PHYSICAL REVIEW A VOLUME 19, NUMBER 2 FEBRUARY 1979

Correlation function near the critical mixing point of a binary liquid

R. F. Chang, H. Burstyn, and J. V. Sengers
*Department of Physics and Astronomy and Institute for Physical Science and Technology,
University of Maryland, College Park, Maryland 20742*

(Received 30 May 1978)

We have determined the order-parameter correlation function near the critical mixing point of 3-methylpentane-nitroethane by measuring the intensity of scattered light as a function of temperature. The data cover a range $10^{-6} < t < 2.7 \times 10^{-3}$ in the reduced temperature $t = (T - T_c)/T_c$, which corresponds to a range $0.18 < k\xi < 25$, where k is the wave number and ξ is the correlation length. The critical exponents deduced from the experimental data agree within combined errors with the values calculated theoretically for the Landau-Ginzburg-Wilson model. However, the data cannot be reconciled with the exponent values deduced from high-temperature series expansions for the three-dimensional Ising model.

I. INTRODUCTION

According to the hypothesis of universality of critical phenomena, systems exhibiting critical-point phase transitions can be grouped into universality classes. Systems within a universality class are expected to have the same critical exponents and scaling functions that characterize the asymptotic behavior of the equation of state and the correlation function in the vicinity of the critical point.[1] It is widely assumed that universality classes for homogeneous isotropic systems with short-range forces are determined by the spatial dimensionality and the number of components of the order parameter. This postulate implies that fluids near the gas-liquid critical point and binary liquids near the critical point of mixing should belong to the same universality class as three-dimensional Ising-like spin systems such as the Ising model itself or its continuous generalizations such as the Landau-Ginzburg-Wilson model. The critical exponents for this universality class have been calculated using series expansion techniques[2,3] and renormalization-group techniques.[4-7] The various calculations yield numerically similar results, although some unresolved discrepancies do exist.[8]

Experimental evidence has been reported in support of the universality hypothesis as applied to the asymptotic behavior of the equation of state of fluids near the gas-liquid critical point[9-11] and the behavior of the coexistence curve of binary liquids near the critical mixing point.[12-14] Subsequent corroborating evidence has been obtained from analyses of coexistence curve[15] and equation-of-state data[16] in larger ranges of temperatures incorporating appropriate correction-to-scaling terms.

This paper is concerned with the question of universality as applied to the correlation function of fluids near a critical point. The correlation function or, more precisely, its Fourier transform, the structure factor χ, can be measured experimentally by determining the intensity of light scattered by the fluid relative to the intensity of the incident light. At the critical density of fluids near the gas-liquid critical point, or at the critical concentration of binary liquids near the critical point of mixing, one expects that sufficiently close to the critical temperature T_c the structure factor has the form[17]

$$\chi(k) = \Gamma t^{-\gamma} g(k\xi). \tag{1.1}$$

Here k is the wave number, t is a reduced temperature difference $t = (T - T_c)/T_c$, γ is the critical susceptibility exponent, $g(x)$ is the correlation scaling function, and ξ is the correlation length which diverges as

$$\xi = \xi_0 t^{-\nu}. \tag{1.2}$$

The amplitude Γ is defined such that $\lim_{x\to 0} g(x) = 1$. For small values of the scaling variable, $g(x)$ assumes the Ornstein-Zernike form $g^{-1}(x) = 1 + x^2$, while for large values of x it becomes asymptotically proportional to $x^{\eta-2}$. The critical exponent η is a measure of the extent to which the actual correlation function differs from the classical behavior predicted by the Ornstein-Zernike theory, and many experimental attempts have been made to determine this exponent.

Most light scattering measurements in fluids have been obtained under conditions that $k\xi$ is small. From such measurements one can determine the exponents γ and ν, and then deduce a value for η by using the Fisher relation[17] $\gamma = (2 - \eta)\nu$. For fluids, the most precise value $\eta = 0.03 \pm 0.03$ was thus obtained by Cannell for sulfurhexafluoride.[18] In view of the small value of η, obtaining it from ν and γ through the Fisher relation does not give very accurate results.[19] For a more direct determination of η from scattering data it is desirable to probe the region of large $k\xi$ with substantial accuracy.[20] This region is entered by making either k or ξ large. Given the small values of k accessible in light scattering, one must approach the critical point very closely so as to make ξ sufficiently large. Under these conditions, however, most fluids become so strongly opalescent that the data are distorted by multiple scattering and turbidity. Much larger k values are accessible with x-ray and neutron scattering. Neutron scattering studies conducted by Mozer *et al.*[21] in neon and helium yielded a surprisingly high value of $\eta = 0.11 \pm 0.03$. This value was to some extent supported by x-ray scattering studies conducted by Lin and Schmidt in argon.[22] It also fell in line with the earlier effective thermodynamic critical exponents found for fluids.[23] However, the result was in definite disagreement with the hypothesis of Ising-like behavior of the critical correlation function of fluids. For the true asymptotic form of the structure factor to be visible, not only should $k\xi$ be large, but also k should be small enough so that the short-range structure of the fluid is not seen. It is doubtful whether the latter condition has been met in the x-ray and neutron scattering studies thus far conducted in fluids.[24]

The question raised by these experiments made it desirable to return to the longer wavelengths accessible with light scattering. In fluids near the gas-liquid critical point, it is difficult to measure the scattering intensities at large $k\xi$ because of the multiple scattering problem. In binary liquids, however, multiple scattering can be greatly reduced by selecting a mixture in which the refractive indices of the two liquid components are matched. Therefore, following a suggestion of McIntyre[25] we chose a mixture of 3-methylpentane and nitroethane. At the wavelength $\lambda = 6328$ Å corresponding to that of a He-Ne laser, the refractive indices of the two pure liquid components at 25 °C are 1.3753 and 1.3882, respectively.[26-28] As a consequence, this mixture has a low cross section for light scattering, and the critical point can be approached very closely with only minor corrections for multiple scattering effects. In addition, a sustained effort was made to substantially increase the accuracy of the scattering intensity measurements as compared to our earlier measurements for the same mixture.[29] In a previous letter we have summarized the principal conclusions deduced from this work.[30] It is the purpose of the present paper to provide the information on how the experimental data were obtained and to present the results of a more complete analysis of these data.

II. EXPERIMENT

A. Binary liquid sample

The experiments were conducted with the same binary liquid sample used in our earlier measurements of the decay rate of the concentration fluctuations.[29] This mixture was prepared from research grade (99.99 mole %) 3-methylpentane obtained commercially and nitroethane obtained from a sample earlier prepared by Wims and co-workers.[31] To reduce any residual traces of water the nitroethane was further dried with a silica gel dessicant. Both liquids were filtered through millipore filters to minimize any amount of dust particles.

The sample cell consists of a 6-cm long pyrex tube with internal and external diameters of 1.0 and 1.3 cm, respectively. It was filled with an equimolar mixture of the two liquids under a nitrogen atmosphere; the cell was then frozen and sealed in vacuo.[32] Further details are documented in a separate technical report.[33]

The critical concentration of 3-methylpentane-nitroethane is 0.500 in mole fraction units, as determined earlier by Wims *et al.* from an analysis of coexistence curve data.[31] An analysis of the position of the meniscus of our sample below the critical temperature as a function of temperature confirmed that the actual concentration of our liquid mixture was within 0.3% of the critical concentration. The critical temperature of our sample is (299.545 ± 0.002) K.[34]

B. Optical arrangement and data acquisition

The light source is a 5-mW He-Ne laser whose output polarization is perpendicular to the plane determined by the incident beam, and the direction in which the scattered light is observed. Special precautions were taken to enhance the stability of the laser light intensity. As shown in the simplified schematic representation in Fig. 1, the laser light, after passing a variable attenuator, is monitored by a photodiode whose output is compared with a reference voltage. The amplified and integrated error signal drives a motor which adjusts the optical density of the attenuator.

The optical arrangement for measuring the light scattering intensities is shown schematically in Fig. 2. The incident light, after passing through the intensity stabilizer, is focused at the center of the sample cell by a lens with a focal length of 16 cm. The waist size of the beam at the focus is about 0.2 mm. The scattered light is detected by a Channeltron (Bendix BX754-A). All scattering measurements were conducted with a scattering angle of 90° to facilitate the evaluation of mul-

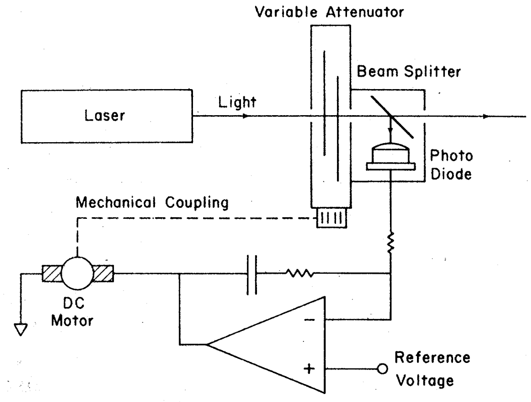

FIG. 1. Schematic representation of intensity stabilizer.

tiple scattering corrections.[35]

In order to improve the accuracy substantially, a provision was made to measure each scattered intensity with respect to the incident light intensity as detected by the same photodetection system, thus eliminating any errors due to small drifts in gain and sensitivity of the photomultiplier. For this purpose a few percent of the incident light is reflected at 45° by a beam splitter. Interference of the beams reflected from the first and the second surface of the beam splitter could lead to instabilities in the reference light intensity. In order to avoid this effect, the surfaces of the beam splitter were sufficiently separated spatially so that the beam reflected from the second surface could be eliminated by a diaphragm. The reference beam is subsequently reflected by the surface of a prism into a diffuser cavity in front of the photocathode of the Channeltron. The purpose of the diffuser cavity is to reduce the intensity of the reference light to a level comparable with that of the scattered light intensity; it is a cylindrical cavity whose inner surface was sprayed with flat gray paint. Shutters were installed in both the path of the incident beam and the reference beam.

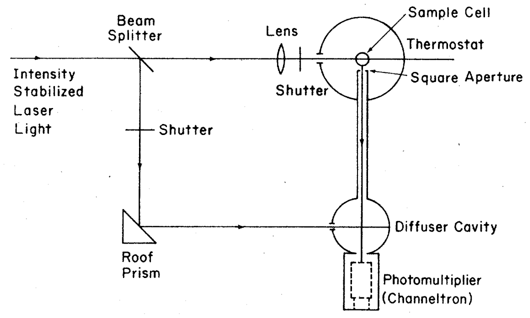

FIG. 2. Schematic representation of optical arrangement.

The scattering volume of the binary liquid sample as seen by the detector is about 0.95 mm^3; it is determined by a 300-μm square aperture adjacent to the cell and a circular cathode of the Channeltron with a diameter of 1 mm located 26 cm from the center of the sample cell. The square aperture, the photocathode, and the illuminated portion of the fluid must be colinear so as to optimize the detected scattering intensity and to account accurately for double scattering effects. Therefore, fine tuning of the alignment was necessary. For this purpose a small glass plate (not shown in Fig. 2), approximately 5 mm thick and 20 mm in diameter, was placed after the focusing lens. By adjusting the tilt of the glass plate, the incident beam could be positioned at the center of the scattering volume seen by the photocathode.

The resolution of our previous light scattering intensity measurements[29] was limited by leakage current effects in the photomultiplier tube. To improve the resolution we adopted photon counting techniques in the present experiment. For this purpose a standard pulse with a width of 42 ns was generated from every photoelectric pulse received by the Channeltron. Each standard pulse was followed by a dead time of the same duration. The Channeltron has a very low dark current yielding approximately 0.1 counts/sec. This level is to be compared with a reference intensity of about 6400 counts/sec and a scattered intensity of approximately 300 counts/sec at $T - T_c \simeq 1$ K and of 8500 counts/sec near T_c.

During the actual experiments, after the sample has reached thermal equilibrium at a desired temperature, the intensities of the reference light and the scattered light were alternatingly registered at 100-sec intervals. The ratio of the intensity of the scattered light to that of the reference light was defined as the normalized scattering intensity. At each temperature the average of 20 consecutive normalized scattering intensities thus obtained was taken as one datum point. A test run of 45 h yielded 41 consecutive data points. The standard deviation of these 41 data points around their average value was 0.17%, indicating the precision with which the normalized scattering intensities could be determined. The data acquisition was automated using a real time operating computer system interfaced with all electronic equipment. The system not only controls the optical shutters and records the readings of the electronic counters, but it also performs the desired calculations of ratios, means, and standard deviations. In addition, by monitoring the normalized scattering intensities continuously after changing the temperature, one can also determine whether thermal equilibrium has been reached. At temperatures more than 10 mK above T_c, the scattered intensity would become constant within 10 min after the desired temperature was reached. At temperatures closer to T_c, the apparent equilibration time still did not exceed 1 h, although in practice we waited 3 h before taking the data. As we shall discuss in Sec. IV B, this equilibration time refers to the approach to local thermodynamic equilibrium, but not total equilibrium.

C. Temperature control and measurement

In order to obtain a high degree of temperature stability, the temperature is controlled in two stages. The sample cell and its surrounding thermostat, the laser, the photodetectors, and some additional electronic instruments are located in an air bath. The temperature of the air bath is regulated using a combination of a refrigerator and an electric heater whose switches are controlled by a thermistor-resistor bridge. The arrangement enabled us to stabilize the air bath temperature, averaged over short term fluctuations, to within 0.01 K. In practice the temperature of the air bath was maintained at approximately 1 °C below the critical temperature to provide a favorable ambient temperature for the second stage. The constant ambient temperature also provides a more stable operation of the electronic instruments and the light source. The air bath is enclosed in a styrofoam box covered with black cloth so as to prevent any extraneous light from reaching the photodetectors.

The sample cell and its surrounding thermostat are shown in Fig. 3. The thermostat consists of a copper cylinder and a copper tubing. The tubing has a wall approximately 0.3 cm thick and a diameter of 9 cm. The cylinder, which is located inside the tubing, has a diameter of 3.8 cm and a height of 15 cm. Its center is bored just large enough to accommodate the sample cell. The space between the tubing and the cylinder is filled with styrofoam.

A heating wire is tightly wound noninductively around the inner cylinder with a thermistor attached to its surface. The thermistor is part of a temperature control system that can maintain the temperature of the inner cylinder to within 0.3 mK over a period of 7 h. The temperature gradient along the vertical axis was found to be within 0.2 mK/cm.

The actual temperature of the sample is measured with the aid of a quartz thermometer probe embedded in the inner cylinder at a location close to where the laser beam passes through the sample cell. The probe is connected to a sensor oscillator. The oscillation frequency is about 28 MHz when the probe is at room temperature, and it varies linearly with the temperature with a rate of 0.986 88 kHz/°C. The oscillating frequency is measured with an electronic counter with a resolution of 0.1 Hz, corresponding to a temperature resolution of 0.1 mK. The temperature of each datum point relative to the critical temperature is determined by the frequency f relative to the frequency f_c when the probe is at T_c. The electronic counter needs a time-base stability of better than 3×10^{-9} over the period of one experimental run (7–14 days). This goal was accomplished by using a rubidium frequency standard whose long-term stability is better than 1×10^{-10} per month. To eliminate any small hysteresis effects in the quartz thermometer, the frequency f_c was redetermined for every experimental run; by monitoring the characteristics of the transmitted beam, the temperature was noted at which the sample passed from the one-phase region into the two-phase region.

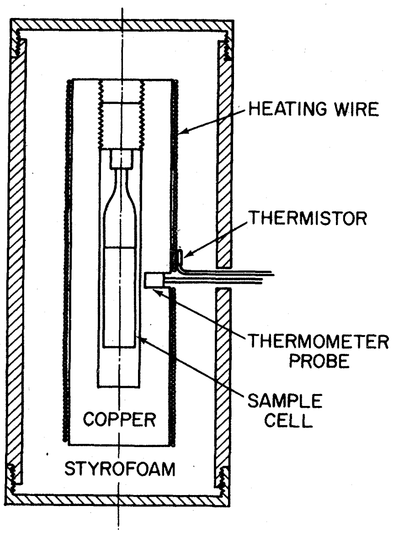

FIG. 3. Sample cell and surrounding thermostat.

In principle, the temperature at which the light scattering intensity is measured may differ from the temperature of the fluid in the optical cell due to local heating by the incident light intensity. We assume that the temperature rise δT is proportional to the incident power per unit area, that is, proportional to the power U of the laser light and inversely proportional to the square of the focusing length l:

$$\delta T = DU/l^2 . \tag{2.1}$$

The intensity measurements were obtained with a focusing length $l = 16$ cm. The sample was illuminated at a 50% duty cycle using laser powers between 1.16 and 1.72 mW, translating into effective average incident power levels U between 0.58 and 0.86 mW. In our earlier analysis of the data[30] we assumed local heating to be negligibly small under these conditions. Subsequently, we measured the Rayleigh linewidth of the scattered light as a function of the incident intensity by raising the laser power to 10 mW and using stronger focusing ($l = 7.5$ cm). These measurements revealed that the temperature rise established after illuminating the fluid for 1 h, corresponded to $D = 0.0056$ K m^2/W in (2.1). For $l = 16$ cm, used in the intensity measurements, we thus applied a temperature correction of 0.22 mK/mW. A similar local heating effect in 3-methylpentane-nitroethane was recently found by Sorensen *et al.*[36]

III. LIGHT SCATTERING INTENSITY AND CRITICAL CORRELATION FUNCTION

A. Dielectric constant and concentration fluctuations

The intensity I of the scattered light is related to the fluctuations of the dielectric constant of the medium by[25]

$$I = I_0 \langle \delta\epsilon_k \delta\epsilon_{-k} \rangle . \tag{3.1}$$

In this relation $I_0 = I_i k_i^4 V \sin^2\psi / 16\pi^2 L^2$, where I_i is the intensity and k_i is the wave number of the incident light in the medium, V is the scattering volume, ψ is the angle between the polarization of the incident light and the observed scattered light direction ($\psi = 90°$ in our experiment), and L is the distance from the scattering volume to the point of observation. For our purpose I_0 can be treated as a constant independent of temperature. The Fourier transform of the dielectric constant correlation function is defined by

$$\langle \delta\epsilon_k \delta\epsilon_{-k} \rangle = \frac{1}{V} \int d\vec{r}_1 \, d\vec{r}_2 \, e^{i\vec{k}\cdot(\vec{r}_1 - \vec{r}_2)} \times \langle \delta\epsilon(\vec{r}_1) \delta\epsilon(\vec{r}_2) \rangle , \tag{3.2}$$

where $\delta\epsilon(\vec{r})$ is the deviation of the local value of the dielectric constant at position $\vec{r}$ from its average equilibrium value.

The fluctuations in the dielectric constant can be related to the fluctuations in the thermodynamic variables of the mixture as indicated by Mountain and Deutch[37,38]:

$$\langle \delta\epsilon_k \delta\epsilon_{-k} \rangle = \left(\frac{\partial\epsilon}{\partial X}\right)^2_{T,P} \langle \delta X_k \delta X_{-k} \rangle + \left(\frac{\partial\epsilon}{\partial T}\right)^2_{P,X} \langle \delta\Phi_k \delta\Phi_{-k} \rangle + \left(\frac{\partial\epsilon}{\partial P}\right)^2_{\Phi,X} \langle \delta P_k \delta P_{-k} \rangle . \tag{3.3}$$

Here X is the mole fraction of either component and Φ is a new variable which is a linear combination of temperature T and pressure P such that

$$\delta\Phi = \delta T - \frac{T}{C_{PX}} \left(\frac{\partial V}{\partial T}\right)_{P,X} \delta P \tag{3.4}$$

and

$$\left(\frac{\partial\epsilon}{\partial P}\right)_{\Phi,X} = \left(\frac{\partial\epsilon}{\partial P}\right)_{S,X} = \left(\frac{\partial\epsilon}{\partial P}\right)_{T,X} + \frac{T}{C_{PX}} \left(\frac{\partial V}{\partial T}\right)_{P,X} \left(\frac{\partial\epsilon}{\partial T}\right)_{P,X} , \tag{3.5}$$

where C_{PX} is the heat capacity at constant pressure and composition.

In order to estimate the effects of the temperature and pressure fluctuations relative to the concentration fluctuations, we note that in the thermodynamic limit $k\xi \to 0$,

$$\langle (\delta X)^2 \rangle = \frac{k_B T}{N} \left(\frac{\partial X}{\partial \mu}\right)_{P,T} , \quad \langle (\delta\Phi)^2 \rangle = \frac{k_B T^2}{C_{PX}} , \quad \langle (\delta P)^2 \rangle = \frac{k_B T}{V K_{SX}} . \tag{3.6}$$

Here k_B is Boltzmann's constant, N is the number of moles of the mixture in the volume V, μ is the difference of the chemical potentials of the two components of the mixture, and K_{SX} is the adiabatic compressibility.[37,38] Many of the required thermodynamic properties are known either for the mixture or for the individual components. The density and thermal expansion coefficient of the mixture has been measured by Greer and Hocken[39] and the excess volume by Reeder *et al.*,[40] while the adiabatic compressibility can be deduced from the sound-velocity measurements of Kruer and Gammon.[41] We estimated the nonsingular part of the heat capacity from the heat capacity of the individual components[41-44] and the amplitude of the singular part from the correlation length using the hypothesis of two-scale-factor universality.[45] The dielectric constant of the mixture was related to the known dielectric constants ϵ_j of the individual components[26-28] using the Clausius-Mossoti formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \left(\frac{\epsilon_1 - 1}{\epsilon_1 + 2}\right) \frac{\rho_1}{\rho_1^0} + \left(\frac{\epsilon_2 - 1}{\epsilon_2 + 2}\right) \frac{\rho_2}{\rho_2^0} , \tag{3.7}$$

where ρ_j are the densities of the components in the mixture and ρ_j^0 is the densities of the pure components at the same temperature and pressure. We find that the second and third terms in (3.3) contribute approximately 7% and 3% to the total scattered intensity at a temperature $T - T_c = 1$ K. These contributions depend weakly on temperature, while the contributions from the concentration fluctuations increase rapidly when the critical temperature is approached more closely. Even allowing for a possible singular behavior of ϵ as a function of temperature,[46] our estimates indicate that in the range $10^{-6} \leqslant t \leqslant 2.7\times10^{-3}$ of our experimental data, the temperature variation of the contributions from the temperature and pressure fluctuations is well within the experimental precision of 0.25%. Thus

$$I = I_0\left(\frac{\partial\epsilon}{\partial X}\right)^2_{T,P}\langle\delta X_k\delta X_{-k}\rangle + \Delta I, \tag{3.8}$$

where ΔI may be treated as a constant independent of temperature. In practice, the constant ΔI will also contain small extraneous contributions such as those due to scattering from the walls of the sample which depend on the optical alignment. For each experimental run we therefore treat ΔI as an adjustable constant. From (3.7), using existing literature data for the densities[39,47] and the volumes of mixing,[40] we conclude that the prefactor $(\partial\epsilon/\partial X)^2_{T,P}$ in (3.8) varies slightly with temperature as

$$\left(\frac{\partial\epsilon}{\partial X}\right)^2_{T,P} = c_X(1+6.4t), \tag{3.9}$$

where c_X represents the value of $(\partial\epsilon/\partial X)^2_{T,P}$ at the critical temperature.

The order parameter near the critical point of mixing is to be identified with the concentration of either component. However, it has been argued that in practice the volume fraction $\phi = V_1/(V_1+V_2)$, where V_1 and V_2 are the volumes of the pure components at the same temperature and pressure, is a more appropriate choice than the mole fraction.[13,48] Hence, instead of (3.8) we consider

$$I = I_0\left(\frac{\partial\epsilon}{\partial \phi}\right)^2_{T,P}\langle\delta\phi_k\delta\phi_{-k}\rangle + \Delta I, \tag{3.10}$$

where $\langle\delta\phi_k\delta\phi_{-k}\rangle$ will be identified with the Fourier transform $\chi(k)$ of the order-parameter correlation function. From the Clausius-Mossoti formula (3.7) we obtain for the prefactor

$$\left(\frac{\partial\epsilon}{\partial \phi}\right)^2_{T,P} = c_\phi(1+6.4t). \tag{3.11}$$

It should be noted that an analysis of coexistence curve data for our mixture has yielded the same results regardless of whether the concentration is expressed in mole fractions or in volume fractions.[40,49] On comparing (3.9) with (3.11) we see also that the analysis of the light scattering data will be insensitive to these particular choices. If we neglect the volume of mixing as is often done in the literature,[13,14,49] the coefficient of the temperature dependence of the prefactor (3.11) changes from 6.4 to 5.5. In principle, different choices of order parameter will lead to slightly different values of the temperature dependence of the prefactor and thus amount to different estimates of the amplitude of a confluent singularity. We shall return to this point in Sec. IV B.

B. Turbidity and multiple scattering

The relationship between the scattered light intensity and the structure factor $\chi(k)$, mentioned above, is only valid if the effects of turbidity and multiple scattering can be neglected. In the vicinity of the critical point this approximation is no longer adequate for a quantitative interpretation of the experimental data. The effects have been considered by a number of authors.[35,50-55] Here we use the approach formulated by Bray and one of the authors.[35] This approach is specifically designed for our case where the scattering angle is 90°, and where the corrections are sufficiently small to justify linearization of the turbidity correction and incorporation of double scattering, but not triple and higher-order scattering. In this approximation the scattered light intensity may be represented by

$$I = I_0\left(\frac{\partial\epsilon}{\partial \phi}\right)^2_{T,P}\chi(k)[1-(1-R)\tau l] + \Delta I, \tag{3.12}$$

where τ is the turbidity per unit length, l is the path length of the scattered beam in the medium, and R is a double scattering correction.[35]

Since for our sample both τ and R turn out to be small at any experimentally accessible temperature, it is sufficient to evaluate these corrections using the Ornstein-Zernike approximation $\chi(k) = \Gamma t^{-\gamma}/(1+k^2\xi^2)$. In this approximation the turbidity correction becomes[56]

$$\tau l = A t^{-\gamma} H(k_i\xi), \tag{3.13}$$

where A is a constant and where the function $H(k_i\xi)$ is given by

$$H(y) = \left(\frac{8y^4+4y^2+1}{8y^6}\right)\ln(1+4y^2) - \left(\frac{2y^2+1}{2y^4}\right). \tag{3.14}$$

For our cylindrical sample cell the path length l of the scattered beam is equal to the path length of the transmitted beam. Hence the turbidity correction can be determined experimentally as a function of temperature by measuring the intensity I_t of the transmitted beam relative to the intensity I_i of the incident beam. In practice we measure a fraction pI_i of the incident beam intensity, and the experimental data are to be compared with

$$I_t/pI_i = (1/p)\exp(-\tau l). \tag{3.15}$$

Using $\gamma = 2\nu = 1.232$ and $\xi_0 = 2.56$ Å as determined earlier for our mixture in the Ornstein-Zernike approximation,[29] we fitted (3.15) with (3.13) to the experimental turbidity data, using p and A as adjustable parameters, and obtained

$$\tau l = 12.3\times 10^{-8} t^{-1.232} H(3.51\times 10^{-3} t^{-0.616}). \tag{3.16}$$

This equation represents the experimental turbidity data within their precision as shown in Fig. 4.

In the same approximation the double scattering correction term R was calculated as a function of $k_i\xi$ from the equations presented in a previous paper[35] noting that in our experiment the parameter $2r_0/h = 32.5$, where r_0 is the inner radius of the cylindrical cell and h is the height of the scattering volume seen by the detector. After converting $k_i\xi$ into $T-T_c$, the value of R as a function of temperature is given in Fig. 5. From Figs. 4 and 5 we note that the combined correction due to turbidity and double scattering amounts to 0.4% at $T-T_c = 0.1$ K and increases up to 3.8% at $T-T_c = 0.3$ mK.

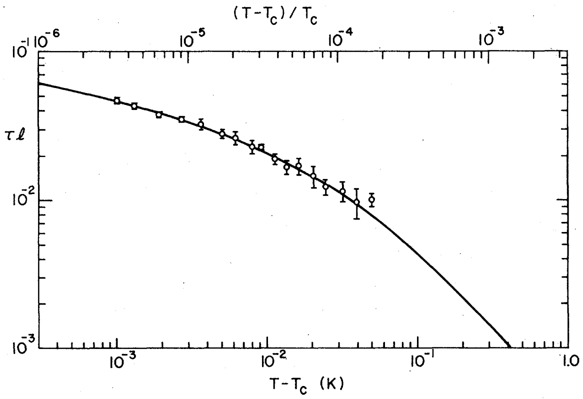

FIG. 4. Turbidity correction τl as a function of temperature. The circles indicate experimental data and the curve represents Eq. (3.16).

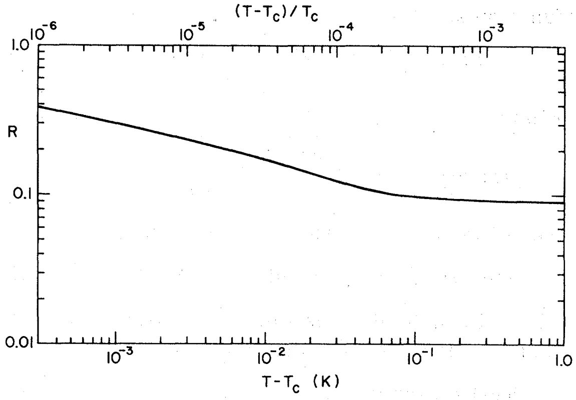

FIG. 5. Double scattering correction term R as a function of temperature.

C. Correlation scaling function

The theory predicts that in the vicinity of the critical point the structure factor $\chi(k)$ will assume the scaled form (1.1), where the correlation scaling function $g(x)$ is a universal function of the scaling variable $x = k\xi$. The scale factor for the correlation length may be normalized by requiring either $\lim_{x\to 0} dg^{-1}(x)/dx^2 = 1$ or $g^{-1}(i) = 0$, where $i = \sqrt{-1}$. The first option defines a scaling variable $x = k\xi$ in terms of the "effective" or "second-moment" correlation length; the second option defines a scaling variable $\tilde{x} = k\tilde{\xi}$ in terms of the "true" or "exact" correlation length.[57] In this paper we shall analyze the experimental data in terms of the second-moment correlation length scaling variable x. The correlation scaling function $g(x)$ should satisfy the boundary conditions[17,58-60]

$$g(x) = 1/(1+x^2), \quad (x \ll 1) \tag{3.17}$$

$$g(x) = \frac{C_1}{x^{2-\eta}}\left(1 + \frac{C_2}{x^{(1-\alpha)/\nu}} + \frac{C_3}{x^{1/\nu}}\right), \quad (x \gg 1). \tag{3.18}$$

The expansion (3.18) for large values of x is often referred to as the Fisher-Langer expansion.[58] Numerical estimates for the coefficients C_1, C_2, and C_3 for the universality class of Ising-like systems have been obtained from a perturbation analysis in terms of $\epsilon = 4-d$, where d is the dimensionality of the system.[61,62]

In order to interpret experimental data at intermediate values of x, one needs a scaling function that interpolates between the small and the large x behavior. Earlier light scattering data have often been interpreted in terms of the Fisher approximant[19,63-65]

$$g_F(x) = 1/(1+x^2)^{1-\eta/2}. \tag{3.19}$$

However, this simple scattering function cannot accommodate simultaneously the correct amplitudes of the leading terms in the small and large x expansions. Therefore, based on an analysis of numerical data for the three-dimensional Ising model, Fisher and Burford proposed the scaling function[57]

$$g_{FB}(x) = \frac{(1+\psi^2 x^2)^{\eta/2}}{1 + (1+\psi^2\eta/2)x^2}. \tag{3.20}$$

For large values of x the leading term in the asymptotic expansion (3.18) is recovered with $C_1 = \psi^\eta/(1+\psi^2\eta/2)$.

The problem was also considered by Ferrell and Scalapino.[66,67] They rewrite the correlation scaling function as

$$g^{-1}(\tilde{x}) = 1 + \tilde{x}^2 [f(\tfrac{1}{9}\tilde{x}^2)/f(-\tfrac{1}{9})], \tag{3.21}$$

where

$$f(z) = \frac{2}{\pi}\sin\left(\frac{\pi\eta}{2}\right)\int_1^\infty \frac{du\,uF(u)}{u^\eta(u^2+z)} . \tag{3.22}$$

Here $F(u)$ is a spectral function defined as

$$F(u) = C_1 \operatorname{Im} g^{-1}(3iu)/\sin(\tfrac{1}{2}\pi\eta)(3u)^{2-\eta}, \tag{3.23}$$

where Im indicates the imaginary part. This spectral function satisfies the conditions

$$F(u) > 0 \text{ for } u > 1,$$

$$F(u) = 0 \text{ for } u \leq 1. \tag{3.24}$$

In this approach the exact correlation length scaling variable $\tilde{x}$ is related to the second-moment correlation scaling variable x by

$$\tilde{x} = x\zeta, \tag{3.25}$$

where

$$\zeta^2 = f(-\tfrac{1}{9})/f(0), \tag{3.26}$$

so that

$$g^{-1}(x) = 1 + x^2\, [f(\tfrac{1}{9}x^2\zeta^2)/f(0)]. \tag{3.27}$$

For the small values of the exponents η to be considered, neglecting terms of order η^2, the scaling function (3.27) can be linearized in η and approximated by

$$g^{-1}(x) = 1 + x^2(1 + \tfrac{1}{9}x^2)^{-\eta/2}[1 + \eta s(x)], \tag{3.28}$$

where the function $s(x)$ is related to the spectral function $F(u)$ by

$$s(x) = \frac{x^2}{9}\int_1^\infty \frac{du[1 - F(u)]}{u(u^2 + x^2/9)} . \tag{3.29}$$

The idea of this approach is to approximate the spectral function $F(u)$. In particular, Ferrell and Scalapino proposed[66]

$$F_{FS}(u) = 1 - u^{-3/2} + 7\omega(u^{-12/7} - u^{-3/2}), \tag{3.30}$$

where ω is a parameter restricted to the range $-\frac{1}{7} \leq \omega \leq 1$. For $\omega = 1$, this procedure yields a scaling function similar to the scaling function of Fisher-Burford over a substantial range of the scaling variable x.

As pointed out by Tracy and McCoy,[20] the Fisher-Burford approximant (3.20) does not reproduce accurately the exactly known correlation function of the two-dimensional Ising model over an appreciable range of the scaling variable x. The correlation scaling function of Ferrell and Scalapino suffers from a similar defect.[68] For this reason, Tracy and McCoy have questioned the reliability of any of the scaling functions mentioned above for determining the exponent η from experimental scattering data.[20,69]

To remedy this deficiency Bray[70,71] proposed to substitute into (3.22) or (3.29) a spectral function derived from the Fisher-Langer expansion (3.18), but truncated so as to vanish for $u < 1$:

$$F_B(u) = [P - Q\cot(\tfrac{1}{2}\pi\eta)]/(P^2 + Q^2), \tag{3.31}$$

with

$$P(u) = 1 + \frac{C_2\cos(\pi p/2\nu)}{(3u)^{p/\nu}} + \frac{C_3\cos(\pi/2\nu)}{(3u)^{1/\nu}} , \tag{3.31a}$$

$$Q(u) = \frac{C_2\sin(\pi p/2\nu)}{(3u)^{p/\nu}} + \frac{C_3\sin(\pi/2\nu)}{(3u)^{1/\nu}} , \tag{3.31b}$$

and where $p = 1 - \alpha$, which in practice may be approximated using the hyperscaling relation $p = d\nu - 1$. The coefficients C_2 and C_3 are the same as those in the asymptotic expansion (3.18), and the coefficient C_1 is determined by

$$C_1 = 3^{-\eta} f(0)\left(\frac{f(-\frac{1}{9})}{f(0)}\right)^{\eta/2} \simeq \frac{1}{3^\eta[1 + \eta s(\infty)]} . \tag{3.32}$$

Bray[71] showed that this procedure yields a scaling function which reproduces the correlation scaling function of the two-dimensional Ising model[72] within 0.03% of any value of x and which also agrees with the theoretical values near four dimensions calculated using ϵ expansion techniques.[61] We shall therefore assume that the correlation scaling function proposed by Bray also yields an adequate representation of the correlation scaling function for three-dimensional Ising-like systems.

IV. RESULTS

A. Experimental data

The light scattering intensities were measured as a function of temperature. In each experimental run we started at temperatures between 1 and 10 K above the critical temperature, and took data at successive lower values of the temperature until the sample would pass the critical temperature. Prior to each experimental run, the sample cell was shaken and the arrangement reassembled so as to guarantee that the fluid sample would be spatially homogeneous.

We obtained six experimental runs with the position of the scattering volume at the level where the meniscus would appear after passing through the critical temperature. The measured scattering intensities relative to the incident intensity are presented in Table I as a function of the temperature difference $\Delta T = T - T_c$. Each individual data point was obtained as the average of 20 consecutive readings. The relative standard deviations $\delta I/I$ thus obtained are also included in Table I. The precision is 0.2%–0.3% for $\Delta T \leq 0.2$ K, gradually increasing up to 0.5% at $\Delta T = 0.8$ K. Because of the decrease in the light scattering intensity, the error grows beyond 1% at temperatures substantially beyond $\Delta T = 1$ K. For the purpose of interpreting the measurements we only consider the data points corresponding to $\Delta T < 0.8$ K.

B. Determination of correlation function parameters

From Eqs. (1.1), (3.11), (3.12), and using the Fisher relation

$$\gamma = (2 - \eta)\nu, \tag{4.1}$$

it follows that the asymptotic behavior of the light scattering intensities I may be represented by

TABLE I. Experimental light scattering intensities relative to the incident intensity as a function of $T - T_c$.

	Run 1			Run 2			Run 3	
$T - T_c$	I	$\delta I/I$	$T - T_c$	I	$\delta I/I$	$T - T_c$	I	$\delta I/I$
0.0003	15.355	0.2%	0.0004	15.410	0.2%	0.0003	15.247	0.3%
0.0006	15.396	0.1%	0.0007	15.482	0.2%	0.0006	15.270	0.2%
0.0009	15.401	0.2%	0.0008	15.511	0.2%	0.0010	15.240	0.2%
0.0012	15.411	0.1%	0.0011	15.518	0.2%	0.0014	15.195	0.2%
0.0016	15.409	0.2%	0.0014	15.465	0.3%	0.0018	15.262	0.2%
0.0021	15.389	0.3%	0.0016	15.468	0.2%	0.0024	15.262	0.2%
0.0025	15.383	0.1%	0.0021	15.392	0.2%	0.0030	15.175	0.2%
0.0032	15.344	0.3%	0.0025	15.407	0.2%	0.0036	15.131	0.2%
0.0034	15.305	0.2%	0.0029	15.381	0.2%	0.0045	15.004	0.2%
0.0041	15.282	0.2%	0.0035	15.311	0.2%	0.0052	14.879	0.2%
0.0053	15.129	0.2%	0.0041	15.331	0.2%	0.0061	14.793	0.2%
0.0063	14.990	0.1%	0.0047	15.226	0.2%	0.0080	14.484	0.2%
0.0070	14.907	0.2%	0.0057	15.052	0.2%	0.0100	14.080	0.3%
0.0087	14.594	0.2%	0.0062	14.959	0.2%	0.0125	13.613	0.2%
0.0103	14.333	0.2%	0.0072	14.822	0.2%	0.0154	13.083	0.3%
0.0127	13.880	0.2%	0.0091	14.547	0.2%	0.0188	12.519	0.2%
0.0159	13.297	0.2%	0.0111	14.203	0.3%	0.0240	11.697	0.2%
0.0200	12.587	0.2%	0.0135	13.753	0.1%	0.0316	10.563	0.2%
0.0248	11.779	0.2%	0.0163	13.225	0.2%	0.0392	9.530	0.2%
0.0252	11.741	0.2%	0.0203	12.531	0.2%	0.0487	8.469	0.2%
0.0315	10.761	0.3%	0.0251	11.724	0.2%	0.0621	7.255	0.3%
0.0400	9.660	0.2%	0.0323	10.631	0.2%	0.0792	6.088	0.3%
0.0501	8.508	0.2%	0.0402	9.617	0.3%	0.0995	5.043	0.4%
0.0631	7.332	0.1%	0.0502	8.506	0.2%	0.1250	4.131	0.3%
0.0792	6.230	0.3%	0.0633	7.316	0.2%	0.1583	3.312	0.2%
0.0977	5.260	0.2%	0.0802	6.153	0.2%	0.1989	2.647	0.3%
0.0977	5.313	0.2%	0.1007	5.114	0.2%	0.2505	2.083	0.3%
0.0985	5.238	0.1%	0.1263	4.189	0.3%	0.3152	1.632	0.4%
0.1260	4.254	0.3%	0.1591	3.337	0.3%	0.3970	1.274	0.5%
0.1583	3.437	0.3%	0.2002	2.678	0.3%	0.5005	0.988	0.4%
0.1998	2.725	0.3%	0.2513	2.109	0.4%	0.6302	0.770	0.5%
0.2510	2.152	0.3%	0.3171	1.649	0.3%	0.7942	0.600	0.5%
0.3166	1.680	0.3%	0.3987	1.287	0.4%	1.0202	0.461	0.6%
0.3981	1.308	0.4%	0.5015	1.005	0.5%	1.2588	0.373	0.8%
0.3985	1.311	0.4%	0.6316	0.784	0.5%	1.5840	0.297	0.7%
0.5010	1.020	0.3%	0.7950	0.609	0.6%	1.9934	0.241	1.0%
0.6299	0.793	0.3%	1.0223	0.466	0.3%	2.5101	0.198	1.0%
0.7954	0.620	0.5%	1.2598	0.377	0.6%	3.1617	0.166	1.1%
1.0220	0.476	0.7%	1.5853	0.302	0.9%	3.9812	0.141	1.6%
			1.9958	0.246	0.9%	5.0118	0.124	1.3%
			2.5125	0.202	0.9%	6.3097	0.110	1.2%
			3.1631	0.169	0.7%	7.0797	0.104	1.8%
			3.9819	0.144	1.2%	7.8916	0.101	1.4%
			5.0131	0.125	1.3%	10.8385	0.092	1.7%
			6.3107	0.112	1.2%			
			7.0802	0.106	0.8%			

TABLE I. *(Continued)*.

	Run 4			Run 5			Run 6	
$T-T_c$	I	$\delta I/I$	$T-T_c$	I	$\delta I/I$	$T-T_c$	I	$\delta I/I$
0.0003	15.120	0.2%	0.0003	15.105	0.2%	0.0003	13.434	0.2%
0.0007	15.200	0.2%	0.0007	15.136	0.3%	0.0006	13.466	0.1%
0.0012	15.207	0.2%	0.0012	15.133	0.2%	0.0012	13.468	0.2%
0.0012	15.224	0.2%	0.0017	15.135	0.3%	0.0019	13.423	0.2%
0.0016	15.176	0.3%	0.0026	15.049	0.2%	0.0027	13.356	0.2%
0.0023	15.158	0.2%	0.0033	14.902	0.3%	0.0032	13.309	0.2%
0.0027	15.157	0.2%	0.0044	14.731	0.3%	0.0039	13.250	0.3%
0.0035	15.038	0.2%	0.0077	14.208	0.2%	0.0048	13.149	0.2%
0.0043	14.938	0.2%	0.0094	13.939	0.2%	0.0053	13.117	0.2%
0.0054	14.785	0.3%	0.0107	13.727	0.1%	0.0058	13.044	0.2%
0.0052	14.863	0.2%	0.0121	13.464	0.2%	0.0068	12.908	0.2%
0.0070	14.531	0.2%	0.0136	13.213	0.2%	0.0072	12.831	0.2%
0.0089	14.164	0.3%	0.0154	12.918	0.2%	0.0080	12.718	0.2%
0.0114	13.710	0.2%	0.0182	12.393	0.3%	0.0085	12.659	0.2%
0.0144	13.206	0.2%	0.0219	11.793	0.2%	0.0099	12.472	0.2%
0.0179	12.577	0.2%	0.0239	11.450	0.2%	0.0113	12.270	0.2%
0.0230	11.736	0.2%	0.0270	10.974	0.3%	0.0140	11.836	0.1%
0.0304	10.574	0.2%	0.0315	10.333	0.3%	0.0158	11.518	0.2%
0.0384	9.530	0.2%	0.0378	9.557	0.2%	0.0174	11.294	0.2%
0.0482	8.430	0.3%	0.0467	8.536	0.3%	0.0205	10.836	0.3%
0.0614	7.251	0.3%	0.0589	7.397	0.3%	0.0237	10.378	0.2%
0.0785	6.079	0.2%	0.0703	6.547	0.3%	0.0301	9.549	0.3%
0.0991	5.046	0.3%	0.0859	5.645	0.3%	0.0361	8.812	0.3%
0.1244	4.132	0.2%	0.1066	4.714	0.2%	0.0441	7.965	0.2%
0.1574	3.316	0.3%	0.1349	3.797	0.3%	0.0565	6.878	0.2%
0.1979	2.637	0.3%	0.1617	3.197	0.3%	0.0666	6.170	0.2%
0.2495	2.079	0.3%	0.2066	2.506	0.4%	0.0727	5.817	0.2%
0.3143	1.631	0.4%	0.2614	1.969	0.2%	0.0820	5.312	0.2%
0.3965	1.272	0.5%	0.3225	1.579	0.4%	0.1020	4.447	0.2%
0.3967	1.267	0.5%	0.4045	1.238	0.4%	0.1337	3.491	0.2%
0.3966	1.268	0.4%	0.5097	0.965	0.4%	0.1562	3.012	0.3%
0.4990	0.989	0.7%	0.6399	0.752	0.7%	0.2049	2.300	0.3%
0.4989	0.989	0.4%	0.7612	0.625	0.8%	0.2521	1.858	0.4%
0.6294	0.769	0.5%	1.0292	0.455	0.8%	0.3080	1.501	0.4%
0.7929	0.601	0.6%	1.2764	0.367	0.7%	0.3953	1.144	0.4%
0.7930	0.602	0.6%	2.1203	0.228	1.1%	0.4959	0.893	0.4%
1.0206	0.460	0.8%	4.2645	0.135	1.3%	0.6273	0.695	0.4%
1.2578	0.374	0.8%				0.7510	0.571	0.6%
1.9939	0.241	1.0%				1.0184	0.414	0.5%
3.1609	0.166	1.5%				1.2615	0.332	0.7%
5.0106	0.122	2.0%				2.0557	0.209	1.1%
7.0797	0.103	1.5%				4.1688	0.122	1.1%
9.4059	0.093	1.4%				6.2469	0.098	1.5%

$$I=\tilde{I}_0(1+6.4t)[1-(1-R)\tau l]t^{-(2-\eta)\nu}g(k\xi)+\Delta I, \tag{4.2}$$

where the constants c_Φ and Γ have been incorporated in the proportionality constant $\tilde{I}_0$.

Assuming that in the experimental temperature range $t \leq 2.7\times10^{-3}$ corrections to scaling can be neglected and that the correlation scaling function $g(x)$ may be represented in terms of the truncated Fisher-Langer spectral function (3.31) as proposed by Bray, we try to deduce from the experimental data optimum values for the correlation function exponent η and the parameters ξ_0 and ν determining the correlation length ξ. For this purpose we consider the spectral function $F_B(u)$ for various values of the exponents η and ν. The procedure is slightly complicated by the fact that this spectral function also depends on the coefficients C_2 and C_3 in the Fisher-Langer expansion, which are known only with limited accuracy.[62] In practice we adopt the sum rule

$$C_2+C_3=-0.9 \tag{4.3}$$

obtained from an ϵ expansion to third order,[71] and determine the individual values of C_2 and C_3 by requiring that $F_B(u)$ be non-negative for $u>1$ and as small as possible at the threshold $u = 1$. For $\eta > 0.028$ this goal can be accomplished by simply requiring $F_B(1) = 0$, as was done by Bray for the three-dimensional Ising model.[71]

A preliminary analysis indicated that ν and η are close to 0.625 and 0.02, respectively. For these exponent values, the spectral function $F_B(u)$ has a minimum at a value of u larger than unity, and the condition $F_B(1) = 0$ would lead to negative values of $F(u)$ in a small range $u > 1$. In practice, we selected the spectral function $F(u)$ corresponding to $\nu = \frac{5}{8}$ and $\eta = \frac{1}{54} \simeq 0.0185$ with the values $C_2 = 1.733$ and $C_3 = -2.745$ derived from the ϵ expansion to second order.[62,73] The behavior of the spectral function $F(u)$ thus obtained is analogous to that of the truncated Fisher-Langer spectral function of the two-dimensional Ising model.[71] It is possible to fine-tune the spectral function by defining[30,71] $F(u) = F_B(u)$ for $u > w$ and $F(u) = v$ for $1 < u < w$, where v is a constant between zero and $F_B(w)$. However, the results of our analysis were insensitive to these refinements, and the spectral function $F_B(u)$ truncated at $u = 1$ was therefore considered adequate for our purpose.

In order to facilitate the determination of the exponent η with the methods of statistical analysis, we substitute the linearized form (3.28) for $g^{-1}(x)$ into (4.2),

$$I = \frac{\tilde{I}_0(1 + 6.4t)[1 - (1 - R)\tau l]t^{-(2-\eta)\nu}}{1 + x^2(1 + x^2/9)^{-\eta/2}[1 + \eta s(x)]} + \Delta I, \tag{4.4}$$

where $x = k\xi$. In the linearized form the dependence of $g^{-1}(x)$, and hence I, on η through the function $s(x)$ is of order η^2 and higher; such terms can be neglected for the small values of η found in our experiment.

The function $s(x)$ and the corresponding correlation scaling function $g(x)$, deduced from the spectral function $F_B(u)$ defined above for $\eta = \frac{1}{54}$ and $\nu = \frac{5}{8}$, are tabulated in Table II. Using this function $s(x)$, Eq. (4.4) was fitted to the experimental data with $\tilde{I}_0$, ΔI, η, ν, and ξ_0 as adjustable parameters. The results thus obtained for the free parameters η, ν, and ξ_0, and the derived parameters

TABLE II. Correlation scaling function for various values of η and ν.

	$\eta = \frac{1}{54}$	$\eta = \frac{1}{54}$	$\eta = 0.0315$	$\eta = 0.0410$
	$\nu = \frac{5}{8}$	$\nu = \frac{5}{8}$	$\nu = 0.6300$	$\nu = 0.6380$
x	$s(x)$	$g(x)$	$g(x)$	$g(x)$
0.1000	0.4715×10^{-3}	0.9901	0.9901	0.9901
0.1259	0.7469×10^{-3}	0.9844	0.9844	0.9844
0.1585	0.1183×10^{-2}	0.9755	0.9755	0.9755
0.1995	0.1874×10^{-2}	0.9617	0.9617	0.9617
0.2512	0.2965×10^{-2}	0.9407	0.9407	0.9407
0.3162	0.4689×10^{-2}	0.9091	0.9091	0.9091
0.3981	0.7406×10^{-2}	0.8632	0.8632	0.8632
0.5012	0.1167×10^{-1}	0.7993	0.7993	0.7993
0.6310	0.1834×10^{-1}	0.7153	0.7153	0.7153
0.7943	0.2868×10^{-1}	0.6132	0.6132	0.6132
0.1000×10	0.4453×10^{-1}	0.5000	0.5001	0.5001
0.1259×10	0.6837×10^{-1}	0.3869	0.3870	0.3870
0.1585×10	0.1034	0.2848	0.2849	0.2850
0.1995×10	0.1529	0.2009	0.2010	0.2011
0.2512×10	0.2198	0.1369	0.1370	0.1371
0.3162×10	0.3054	0.9102×10^{-1}	0.9114×10^{-1}	0.9124×10^{-1}
0.3981×10	0.4082	0.5946×10^{-1}	0.5958×10^{-1}	0.5968×10^{-1}
0.5012×10	0.5239	0.3839×10^{-1}	0.3850×10^{-1}	0.3859×10^{-1}
0.6310×10	0.6465	0.2459×10^{-1}	0.2469×10^{-1}	0.2478×10^{-1}
0.7943×10	0.7695	0.1568×10^{-1}	0.1577×10^{-1}	0.1584×10^{-1}
0.1000×10^2	0.8871	0.9968×10^{-2}	0.1004×10^{-1}	0.1010×10^{-1}
0.1259×10^2	0.9954	0.6325×10^{-2}	0.6383×10^{-2}	0.6429×10^{-2}
0.1585×10^2	0.1092×10	0.4010×10^{-2}	0.4055×10^{-2}	0.4091×10^{-2}
0.1995×10^2	0.1175×10	0.2540×10^{-2}	0.2575×10^{-2}	0.2602×10^{-2}
0.2512×10^2	0.1246×10	0.1609×10^{-2}	0.1635×10^{-2}	0.1655×10^{-2}
0.3162×10^2	0.1305×10	0.1019×10^{-2}	0.1038×10^{-2}	0.1053×10^{-2}
		$C_1 = 0.9529$	$C_1 = 0.9268$	$C_1 = 0.9089$
		$C_2 = 1.733$	$C_2 = 2.403$	$C_2 = 3.591$
		$C_3 = -2.745$	$C_3 = -3.303$	$C_3 = -4.491$

TABLE III. Results of analysis in terms of simple scaling.

Run	Free parameters			Derived parameters		σ_I
1	$\eta = 0.028 \pm 0.002$	$\nu = 0.622 \pm 0.001$	$\xi_0 = (2.33 \pm 0.02)$ Å	$\gamma = 1.227$	$C_1 = 0.93$	0.25%
2	$\eta = 0.021 \pm 0.002$	$\nu = 0.630 \pm 0.001$	$\xi_0 = (2.20 \pm 0.02)$ Å	$\gamma = 1.246$	$C_1 = 0.95$	0.23%
3	$\eta = 0.018 \pm 0.002$	$\nu = 0.625 \pm 0.001$	$\xi_0 = (2.28 \pm 0.02)$ Å	$\gamma = 1.239$	$C_1 = 0.95$	0.22%
4	$\eta = 0.017 \pm 0.001$	$\nu = 0.622 \pm 0.001$	$\xi_0 = (2.33 \pm 0.01)$ Å	$\gamma = 1.234$	$C_1 = 0.96$	0.12%
5	$\eta = 0.006 \pm 0.002$	$\nu = 0.625 \pm 0.001$	$\xi_0 = (2.33 \pm 0.02)$ Å	$\gamma = 1.246$	$C_1 = 0.98$	0.20%
6	$\eta = 0.012 \pm 0.001$	$\nu = 0.629 \pm 0.001$	$\xi_0 = (2.27 \pm 0.01)$ Å	$\gamma = 1.250$	$C_1 = 0.97$	0.15%
Average	$\eta = 0.017 \pm 0.002$	$\nu = 0.625 \pm 0.001$	$\xi_0 = (2.29 \pm 0.02)$ Å	$\gamma = 1.240$	$C_1 = 0.96$	0.19%

$\gamma = (2 - \eta)\nu$ and $C_1 = 3^{-\eta}/[1 + \eta s(\infty)]$ for the six experimental runs are presented in Table III. It turns out that Eq. (4.4) fits the data of each experimental run with a standard deviation $\sigma_I = 0.2\%$. The fact that the average values $\eta = 0.017$ and $\nu = 0.625$ are close to the exponent values used in the evaluation of the spectral function confirms *a posteriori* the consistency of the analysis. Moreover, the values found for the extraneous scattering contribution ΔI were of the same order of magnitude as the theoretical estimates for the contributions from temperature and pressure fluctuations discussed in Sec. III A.

The standard deviations $\sigma_\eta = 0.002$, $\sigma_\nu = 0.001$, and $\sigma_{\xi_0} = 0.02$ Å obtained by fitting (4.4) to the individual experimental runs do not yield realistic error estimates, as can be seen from the variations in the parameter values obtained from different runs. In order to take into account effects of systematic errors between different experimental runs, we adopt in this paper the convention of quoting as error two standard devations when the parameter values are averaged over the six experimental runs. We thus obtain

$$\eta = 0.017 \pm 0.015, \quad \nu = 0.625 \pm 0.006,$$
$$\xi_0 = (2.29 \pm 0.10) \text{ Å}, \quad \gamma = 1.240 \pm 0.017,$$
$$C_1 = 0.96 \pm 0.04, \quad \sigma_{\text{tot}} = 0.4\%. \tag{4.5}$$

One possible source of error, causing differences between the results deduced from the various experimental runs, is the frequency f_c of the quartz thermometer attributed to the critical temperature T_c. The measurements were conducted by lowering the temperature of the thermostat, the step size being approximately $\frac{1}{10}$ decade on a logarithmic scale. When the temperature was close to T_c, the step size was typically about 0.3 mK. In our previous analysis,[30] T_c was identified with the step value at which the fluid separated. However, strictly speaking, this temperature must be below T_c, whereas the previous step value of the temperature must be above T_c. For our present analysis, T_c was defined as the midpoint between these two temperatures. This procedure determines T_c with an accuracy of about 0.15 mK. Local heating may cause an additional uncertainty of 0.1 mK in temperature. Repeating our analysis we concluded that a shift of 0.25 mK in T_c changes η by 0.006, ν by 0.0003, and ξ_0 by 0.02 Å. These errors are well within the error estimates quoted in (4.5).

The constants $\tilde{I}_0$ and ΔI depend to some extent on the detailed geometry of the optical arrangement. Since between each run the cell with the sample fluid had to be removed to mix the phases, we must allow for small differences in $\tilde{I}_0$ and ΔI for different experimental runs. However, the critical exponents and the correlation length amplitude are physical properties of the fluid and they must be the same in all runs. Therefore, as a second step we fixed these physical parameters at the average values quoted in (4.5) and fitted (4.4) to the data points of all six runs simultaneously, leaving I_0 and ΔI of each run as adjustable parameters. We thus obtained a standard deviation $\sigma_{\text{tot}} = 0.4\%$; this standard deviation does include the effect of systematic differences between data points of different runs. A deviation plot of the experimental and calculated data points is presented in Fig. 6(a). The data points cover a range $1 \times 10^{-6} < t < 2.7 \times 10^{-3}$ in temperature which corresponds to a range $0.18 < k\xi < 25$ in the scaling variable $x = k\xi$.

The factor $1 + 6.4t$ in (4.4) represents a correction due to the temperature variation of the derivative of the dielectric constant with respect to the order parameter ϕ. We also repeated the analysis replacing this factor by unity, and obtained

$$\eta = 0.018 \pm 0.015, \quad \nu = 0.625 \pm 0.006,$$
$$\xi_0 = (2.30 \pm 0.10) \text{Å}, \quad \gamma = 1.239 \pm 0.018,$$
$$C_1 = 0.96 \pm 0.04, \quad \sigma_{\text{tot}} = 0.4\%. \tag{4.6}$$

On comparing (4.6) with (4.5), we conclude that the results are insensitive to small changes in the definition of the order parameter. The results also indicate that contributions from a confluent sin-

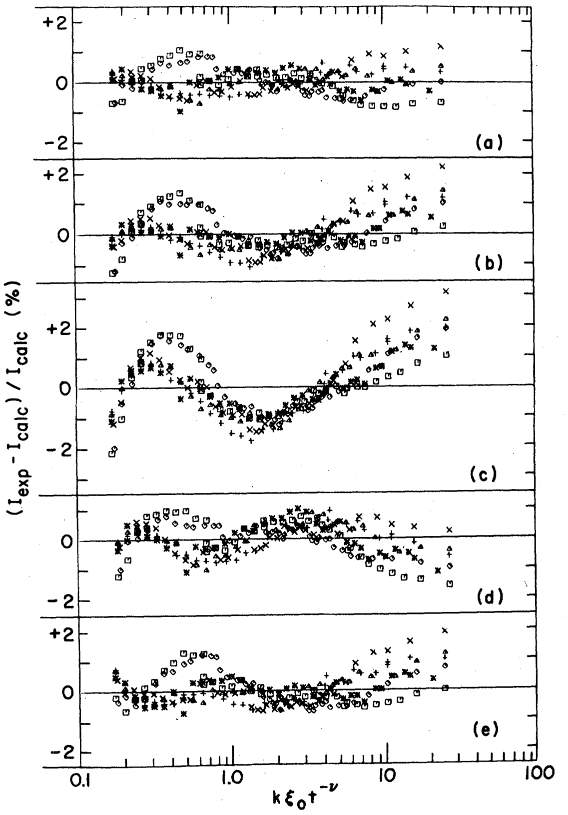

FIG. 6. Plot of the deviations $(I_{\rm exp}-I_{\rm calc})/I_{\rm calc}$ in percent as a function of the scaling variable $x=k\xi_0 t^{-\nu}$.
(a) $\eta=0.017$, $\nu=0.625$, $\xi_0=2.29$ Å simple scaling;
(b) $\eta=0.0315$, $\nu=0.630$, $\xi_0=2.16$ Å, simple scaling;
(c) $\eta=0.041$, $\nu=0.638$, $\xi_0=2.00$ Å, simple scaling;
(d) $\eta=0$, $\nu=0.633$, $\xi_0=2.22$ Å, simple scaling;
(e) $\eta=0.0315$, $\nu=0.630$, $\xi_0=2.13$ Å, $\Gamma_1=3.4$.

gularity proportional to $t^{-\gamma+1}$ are negligibly small within the temperature range of our experiment.

Near the critical point the earth's gravitational field will induce a concentration gradient in the fluid. For our mixture of 3-methylpentane-nitroethane the effect was studied experimentally by Greer *et al.*[74] They observed the formation of gravitationally induced concentration profiles for a period of 15 days, which is comparable to the time scale of our experimental runs. It was found that gradients are formed rapidly at the bottom and top of the cell, but the concentration remained constant near the center of the cell during the entire period. Since the six experimental runs discussed earlier were all obtained with the scattering volume located at the position where the meniscus would appear, we may thus assume that the data were indeed obtained at the critical concentration.

In order to investigate the validity of this assumption we studied the scattered light intensities with the scattering volume located at different heights. Defining the height $z=0$ at the position where the meniscus would appear, the height z was +2, −5, and −11 mm, respectively. These experimental data were subjected to the same analysis described earlier and the results are presented in Table IV. These results should be compared with the results presented in Table III for the data taken at $z=0$. The parameter values deduced from the runs at $z=+2$ mm and $z=-5$ mm are in good agreement with the values obtained earlier from the runs at $z=0$, and no systematic dependence on the height is found. The run at $z=-11$ mm yields slightly smaller values for η and ν, indicating the possible influence of a concentration gradient at 1 cm from the center. This is precisely what one would expect from the work of Greer *et al.*,[74] and we conclude that data taken within 5 mm from the level of meniscus appearance are unaffected by gravitationally induced concentration changes.

Tracy and McCoy have emphasized that a convincing determination of the exponent η requires the use of a correlation scaling function that does reproduce the exactly known correlation function of the two-dimensional Ising model.[20,69] Although the Fisher-Burford approximant (3.20) fails to satisfy this criterion, it does not necessarily follow that this approximant yields also an inadequate representation of the critical correlation function of three-dimensional systems. To investigate this question we substituted the Fisher-Burford correlation scaling function (3.20) into (4.2) and fitted the resulting equation to the six experimental runs taken at $z=0$. We used as adjustable parameters $\tilde{I}_0$, ΔI, η, ν, ξ_0, and ψ, but required that η, ν, ξ_0, and ψ be the same in all experimental runs. We thus obtained

TABLE IV. Results of analysis of runs at different heights.

Run	z	Free parameters			Derived parameters		σ_I
7	+2 mm	$\eta=0.009$	$\nu=0.625$	$\xi_0=2.32$ Å	$\gamma=1.245$	$C_1=0.98$	0.17%
8	−5 mm	$\eta=0.016$	$\nu=0.625$	$\xi_0=2.30$ Å	$\gamma=1.240$	$C_1=0.96$	0.19%
9	−11 mm	$\eta=0.002$	$\nu=0.621$	$\xi_0=2.45$ Å	$\gamma=1.241$	$C_1=1.00$	0.16%

$$\eta = 0.024 \pm 0.022, \quad \nu = 0.625 \pm 0.006,$$
$$\xi_0 = (2.28 \pm 0.12)\ \text{Å}, \quad \gamma = 1.235 \pm 0.016, \tag{4.7}$$
$$C_1 = 0.95 \pm 0.04, \quad \psi = 0.14 \pm 0.11, \quad \sigma_{\text{tot}} = 0.4\%.$$

As a third alternative we considered the correlation scaling function proposed by Ferrell and Scalapino. For this purpose we adopted the spectral function (3.30) for $\omega = 1$, evaluated the function $s(x)$ defined in (3.29), and then fitted the experimental data to (4.4). Using as adjustable parameters $\tilde{I}_0$, ΔI, η, ν, and ξ_0 and again requiring η, ν, and ξ_0 to be the same in all six experimental runs, we find

$$\eta = 0.020 \pm 0.017, \quad \nu = 0.625 \pm 0.006,$$
$$\xi_0 = (2.28 \pm 0.10)\text{Å}, \quad \gamma = 1.238 \pm 0.018, \tag{4.8}$$
$$C_1 = 0.95 \pm 0.04, \quad \sigma_{\text{tot}} = 0.4\%.$$

Repeating the analysis using $\omega = 0$ in the correlation scaling function of Ferrell and Scalapino, we obtain

$$\eta = 0.030 \pm 0.025, \quad \nu = 0.626 \pm 0.006,$$
$$\xi_0 = (2.26 \pm 0.10)\text{Å}, \quad \gamma = 1.232 \pm 0.020, \tag{4.9}$$
$$C_1 = 0.95 \pm 0.04, \quad \sigma_{\text{tot}} = 0.4\%.$$

On comparing (4.7), (4.8), and (4.9) with (4.5), we conclude that the correlation scaling functions, proposed by Bray, Fisher and Burford, and Ferrell and Scalapino, give equally satisfactory representations of the experimental scattering data; they all lead to values for the critical exponents and the correlation-length amplitude that are the same within experimental error.

C. Comparison with theoretical predictions

The critical exponents for the universality class of Ising-like systems have been calculated quite accurately by Le Guillou and Zinn-Justin[6] and by Baker, Nickel, and Meiron[7] from an asymptotic analysis of the Callan-Symanzik equation for the Landau-Ginzburg-Wilson model. They found

$$\eta = 0.0315 \pm 0.0025, \quad \nu = 0.630 \pm 0.001,$$
$$\gamma = 1.240 \pm 0.001\ . \tag{4.10}$$

On comparing with (4.5) we conclude that the critical exponent values found experimentally for our binary liquid mixture agree within combined error with the exponent values predicted theoretically for the universality class of Ising-like systems. In fact, agreement is found using any proposed correlation scaling function approximant that accommodates the Ornstein-Zernike behavior for small $k\xi$ and the leading term in the Fisher-Langer expansion for large $k\xi$. The value 0.96 ± 0.04 found experimentally for the coefficient C_1 may be compared with the values $C_1 = 0.962$ and $C_1 = 0.922$ calculated theoretically[62] in second and third order, respectively, from an expansion in terms of $\epsilon = 4 - d$.

To investigate further the comparison with the theoretical predictions we also fitted the experimental data to (4.2) fixing the critical exponents at the theoretical values quoted in (4.10) and using again Bray's procedure for calculating the correlation function. For these exponent values the sum rule (4.3) and the condition $F_B(1) = 0$ implies $C_1 = 0.9268$, $C_2 = 2.403$, and $C_3 = -3.303$. Numerical values for the resulting correlation scaling functions are included in Table II. Using $\tilde{I}_0$, ΔI, and ξ_0 as adjustable parameters, but requiring ξ_0 to be the same for all six experimental runs, we obtained $\xi_0 = (2.16 \pm 0.03)$ Å, and $\sigma_{\text{tot}} = 0.6\%$. A plot of the deviations of the experimental data from the calculated values is presented in Fig. 6(b).

The critical exponents for the three-dimensional Ising model have been estimated theoretically from numerical analyses of high-temperature series expansions[3,75]

$$\eta = 0.041 \pm^{0.006}_{0.003}, \quad \nu = 0.638 \pm^{0.002}_{0.008},$$
$$\gamma = 1.250 \pm^{0.003}_{0.007}\ . \tag{4.11}$$

We have also fitted the data to (4.2) with the critical exponents fixed at the series expansion values quoted in (4.11). The corresponding correlation scaling function $g(x)$ was earlier evaluated by Bray,[71] and it is reproduced in the last column of Table II in terms of the second-moment correlation scaling variable. Using as adjustable parameters $\tilde{I}_0$, ΔI, and ξ_0 and again requiring ξ_0 to be the same for different experimental runs, we find $\xi_0 = (2.00 \pm 0.03)$ Å, and $\sigma_{\text{tot}} = 1.0\%$. A deviation plot is shown in Fig. 6(c). The deviations are quite systematic and the standard deviation of $\sigma_{\text{tot}} = 1.0\%$ seems well beyond the error of the experimental data. We conclude that the critical exponent values (4.11) are not in good agreement with the experimental data.

While our data are consistent with the predictions from the renormalization-group theory which imply a finite value of the exponent η, one could also ask the question whether the experimental data exclude the possibility $\eta = 0$. To investigate this question we also fitted the experimental data to (4.2) using the Ornstein-Zernike form $g^{-1}(x) = 1 + x^2$ for the corrections scaling function, and obtained $\nu = 0.633 \pm 0.008$, $\gamma = 2\nu = 1.266 \pm 0.017$, and $\xi_0 = (2.22 \pm 0.13)$ Å. The total standard deviation σ_{tot} is still only 0.5% and the deviation plot is shown in Fig. 6(d). Without theoretical guidance, we cannot prove on the basis of the experimental data alone that η must be finite.

D. Corrections to scaling

So far we have represented the experimental scattering data in terms of the asymptotic behavior predicted by the theory. The question arises whether correction-to-scaling terms can be neglected in the range covered by our experimental data. Including the first correction term the function $g(x)$ in (4.2) is predicted to become[76]

$$g(x)=g_0(x)+\Gamma_1 t^{\Delta_1} g_1(x)\,, \tag{4.12}$$

where the scaling variable x is now defined as

$$x=k\xi_0 t^{-\nu}. \tag{4.13}$$

The function $g_0(x)$ is the correlation scaling function discussed earlier, Γ_1 is a system-dependent correction-to-scaling amplitude, Δ_1 is a universal correction-to-scaling exponent, and $g_1(x)$ is a new universal function subject to the boundary conditions

$$g_1(x)=1/[1+D_0x^2],\quad (x\ll 1) \tag{4.14}$$

$$g_1(x)=\frac{D_1}{x^{2-\eta-\Delta_1/\nu}}\left[1+\frac{D_2}{x^{(1-\alpha)/\nu}}+\frac{D_3}{x^{1/\nu}}\right],\quad (x\gg 1). \tag{4.15}$$

In the absence of theoretical information concerning the values of the universal coefficients D_i, we approximate $g_1(x)$ by an approximant analogous to (3.19),

$$g_1(x)\simeq 1/(1+x^2)^{(2-\eta-\Delta_1/\nu)/2}\quad . \tag{4.16}$$

This choice is motivated by the following considerations. First, the effect of the correction term turns out to be very small and therefore will not be sensitive to the choice of approximant. Second, the Fisher-like approximant (4.16) is the simplest function that reproduces qualitatively the correct analytic behavior in the limit of small and large x without introducing new unknown constants.

In order to investigate the effect of the correction-to-scaling term on the determination of the critical exponents, we take $\Delta_1=0.5$ as predicted theoretically,[6,7] substitute (4.12) into (4.2), and approximate $g_0(x)$ by the linearized expression (3.28), using again the function $s(x)$ with $\eta=\frac{1}{54}$ and and $\nu=\frac{5}{8}$. When the data are then fitted to (4.2), using $\bar{I}_0$, ΔI, η, ν, ξ_0, and Γ_1 as adjustable parameters, one obtains

$$\begin{gathered}\eta=0.016\pm0.016,\quad \nu=0.628\pm0.013,\\ \xi_0=(2.23\pm0.25)\ \text{Å},\quad \Gamma_1=1.1\pm3.5,\\ \gamma=1.246\pm0.033,\quad C_1=0.96\pm0.04,\quad \sigma_{\text{tot}}=0.4\%,\end{gathered} \tag{4.17}$$

to be compared with the values obtained earlier in (4.5). We conclude that inclusion of a correction-to-scaling term does not change the critical exponent values deduced experimentally, while the correction-to-scaling term is clearly not significant. Thus we do not find any evidence for correction-to-scaling contributions in the temperature range of our experimental data.

The analysis was repeated, but now with the critical exponents fixed at the values (4.10) calculated theoretically for the Landau-Ginzburg-Wilson model, and again with the appropriate spectral function to evaluate $g_0(x)$. Using, in addition to $\bar{I}_0$ and ΔI, ξ_0 and Γ_1 as free parameters, we obtained

$$\begin{gathered}\eta=0.0315\ \text{(fixed)},\quad \nu=0.630\ \text{(fixed)},\\ \xi_0=(2.13\pm0.05)\ \text{Å},\quad \gamma=1.240\ \text{(fixed)},\\ \Gamma_1=3.4\pm3.0,\quad \sigma_{\text{tot}}=0.5\%\ .\end{gathered} \tag{4.18}$$

The corresponding deviation plot is shown in Fig. 6(e). This equation represents the experimental data almost equally well as when the critical exponents are treated as unknown parameters. We conclude that the experimental data are consistent with the predictions from the renormalization-group theory for Ising-like systems and thus consistent with the hypothesis of critical-point universality.

Finally, we repeated the analysis fixing the critical exponents at the values (4.11) calculated from series expansions for the three-dimensional Ising model. In all our previous fits we obtained values for the extraneous scattering contribution ΔI of an acceptable order of magnitude; that is, compatible with the limited accuracy we were able to estimate the contributions from temperature and pressure fluctuations. However, when we fit the data using the critical exponent values (4.11) and including the correction-to-scaling term, we obtain a negative value for ΔI which is physically unacceptable. Thus we are not able to reduce the systematic deviations shown in Fig. 6(c) using series expansions results by introducing a correction-to-scaling term of a form consistent with theory. We conclude that our experimental data are consistent with the critical exponent values predicted from the renormalization-group theory, but not with the values predicted from series expansions for the three-dimensional Ising model.

ACKNOWLEDGMENTS

We thank C. O. Alley for enabling us to use some of his laboratory facilities and for his encouraging support. A. J. Bray gave us advice concerning the interpretation of the data, H. J. M. Boots assisted us in estimating the effects of pressure and temperature fluctuations, and R. W. Gammon helped with collecting physical property data for our mixture. We acknowledge technical assistance received from E. Barrett, L. A. Buennagel, F. Meraldi, J. D. Rayner, and C. A. Steggerda. We have also appreciated valuable discussions with W. J. Camp, R. A. Ferrell, S. C. Greer, and P. C. Hohenberg. This research was supported by NSF Grant No. DMR 76-82345. Computer time was provided by the Computer Science Center at the University of Maryland. The collaboration with H. J. M. Boots of the University of Leiden was supported by NATO Research Grant 1065. The work will be included in a dissertation to be submitted by H. Burstyn in partial fulfillment of the requirements for the Ph.D. degree in Physics at the University of Maryland.

---

[1] L. P. Kadanoff, in "Critical Phenomena," Proceedings of the International School of Physics, "Enrico Fermi," Course LI, edited by M. S. Green (Academic, New York, 1971) p. 100; in *Phase Transitions and Critical Phenomena*, Vol. 5A, edited by C. Domb and M. S. Green (Academic, New York, 1976), Chap. 1.

[2] C. Domb, in *Phase Transitions and Critical Phenomena*, Vol. 3, edited by C. Domb and M. S. Green (Academic, New York, 1974), Chap. 6.

[3] W. J. Camp, D. M. Saul, J. P. VanDyke, and M. Wortis, Phys. Rev. B 14, 3990 (1976).

[4] G. R. Golner and E. K. Riedel, Phys. Lett. A 58, 11 (1976).

[5] G. A. Baker, B. G. Nickel, M. S. Green, and D. I. Meiron, Phys. Rev. Lett. 36, 1351 (1976).

[6] J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. Lett. 39, 95 (1977).

[7] G. A. Baker, B. G. Nickel, and D. I. Meiron, Phys. Rev. B 17, 1365 (1978).

[8] G. A. Baker, Phys. Rev. B 15, 1552 (1977).

[9] D. A. Balzarini and K. Ohrn, Phys. Rev. Lett. 29, 840 (1972).

[10] R. J. Hocken and M. R. Moldover, Phys. Rev. Lett. 37, 29 (1976).

[11] C. E. Hayes and H. Y. Carr, Phys. Rev. Lett. 39, 1558 (1977).

[12] D. A. Balzarini, Can. J. Phys. 52, 499 (1974).

[13] S. C. Greer, Phys. Rev. A 14, 1770 (1976).

[14] D. T. Jacobs, D. L. Anthony, R. C. Mockler, and W. J. O'Sullivan, Chem. Phys. 20, 219 (1977).

[15] M. Ley-Koo and M. S. Green, Phys. Rev. A 16, 2483 (1977).

[16] F. W. Balfour, J. V. Sengers, M. R. Moldover, and J. M. H. Levelt Sengers, Phys. Lett. A 65, 223 (1978); in *Proceedings of the Seventh Symposium on Thermophysical Properties*, edited by A. Cezairliyan (ASME, New York, 1977), p. 786.

[17] M. E. Fisher, J. Math. Phys. 5, 944 (1964).

[18] D. S. Cannell, Phys. Rev. A 12, 225 (1975).

[19] B. Chu, Ber. Bunsenges. Phys. Chem. 76, 202 (1972).

[20] C. A. Tracy and B. M. McCoy, Phys. Rev. B 12, 368 (1975).

[21] V. P. Warkulwiz, B. Mozer, and M. S. Green, Phys. Rev. Lett. 32, 1410 (1974).

[22] J. S. Lin and P. W. Schmidt, Phys. Lett. A 48, 75 (1974).

[23] J. M. H. Levelt Sengers and J. V. Sengers, Phys. Rev. A 12, 2622 (1975).

[24] H. D. Dale, J. S. Lin, D. A. Dolejsi, J. L. Casteel, O. A. Pringle, and P. W. Schmidt, Phys. Rev. A 15, 2513 (1977).

[25] D. McIntyre and J. V. Sengers, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (North-Holland, Amsterdam, 1968), Chap. 11.

[26] *International Critical Tables of Numerical Data, Physics, Chemistry, and Technology*, edited by E. W. Washburn, Vol. VII (McGraw-Hill, New York, 1930).

[27] J. P. Wibaut, H. Hoog, S. L. Langedijk, J. Overhoff, and J. Smittenberg, Recueil Travaux Chim. Pays-Bas 58, 329 (1939).

[28] A. L. Vogel, J. Chem. Soc. Lond. 1833 (1948).

[29] R. F. Chang, P. H. Keyes, J. V. Sengers, and C. O. Alley, Phys. Rev. Lett. 27, 1706 (1971); Ber. Bunsenges. Phys. Chem. 76, 260 (1972).

[30] R. F. Chang, H. Burstyn, J. V. Sengers, and A. J. Bray, Phys. Rev. Lett. 37, 1481 (1976).

[31] A. M. Wims, D. McIntyre, and F. Hynne, J. Chem. Phys. 50, 616 (1969).

[32] The authors are indebted to P. H. Keyes and J. Maurey for preparing the sample.

[33] P. H. Keyes, R. F. Chang, J. V. Sengers, and C. O. Alley, *Concentration Fluctuations in the Critical Region of the Binary Liquid 3-Methylpentane-Nitroethane*, Technical Report No. 73-018, (Dept. of Physics and Astronomy, Univ. of Maryland, College Park, Maryland, 1972).

[34] The authors are indebted to S. C. Greer of the Natl. Bur. Stand. for determining the value of the critical temperature of our sample on the international practical temperature scale.

[35] A. J. Bray and R. F. Chang, Phys. Rev. A 12, 2594 (1975).

[36] C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 40, 777 (1978).

[37] R. D. Mountain and J. M. Deutch, J. Chem. Phys. 50, 1103 (1969).

[38] C. Cohen, J. W. H. Sutherland, and J. M. Deutch, Phys. Chem. Liq. 2, 213 (1971).

[39] S. C. Greer and R. Hocken, J. Chem. Phys. 63, 5067 (1975).

[40] J. Reeder, T. E. Block, and C. M. Knobler, J. Chem. Thermody. 8, 133 (1976).

[41] M. R. Kruer, Ph.D. thesis (Catholic University of America, Washington, D. C., 1971) (unpublished).

[42] D. R. Stull, J. Am. Chem. Soc. 59, 2726 (1937).

[43] D. R. Douslin and H. M. Huffman, J. Am. Chem. Soc. 68, 1704 (1946).

[44] N. S. Osborne and D. C. Ginnings, J. Res. Natl. Bur. Stand. 39, 453 (1947).

[45] D. Stauffer, M. Ferer, and M. Wortis, Phys. Rev. Lett. 29, 345 (1972).

[46] C. L. Hartley, D. T. Jacobs, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 33, 1129 (1974).

[47] "*Selected Values of Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44*" (Thermodynamics Research Center, Texas A & M University, College Station, Texas, 1976).

[48] R. L. Scott, in *Specialists Periodical Report, Chemical Thermodynamics*, edited by M. L. McGlashan (The Chemical Society, London, 1977), Vol. 2, Chap. 8.

[49] A. Stein and G. F. Allen, J. Phys. Chem. Ref. Data 2, 443 (1974).

[50] A. V. Chalyi, Ukr. Phys. J. 13, 828 (1969).

[51] D. W. Oxtoby and W. M. Gelbart, Phys. Rev. A 10, 738 (1974).

[52] L. A. Reith and H. L. Swinney, Phys. Rev. A 12, 1094 (1975).

[53] H. M. J. Boots, D. Bedeaux, and P. Mazur, Physica 84A, 217 (1976).

[54] H. M. J. Boots, Physica 87A, 185 (1977).

[55] C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. A 16, 365 (1977).

[56] V. G. Puglielli and N. C. Ford, Phys. Rev. Lett. 25, 143 (1970).

[57] M. E. Fisher and R. J. Burford, Phys. Rev. B 10, 2818 (1974).

[58] M. E. Fisher and J. S. Langer, Phys. Rev. Lett. 20, 665 (1968).

[59] G. Stell, Phys. Lett. A 27, 550 (1968).

[60] E. Brézin, D. J. Amit, and J. Zinn-Justin, Phys. Rev. Lett. 32, 151 (1974).

[61] M. E. Fisher and A. Aharony, Phys. Rev. B 10, 2818 (1974).

[62] A. J. Bray, Phys. Lett. A 55, 453 (1976).

[63] P. Calmettes, I. Lagües, and C. Laj, Phys. Rev. Lett. 28, 478 (1972).

[64] C. C. Lai and S. H. Chen, Phys. Lett. A 41, 259 (1972).

[65] B. Volochine, Ber. Bunsenges. Phys. Chem. 76, 217 (1972).

[66] R. A. Ferrell and D. J. Scalapino, Phys. Rev. Lett. 34, 200 (1975).

[67] R. A. Ferrell, in *Theory of Light Scattering in Condensed Matter*, edited by B. Bendow, J. L. Birman, and V. M. Agranovich (Plenum, New York, 1976), p. 509.

[68] A. J. Bray (private communication).

[69] C. A. Tracy, in *AIP Conference Proceedings No. 29*, edited by J. J. Becker, G. H. Lander, and J. J. Rhyne (American Institute of Physics, New York, 1975), p. 483.

[70] A. J. Bray, Phys. Rev. Lett. 36, 285 (1976).

[71] A. J. Bray, Phys. Rev. B 14, 1248 (1976).

[72] T. T. Wu, B. M. McCoy, C. A. Tracy, and E. Barouch, Phys. Rev. B 13, 316 (1976).

[73] The difference between second-moment correlation length and exact correlation length has a negligible effect on the values of C_2 and C_3.

[74] S. C. Greer, T. E. Block, and C. M. Knobler, Phys. Rev. Lett. 34, 250 (1975).

[75] M. A. Moore, D. Jasnow, and M. Wortis, Phys. Rev. Lett. 22, 940 (1969).

[76] F. J. Wegner, J. Phys. A 8, 710 (1975).