is as given in the text, then its slope in terms of mole fractions is of the form $(\partial/\partial t)\frac{1}{2}(X'+X'')=3.05t^{-\alpha}+0.0012t^{2\beta-1}$ for the present case, where $1-\alpha=0.86=f$. Even though $t^{2\beta-1}$ diverges faster as $t\to 0$, the coefficients make this term negligible even in the limit of the present resolution. In fact, an analysis of the diameter in terms of mole fractions apparently gives the same fit as for volume fractions with $b=-0.000\,85$, $F=5.0$, $f=0.87$, $G=5.8$, $h=0.19$.

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Critical Behavior of Polar Fluids

G. Stell*
Mathematics Department, The Rockefeller University, New York, New York 10021

(Received 26 November 1973)

A simple argument demonstrates that one should expect polar and nonpolar fluids to have the same critical exponents.

There has been no adequate theory as yet to cope with the critical behavior of a polar fluid, and existing clues have been ambiguous. On the one hand, it has been known for some time[1] that if the pair potential $w(12)$ of a system is of sufficiently long range, one must expect the range to be an active parameter in determining the critical behavior of the system. More precisely, if $w(12)\sim\text{const}\times r^{-\sigma-d}$ for large r (d = dimension and $\sigma>0$), then we expect the critical exponents to depend upon σ whenever σ is less than a certain value $\sigma_m(d)$, which is a bit less than 2 for $d=3$.[1,2] For $\sigma\to 0$, we further expect to recover mean-field behavior.[1-3] For polar fluids, $w(12)\sim f(\varphi,\theta_1,\theta_2)r^{-3}$, where φ, θ_1, θ_2 are angles that describe the relative orientation of two dipolar molecules; thus, one might naively predict mean-field behavior, or at least a considerable departure from the large-σ behavior characteristic of nonpolar molecules. On the other hand, there appears to be no compelling experimental evidence that the critical exponents of polar fluids differ in any substantial way from those of nonpolar fluids.[4] One would guess that the angular-dependent $f(\varphi,\theta_1,\theta_2)$ must be crucial in tempering the effect of the r^{-3} in this connection, and the results of recent theoretical studies[5] of dipolar spin systems indeed show that the angular dependence reduces (but does not completely eliminate) the effect of the long range of the potential. However, fundamental symmetry differences between such spin systems and a fluid of freely rotating dipolar molecules rule out the direct use of those results in treating polar fluids.

Our treatment here begins with the observation that the thermodynamics of a polar system can be identified with the thermodynamics of an exactly equivalent hypothetical nonpolar system with many-body temperature-dependent forces among molecules.[6] Let the configuration integral of the polar system of N particles be

$$Q_N=(N!\Omega^N)^{-1}\int d(1)\cdots d(N)\exp[-\beta W(1,\dots,N)],$$

where $\beta=1/kT$, $i=(\vec{r}_i,\vec{\omega}_i)$ describes both the orientation $\vec{\omega}_i$ and location $\vec{r}_i$ of the ith particle, and $\Omega=\int d^3\omega_i$. In general we have

$$W(1,\dots,N)=\sum_{i<j}w_2(ij)+\sum_{i<j<k}w_3(ijk)+\dots\ . \tag{1}$$

It is often convenient to further decompose each w_n into the sum of an orientation-independent term, call it $q_n(\vec{r}_1,\dots,\vec{r}_N)$, and a term that includes all the $\vec{\omega}_1$ dependence. For example, in the simplest case of interest, $w_n=0$ for $n>2$ and

$$w_2(12)=q(r)+w^{\mathrm{ID}}(12), \tag{2}$$