cessfully recovered even in the presence of the apparent excess background if α is accurately known.

We gratefully acknowledge helpful discussions with S. H. Koenig, D. E. Koppel, and P. N. Pusey. One of us (B.J.B.) gratefully acknowledges opportunities provided by IBM at the T. J. Watson Research Center.

*Alfred P. Sloan Foundation Fellow.

†Work partially supported by the National Science Foundation under Grant No. NSF GP22881.

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Evidence of Nonzero Critical Exponent η for a Binary Mixture from Turbidity and Scattered Light Intensity Measurements

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(Received 12 February 1971)

Measurements of the turbidity and of the intensity of light scattered by a cyclohexane-aniline mixture in the vicinity of the critical point allow us to verify that scaling laws correctly describe the observed phenomena and yield precise values of the critical exponents γ, ν, and η, of the correlation length ξ, and of $(\partial\mu/\partial c)_{P,T}$.

Most of the optical studies of the critical properties of a binary mixture or of a pure fluid have been performed by measuring either the linewidth or the intensity of the scattered light. Puglielli and Ford,[1] however, have shown that very valuable information can also be obtained from turbidity measurements in a pure liquid. This technique has the primary advantage that the angular acceptance of the photomultiplier measuring the intensity of the transmitted light can be reduced to such an extent that any contribution due to forward or multiple scattering is completely negligible.

In the case of an aniline-cyclohexane mixture throughout the temperature range which we explored, the dominant process contributing to the turbidity is Rayleigh scattering. Furthermore, previous experiments performed in our laboratory showed that any contribution other than that due to concentration fluctuations is completely negligible.

In a wide range of temperatures above the critical temperature the intensity scattered by this binary mixture can be expressed by[2]

$$I_s(K) = I_0 \frac{\pi^2}{\lambda_0^4}\left(\frac{\partial n^2}{\partial c}\right)_{P,T}^2 \frac{k_B T}{(\partial\mu/\partial c)_{P,T}} \frac{\sin^2\varphi}{(1+K^2\xi^2)^{1-\eta/2}}, \tag{1}$$

where all the symbols have their usual significance and η is the critical exponent introduced by Fisher to account for an eventual departure from the Ornstein-Zernicke theory. The turbidity is then readily obtained by integrating expression (1) over all angles:

$$\tau = \frac{2\pi^3}{\lambda_0^4}\left(\frac{\partial n^2}{\partial c}\right)_{P,T}^2 \frac{k_B T}{(\partial\mu/\partial c)_{P,T}} \frac{[(1+2a)^{\eta/2}-1][1+a(2-\frac{1}{2}\eta+a^2(2+\frac{1}{2}\eta+\frac{1}{4}\eta^2)] - \eta a(1+a)}{a^3\tfrac{1}{2}\eta(1+\frac{1}{2}\eta)(2+\frac{1}{2}\eta)}, \tag{2}$$

where $a = 2k_0^2\xi^2$. The scaling theory predicts, and a number of experiments show, that ξ and $(\partial\mu/\partial c)_{P,T}$ vary according to

$$\xi = \xi_0\left(\frac{T-T_c}{T_c}\right)^{-\nu}, \qquad \left(\frac{\partial\mu}{\partial c}\right)_{P,T} = \left(\frac{\partial\mu}{\partial c}\right)_{P,T}^{0}\left(\frac{T-T_c}{T_c}\right)^{\gamma}. \tag{3}$$

Thus measurements of the scattered intensity and of the turbidity allow us to calculate the values of the critical exponents γ, ν, and η_0 and of the critical constants ξ_0 and $(\partial\mu/\partial c)_{P,T}^{0}$.

Our equipment is extremely simple. A thermostatic bath, containing about 50 liters of distilled water, insures a temperature stabilization of 1 mdeg. The temperature is measured using a Hewlett-Packard quartz thermometer. The sample cell, which has the form of a right-angled parallelepiped, can slide vertically along a guide track: In the upper position the beam, originating from a He-Ne laser, is not intercepted and the incident power (a fraction of a milliwatt) falls directly on the photomultiplier. The cell is then lowered for the measurement of the intensity of the transmitted beam. Spurious contributions due to reflections on the cell windows were found to be negligible both by direct measurements and computer simulation. A second photomultiplier measured the intensity of the light scattered at 90°. For intensity measurements the incident power ranged from about 0.3 mW for $T - T_c < 0.01$° C to 2 mW for $T - T_c \geq 2$°C. This second photomultiplier was not calibrated with respect to the other, and thus our intensity measurements only yielded the relative variation of the scattered intensity with temperature.

The results of the measurements of the intensity scattered at 90° are reported in Fig. 1, which shows the variation of the reciprocal of the scattered intensity multiplied by the temperature as a function of $T - T_c$. Near the critical point there is an appreciable amount of multiple-scattered light, giving a discrepancy between the theoretical curve and the experimental points. These points were thus neglected and only the linear portion of this curve was used, insuring at least a good determination of the critical exponent γ.

Figure 2 shows the plot of the turbidity as a function of $T - T_c$ on a log-log scale. The different experimental points were obtained using four cells of different thickness as illustrated in Fig. 2, and each cell was filled at least twice with the critical mixture to check the reproducibility of

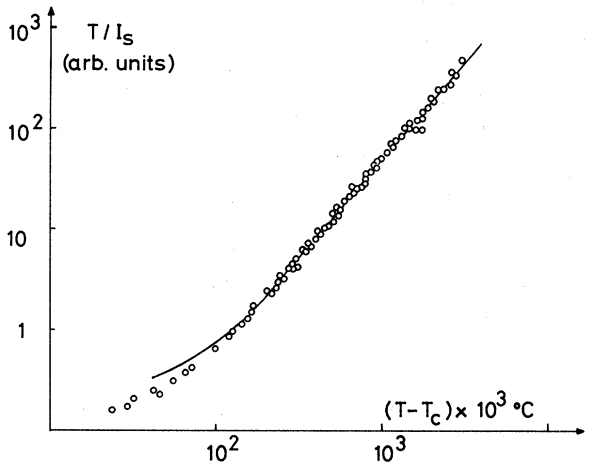

FIG. 1. Plot of the reciprocal of the intensity scattered at 90° multiplied by the absolute temperature as a function of $T - T_c$.

the data. The critical temperature was determined by the vanishing of the transmitted beam and was found to be $\simeq 30.300$°C. For the 5-mm and 10-mm cells, T_c could be determined to better than 10^{-3} °C; for the thicker ones the accuracy was poorer. The maximum difference found between the T_c corresponding to different cells was of the order of 0.1°C. Within these limits it was found that the curves corresponding to different cells giving the turbidity per unit length are exactly the same when plotted as functions of $T - T_c$ even though the T_c's relative to different cells are slightly different.

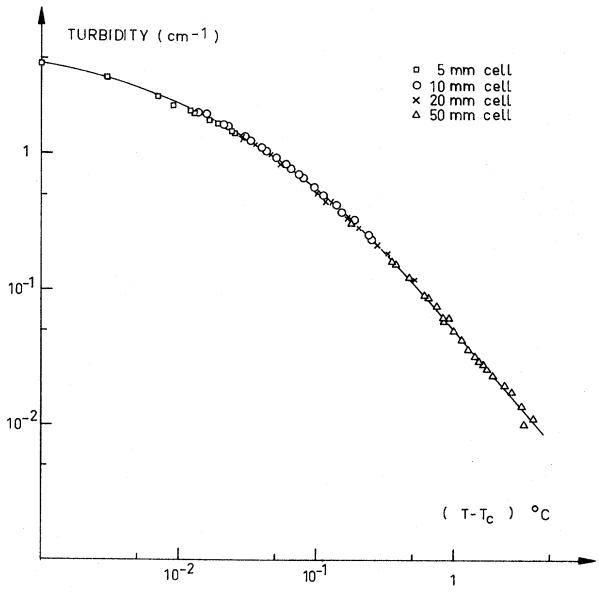

FIG. 2. Plot of the turbidity as a function of $T - T_c$.

The results of these two experiments were compared by computer with expressions (1) and (2) *simultaneously*, using a nonlinear statistical refining program due to Tournarie[3]. To do this the two expressions (3) were introduced in (1) and (2). Then the critical exponents γ, ν, and η and the critical constants ξ_0 and $(\partial\mu/\partial c)_{P,T}{}^0$ were treated as variables which the computer had to adjust in order to obtain the best agreement between the experimental points and the theoretical expressions (1) and (2).

We insist on the fact that in this calculation we have not imposed on the different parameters *any restrictions whatsoever*, except that they should all be positive. In particular we have *not supposed the existence of any relation* between γ, ν, and η in spite of the relation

$$\gamma = (2-\eta)\nu \tag{4}$$

predicted by scaling theories, since if this relation were imposed during the fitting process, then even a weak breakdown of scaling could give a completely *fictitious* nonzero value of η. The results obtained under these conditions are the following:

$$\xi_0 = 2.20 \pm 0.1 \text{ Å}, \quad \nu = 0.63 \pm 0.01,$$
$$\gamma = 1.22 \pm 0.01, \quad \eta = 0.08 \pm 0.5,$$
$$(\partial\mu/\partial c)_{P,T}{}^0 = 112 \pm 7 \text{ J/cm}^3.$$

To obtain this last value we have used the Lorentz-Lorenz relation to find $(\partial n^2/\partial c) = 0.48$.

We remark that, with the exception of η, the values of the different critical parameters are obtained with good accuracy. Moreover all these values are in extremely good agreement with those already found in our laboratory by two different techniques.[4,5] We also remark, in particular, that γ is significantly different from 2ν, in contrast with the Ornstein-Zernicke theory, while the poor accuracy obtained on the direct determination of η would not allow us to reject this theory.

There are thus good reasons to think that η is nonzero, and the central value obtained for η should be regarded as significant. First of all, using this value and that obtained for ν, expression (4) gives $\gamma = 1.21 \pm 0.02$ and this value differs by less than 1% from the value $\gamma = 1.22 \pm 0.01$ determined directly. Furthermore, using scaling theory one can directly derive the relation

$$2\beta = (1+\eta)\nu, \tag{5}$$

where β is the critical exponent describing the coexistence curve

$$C_1 - C_2 \sim (T_c - T)^\beta,$$

C_1 and C_2 being the mass concentration of one component in each of the two phases.

A very accurate value of β can be deduced from the results obtained by Atak and Rice by density measurements in the two phases of this same binary mixture below the critical point.[6] One obtains $\beta = 0.346 \pm 0.005$. Using the relation (5), this value of β, and our value of ν, one obtains $\eta = 0.09 \pm 0.04$, while a zero value for η would lead to $\beta = \nu/2$ which clearly is not verified to the precision of the two experiments. There is no reason to suspect an even weak breakdown of scaling in the vicinity of the critical temperature.

We may then, *a posteriori*, repeat the computer calculation using relation (4) as supplementary information. This will not significantly change the central values and thus will not introduce a distortion but only increase the accuracy. Eliminating γ by the use of (4), we obtain indeed

$$\xi_0 = 2.10 \pm 0.02 \text{ Å}, \quad (\partial\mu/\partial c)_{P,T}{}^0 = 113 \pm 6 \text{ J/cm}^3,$$
$$\nu = 0.633 \pm 0.01, \quad \eta = 0.08 \pm 0.01,$$

whence

$$\gamma = (2-\eta)\nu = 1.22 \pm 0.02.$$

In conlucsion we have shown that parallel intensity and turbidity measurements allow direct and independent determinations of all the critical parameters. It is also possible, by comparison with other measurements, to show that there is no significant breakdown of scaling and consequently that the critical exponent η is nonzero and equal to 0.08 ± 0.01.

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