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Refractive index near the critical point and pressure dependence of the critical temperature of a water–sodium di-2-ethylhexylsulfosuccinate–decane microemulsion

C. Pépin and T. K. Bose
Groupe de Recherche sur les Diélectriques, Département de Physique, Université du Québec à Trois-Rivières,
Case Postale 500, Trois-Rivières, Québec, Canada G9A 5H7

J. Thoen
Laboratorium voor Akoestiek en Warmtegeleiding, Departement Natuurkunde, Katholieke Universiteit Leuven,
Celestijnenlaan 200D, 3030 Leuven, Belgium

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Experimental data are presented for the refractive-index behavior in the homogeneous phase below the cloud-point temperature of a critical microemulsion composed of sodium di-2-ethylhexylsulfosuccinate (AOT), water, and decane. The pressure dependence of the critical temperature (dT_c/dP) is also reported. Fitting the refractive-index data as a function of temperature, we find a $(1-\alpha)$ power-law singularity with an α value consistent with the Ising value $\alpha_I=0.11$. It is shown that the refractive-index anomaly observed in this microemulsion is an intrinsic effect, most likely related to the electric field dependence of the critical temperature (dT_c/dE^2). Further, using two-scale-factor universality and experimental values for dT_c/dP and the correlation-length critical amplitude ξ_0, we also found that the density contribution to the refractive-index anomaly is negligibly small.

I. INTRODUCTION

Considerable experimental and theoretical effort has recently been devoted to the study of phase transitions and critical phenomena in liquid mixtures involving surfactants. Apart from their importance in many chemical applications, they offer challenging complex cases to test recent concepts of universality of critical phenomena. Two-, three- , four- , and even five-component systems have been investigated.[1,2] In these types of multicomponent systems, micellar, microemulsion, and liquid-crystalline phases can be observed. In particular, binary micellar[3-6] and multicomponent microemulsion systems[1,2,7-13] have attracted much attention because they exhibit critical phase-separation behavior quite similar to that at consolute points in mixtures of ordinary liquids.

The critical behavior of binary fluids near liquid-liquid consolute points has been rather well characterized in recent years and found to be in accordance with the general concepts of scaling and universality, and the critical exponents obtained experimentally are in generally good agreement with the renormalization-group values for the Ising model.[14,15]

For some of the micellar and microemulsion systems, the analogy with the ordinary binary liquid mixtures seems to hold and Ising values[4,8-12,16] for critical exponents are obtained. For other systems, however, light scattering experiments yield what appear to be nonuniversal values[1-6,13,17] for the order-parameter susceptibility exponent γ (Ising value 1.24) and the correlation-length exponent ν (Ising value 0.63). The critical points of aqueous solutions of the nonionic amphiphilic molecules *n*-alkyl-polyoxyethylene glycol monoethers (labelled C_iE_j), seem to belong to the Ising universality class for $i \le 6$ and $j \le 3$, while for larger i and j, nonuniversal γ and ν values are obtained.[3-6] In some cases, values even lower than the mean-field values $\gamma_0=1$ and $\nu_0=0.5$ are obtained. A theoretical explanation has been given by Fisher[18] in terms of a model of stable micelles of radius R undergoing ordinary criticality with (nonmonotonic) crossover to Ising behavior delayed by an increasing range of interaction (measured by observed correlation-length amplitudes ξ_0). Microemulsion systems composed of dodecane, water, pentanol, and the surfactant sodium dodecyl sulfate (SDS) exhibit a line of critical points as the composition is varied. Along this line, the effective exponents γ and ν vary continuously from the Ising values ($\gamma_I=1.24$ and $\nu_I=0.63$) to values as low as 0.40 for γ and 0.21 for ν as the composition is varied.[2] Although these microemulsions have very large correlation-length amplitudes,[2] it is unclear whether the large deviations from Ising can also be explained here in terms of the crossover description of Fisher.[18]

The very recent light scattering measurements of Dietler and Cannell[19] seem to indicate that the non-Ising behavior of certain microemulsions (C_iE_j with H_2O and D_2O) could well be due to impure samples. They have concluded from the measurements of osmotic susceptibility χ and long-range correlation length ξ of binary mixtures of nonionic surfactant $C_{12}E_8$ with H_2O and D_2O that regardless of which solvent is used, three-dimensional (3D) Ising exponent values are obtained for both γ and ν. This strongly suggests Ising-like exponents for the binary microemulsions with the C_iE_j surfactants, probably reducing the non-Ising cases to the multicomponent systems.[1-6,13]

The vast majority of experimental results on the critical behavior of micellar and microemulsion systems have been obtained from light scattering experiments and have thus concentrated on the critical exponents γ and ν. In view of testing scaling relations, results for other critical exponents are highly desirable. In particular, values for the order-parameter exponent β and for the heat-capacity singularity exponent α are very much needed.

Recently, Hamano *et al.*[17] used a differential refractometer to determine the temperature dependence of the concentration of the two coexisting phases for the system $C_{12}E_5$ and H_2O. For the critical exponent β they obtained a value of 0.249 ± 0.007, which is substantially different from the Ising value $\beta_I = 0.325$. They also carried out light scattering measurements and found $\gamma = 1.035 \pm 0.028$ and $\nu = 0.514 \pm 0.012$ for the low-temperature homogeneous phase. These γ, ν, and β values are consistent with the tricritical ones and would require a rather large α of 0.5 if the scaling relations $\alpha + 2\beta + \nu = 2$ were to be satisfied. No heat-capacity data are available for this system. If the analogy with ordinary binary critical mixtures holds, α can also be obtained from density, dielectric constant, or refractive index measurements. For the critical concentration as a function of temperature one expects an anomaly with a critical exponent $\Theta = 1 - \alpha$ for the above quantities.[20]

If two-scale-factor universality[21,22] holds, one can also relate, as in the case of ordinary binary mixtures, the critical heat-capacity amplitude A_v (per unit volume) to the correlation-length amplitude ξ_0 via the universal constant

$$X \equiv \frac{A_v \xi_0^3}{\alpha k_B} , \tag{1.1}$$

with k_B the Boltzmann constant. If in addition, one also has information on dT_c/dP, the change of the critical temperature with pressure, A_v values can be derived from density measurements. These results for A_v can also be obtained from measurements of the refractive index n and the dielectric constant ϵ, provided the density anomaly is the only relevant contribution to the observed anomaly in n or ϵ [see Eqs. (2.4) and (2.8) below]. For binary mixtures this seems generally[23] to be the case for the refractive index, although an intrinsic[20] contribution to n has recently been demonstrated for the critical mixture of triethylamine-water.[24] However, for binary liquid mixtures involving polar molecules, the intrinsic contribution to the dielectric constant is usually larger than the density effect.[25]

For microemulsion systems, most of the amplitude relationships cannot be verified because values for one or more of the relevant physical parameters are lacking. Hamano *et al.*[17] carried out density measurements in the reduced temperature range of $2.44 \times 10^{-5} < t < 9.62 \times 10^{-3}$ for their $C_{12}E_5$ microemulsion system by using an Anton Paar densimeter [$t = (T_c - T)/T_c$ and T_c is the critical temperature]. They report a small critical anomaly in the density close to T_c (e.g., $1.8 \times 10^{-3}\%$ at $t = 8.11 \times 10^{-4}$ and $2.5 \times 10^{-3}\%$ at $t = 2.44 \times 10^{-5}$) for which no critical exponent value was given. Because of the large $\epsilon_0 = 32.7$ Å, it is to some extent surprising that a density anomaly is observed at all. If Eq. (1.1) holds this would require a very large dT_c/dP, for which, however, there is no value available. For some other microemulsion systems with large ξ_0 values the absence of a heat capacity and density anomaly has been verified experimentally.[26] Rather unexpectedly, however, such a microemulsion system, recently investigated by Rebbouh *et al.*,[27] showed a substantial critical anomaly in the refractive index. This anomaly could not be characterized in a satisfactory way in terms of power-law expressions and is not understood at the present time.

In this paper we report on high-resolution refractive-index measurements for a critical three-component microemulsion of sodium di-2-ethylhexylsulfosuccinate, a surfactant commercially known as AOT, and water and n-decane. We also report on measurements for dT_c/dP, the pressure coefficient for the critical temperature. The γ and ν values for this system obtained from light scattering by Huang and Kim[8] indicate that it belongs to the Ising universality class. It was our purpose to test whether an Ising value for the critical exponent α would be consistent with the data, or whether on the contrary here also an unexpected exponent (as seen by Rebbouh *et al.*[27]) would be observed. The results for dT_c/dP could possibly allow a link, via two-scale-factor universality, with the amplitude of the heat-capacity anomaly.

II. THEORETICAL BACKGROUND

Modern theory of critical phenomena predicts that the mass density ρ and the refractive index n in the one-phase region near a critical demixing point can be represented by the following expressions:[14,20]

$$\rho = R_1 + R_2 t + R_3 t^{1-\alpha} + R_4 t^{1-\alpha+\Delta} + R_5 t^{1-\alpha+2\Delta} + \cdots , \tag{2.1}$$

$$n = N_1 + N_2 t + N_3 t^{1-\alpha} + N_4 t^{1-\alpha+\Delta} + N_5 t^{1-\alpha+2\Delta} + \cdots , \tag{2.2}$$

where for a lower critical point (as in our case here), t is the reduced temperature difference $(T_c - T)/T_c$ with the critical temperature T_c. The critical exponent α characterizes also the divergence of the heat capacity at constant pressure and concentration $C_{p,x}$ and Δ is the first correction-to-scaling exponent. The most recent renormalization-group calculations[28] find $\alpha = 0.11$ and $\Delta = 0.50$ for systems belonging to the Ising universality class. in Eqs. (2.1) and (2.2), one has $R_1 = \rho_c$ and $N_1 = n_c$, where ρ_c and n_c are, respectively, the density and refractive index at the critical point. For the heat capacity $C_{p,x}$ one can write the following expression:[14,29]

$$C_{p,x} = C_1 + C_2 t + C_3 t^{-\alpha} + C_4 t^{-\alpha+\Delta} + C_5 t^{-\alpha+2\Delta} + \cdots . \tag{2.3}$$

Asymptotically, close to the critical point, the singular parts of $C_{p,x}$ and of the thermal expansion at constant pressure and composition $\alpha_{p,x} = -\rho^{-1}(\partial\rho/\partial T)p,x$ are related to the slope dT_c/dP of the critical line.[30] For the mass density ρ and the heat capacity per unit of mass in Eq. (2.3), one arrives then for a lower critical point at the following relationship between R_3 and C_3 in Eqs. (2.1) and (2.3):

$$R_3=\frac{\rho_c^2 C_3}{1-\alpha}\frac{dT_c}{dP}\ . \tag{2.4}$$

Using Eq. (1.1) and taking into account that $A_v=\rho_c C_3$, one can write this expression as

$$R_3=\frac{\rho_c k_B X}{\alpha(1-\alpha)\xi_0^3}\frac{dT_c}{dP}\ . \tag{2.5}$$

According to the theory,[20] the leading critical contributions to the refractive index, arising from the density anomaly and from dT_c/dE^2, have both a $t^{1-\alpha}$ temperature dependence, and an amplitude N_3 in Eq. (2.2). If one assumes, as is quite often done,[23] that only the density contribution is important, then one can obtain a simple relationship between N_3 and R_3. From

$$\begin{aligned}(\partial n/\partial T)_{p,x}&=(\partial n/\partial \rho)_{p,x}(\partial \rho/\partial T)_{p,x}\\ &=-\rho(\partial n/\partial \rho)_{p,x}\alpha_{p,x}\end{aligned} \tag{2.6}$$

it follows that

$$\begin{aligned}\rho(T)-\rho(T_c)&=\int_{T_c}^{T}(\partial\rho/\partial n)_{p,x}(\partial n/\partial T)_{p,x}dT\\ &\approx\left[\frac{\partial\rho}{\partial n}\right]_{p,x}^{\mathrm{reg}}[n(T)-n(T_c)]\ .\end{aligned} \tag{2.7}$$

In the last part of Eq. (2.7), the additional assumption[23] of a regular temperature-independent $(\partial\rho/\partial n)_{p,x}$ value is made. This then results immediately in

$$R_3'=\left[\frac{\partial\rho}{\partial n}\right]_{p,x}^{\mathrm{reg}}N_3\ . \tag{2.8}$$

A value for $\partial\rho/\partial n$ is usually estimated via the Lorentz-Lorenz formula analysis away from T_c. From an analysis of the refractive index in several liquids, Beysens and Calmettes[31] arrived at the following expression:

$$\frac{1}{\rho}\left[\frac{\partial\rho}{\partial n}\right]_{p,x}=\frac{6n}{(n^2-1)(n^2+2)}(1+f_p)^{-1}\ . \tag{2.9}$$

For $f_p=0$ the result is a straightforward derivation of the Lorentz-Lorenz formula. f_p is an empirical correction term typically of the order of 0.05 and given by

$$f_p\approx-\frac{7}{8}\left[\frac{n^2-1}{n^2+2}\right]^2\ . \tag{2.10}$$

If there is, however, an additional intrinsic contribution to the critical anomaly of the refractive index, the above procedure will result in a violation of Eq. (2.7) and the R_3' derived from Eq. (2.8) will not correspond with R_3 values obtained from experimental density data via Eq. (2.1) or calculated with Eqs. (2.4) or (2.5). Conversely, different values for R_3 and R_3' will indicate intrinsic critical contributions to the refractive index.

III. EXPERIMENTAL TECHNIQUES

The experimental study of the critical behavior of the refractive index along the critical isochore is quite difficult because of the weak $1-\alpha$ expected singularity. Such a study therefore requires stringent temperature control and very precise measurement of the refractive index.

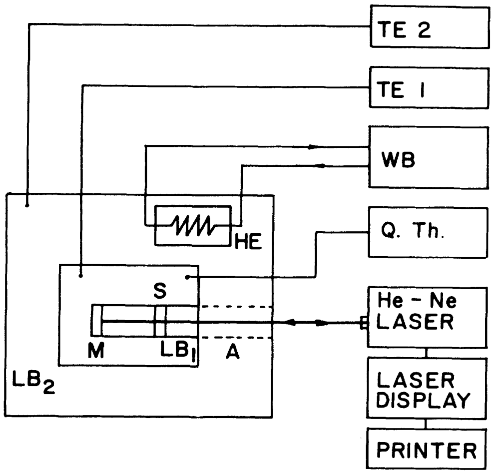

FIG. 1. Experimental setup for studying the refractive index variation. A, aluminum cylinder; S, sample cell; M, reflector; LB_1,LB_2 are, respectively, the inside and the outside liquid baths; HE, heat exchanger; Q.Th, quartz thermometer; WB, temperature regulated water; TE1 and TE2 are temperature controllers for the inside and the outside baths.

The present work consists in measuring the refractive index of a microemulsion composed of AOT, water, and decane in the vicinity of the critical temperature. Details of the experimental system are shown schematically in Fig. 1. As can be seen, the experimental system consists of two essential parts: the laser interferometer and the optical cell with the temperature control and the temperature-measuring systems.

A. Refractive-index measurement

The refractive-index measurements were made with a Hewlett-Packard (HP) laser interferometer (model 5525 A). The laser interferometer, which is of the Michelson type, has three components: a laser head, a reflector, and a display unit that computes and displays the readings. A digital recorder was attached to the output of the display for permanent recording. The light from the He-Ne laser head enters the optical cell through a small window in the center and, after traversing the cell, is reflected from a plane minor and retraces the same path back to the laser interferometer. The interferometer is based on the heterodyne principle and has the advantage of counting fringes in both directions. This is particularly important as fluctuations in temperature do not give rise to false count.

The measuring cell consists of a brass cylinder with the inside coated in gold. Two glass windows, each 5.8 mm wide, are glued with epoxy resin on the two opposite sides of the brass cylinder covering two apertures through which light can pass. The glass windows are optically polished to the order of $\lambda/10$. The microemulsion was introduced through a small opening on the top. The

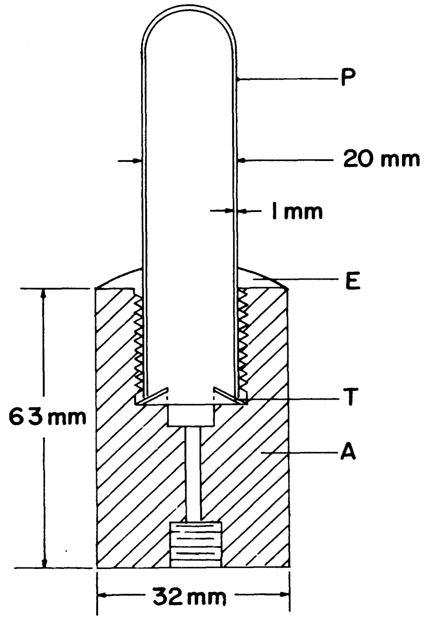

FIG. 2. Experimental cell for dT_c/dP measurements. P, Pyrex cell; E, epoxy resin: T, Teflon O ring; A, Aminco connector.

opening was closed with a small nylon screw after the introduction of the liquid. The screw was later sealed hermetically with epoxy resin. There is also a small opening at the bottom to facilitate cleaning which was likewise sealed during the measurement. The brass cylinder was then held fixed along the cylindrical axis of an aluminum cylinder. A reflector (plane mirror) was placed on one end of the aluminum encasement and the other end was terminated with a glass window at the junction of the inside and the outside temperature-controlled baths. The glass window was, however, not in touch with the liquid. The aluminum cylinder was simply extended to the end of the second bath.

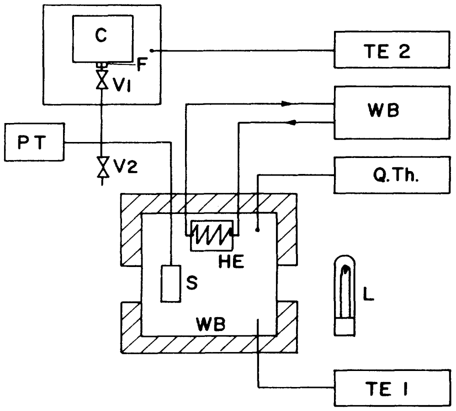

FIG. 3. Schematic diagram for dT_c/dP measuring system. C, compressor; F, 15-μm filter; V_1,V_2 valves; P.T., pressure transducer; S, sample cell; WB, temperature regulated distilled water bath; TE1, temperature controller for the sample bath; TE2, temperature controller for the compressor bath; Q.Th, quartz thermometer; L, light.

The inside bath containing the optical cell is made up of a rectangular aluminum sheet (15 mm thick) which is 42 cm high, 44 cm long, and 40 cm wide. The internal bath was put inside a second retangular bath also made of aluminum sheet 58 cm high, 70 cm long, and 61.5 wide. The second bath was insulated from outside by covering on all sides, with polystyrene 24 mm thick. Liquid in both the inside and the outside baths was polyethylene glycol, which has a high thermal capacity and low evaporation. The outside bath was controlled with water from a temperature controller (Neslab, model RTE-8DD)

TABLE I. Experimental values for the refractive-index changes as a function of temperature for sample *A* of a critical microemulsion of AOT-water-decane.

T (°C)	$10^3\Delta n$	T (°C)	$10^3\Delta n$
Run I		Run II	
23.8660	5.4676	22.1550	6.2523
24.3970	5.2250	22.6410	6.0286
24.8260	5.0296	23.1230	5.8080
25.2890	4.8153	23.6050	5.5874
25.4950	4.7239	23.9970	5.4077
25.8570	4.5569	24.3920	5.2281
26.8370	4.1094	24.8350	5.0233
27.9020	3.6241	25.3360	4.7932
30.4200	2.4801	25.8120	4.5758
30.9220	2.2532	26.1020	4.4434
31.4280	2.0263	26.6610	4.1882
32.8950	1.3645	28.3630	3.4129
33.4060	1.1376	29.8640	2.7322
33.7700	0.9737	30.1020	2.6251
34.5130	0.6128	30.6740	2.3635
35.0001	0.4285	31.1820	2.1366
35.1150	0.3781	31.6050	1.9444
35.1651	0.3561	32.0880	1.7269
35.2003	0.3403	33.6860	1.0115
35.2410	0.3245	34.0790	0.8351
35.2922	0.3025	34.5120	0.6428
35.3904	0.2584	35.0011	0.4285
35.5021	0.2111	35.0890	0.3907
35.6543	0.1449	35.1292	0.3718
35.7019	0.1260	35.2291	0.3277
35.7519	0.1039	35.2830	0.3056
35.8011	0.0819	35.3316	0.2867
35.8504	0.0630	35.3809	0.2647
35.8881	0.0441	35.4302	0.2426
35.9071	0.0378	35.2838	0.2205
35.9130	0.0346	35.5856	0.1733
35.9420	0.0220	35.6811	0.1355
35.9649	0.0126	35.7329	0.1134
35.9861	0.0063	35.7809	0.0913
35.9951	0.0031	35.8301	0.0724
36.0028	0.0000	35.8557	0.0598
		35.8803	0.0504
		35.9123	0.0378
		35.9400	0.0252
		35.9710	0.0126
		35.9901	0.0063
		36.0015	0.0000

circulating inside a copper coil. The temperature of the outside bath was controlled to within 0.04 °C. The internal bath was controlled with a proportional temperature control made by Mellab. It contained a very small heating element of 10 W, enough to respond to small fluctuations of the outside bath. This dual-control system enabled us to control the inside bath to within 0.0005K per 8 h. The temperature was measured with a quartz thermometer with a precision of 1 in 10^4 (HP model 2801A).

B. Measurements of dT_c/dP

Figure 2 shows the sample cell used for dT_c/dP experiments. The cell is made of Pyrex and is glued at the bottom by epoxy to a stainless-steel Aminco connector. A teflon *O* ring is used at the junction of the pyrex cell and the Aminco connector. A high-pressure tubing emanating from the Aminco connector is connected to a compressor for introducing pressures up to 14 atm. The sample cell was thermostated in a constant-temperature bath. The compressor and the sample cell contained the same liquid. A calibrated pressure transducer was used to measure pressures. A schematic diagram of the system is shown in Fig. 3. The precision in pressure and temperature is, respectively, $\Delta P = \pm 0.5$ psi and $\Delta T = \pm 0.003$ °C. The change in the critical temperature T_c with pressure was noted visually. The variation $T_c(P) - T_c(P_0)$, where $P_0 = 1$ atm, is plotted versus $P - P_0$. The slope of the curve gives the value of dT_c/dP.

C. Sample preparation

The microemulsion system that we have studied contains 3 wt. % of surfactant, sodium di-2-ethylhexyl-sulfosuccinate (AOT), in 5 vol % of distilled water and 95 vol % of decane. Decane (gold label) was more than 99% pure and was supplied by Aldrich Chemical Company. Distilled water was deionized in the laboratory. AOT also supplied by Aldrich Chemical Company was 96% pure and was further purified to remove water. The mixture of AOT and methanol was evaporated in a vacuum in order to remove the water dissolved in methanol. The process was repeated three times. The pure AOT was then mixed in exact proportion with deionized water and decane. The microemulsion thus prepared was left in a hermetically sealed container for 12 h. The microemulsion sample was then carefully introduced with a syringe into the measuring cell. After the introduction of the microemulsion, the measuring cell was hermitically sealed. For the purpose of our refractive-index measurements, two separate samples with the same nominal concentrations have been prepared.

IV. RESULTS AND DISCUSSION

We have investigated the temperature dependence of the refractive index of two samples of a critical AOT-water-decane microemulsion mixture in the temperature range between 20 °C and the critical temperature at 36 °C. Since the critical point is a lower critical one, all the data have thus been obtained for the critical concentration in the homogeneous phase. With the interferometric technique described in Sec. III, one can only record changes in refractive index, e.g., as a function of temperature. This is, however, sufficient to arrive at most of the relevant information on the critical behavior. In Table I results for the two runs in sample *A* have been given. The quantity Δn is defined as

$$\Delta n = n(T) - n(T_r) , \tag{4.1}$$

where T_r is a reference temperature. This reference temperature was chosen as close as possible to the critical temperature. For each run it is the last entry in the Table I. The Δn values for sample *B* are given in Table II. These refractive-index changes were measured with a precision of 1 part in 10^6, using the above-described Hewlett-Packard laser interferometer. As mentioned earlier, the temperature of the sample was kept constant to within ± 0.0005 K per 8 h.

In Fig. 4 Δn values for the two runs of sample *A* are given. Results for the three runs of sample *B* are displayed in Fig. 5. For display reasons not all the data could be plotted in these figures. Compared to the binary liquid system of triethylamine-water,[24] the anomaly in this microemulsion is very small and barely visible. Moreover, the anomaly has a different sign. Here there is a very slight upward curvature, while for the binary mixture there is a clearly visible downward bending on approaching T_c. The small refractive-index anomaly can be made more clearly visible by introducing, via Eq. (2.2), the following new quantity:

$$D_n \equiv - \left[\frac{n - n_c}{t} \right] = -(N_2 + N_3 t^{-\alpha} + N_4 t^{-\alpha+\Delta} + \cdots) . \tag{4.2}$$

The minus sign in the definition of D_n is introduced for display reasons only. In Fig. 6 a plot of D_n versus temperature is given for the two runs of sample *A*. From Eq. (4.2) it follows that at T_c the quantity D_n should exhibit a weak α-type critical divergence. In Fig. 5 the data indicate a divergence at the critical point.

As pointed out in Sec. II, one expects theoretically that the behavior of the refractive index can be described by means of the Eq. (2.2). The last two terms (and additional higher-order ones) represent corrections to scaling.[32] Sufficiently close to the critical point, it is expected that the contributions from the correction-to-scaling terms and also from nonlinear terms in background behavior of *n* can be neglected. These assumptions can be verified by the procedure of range shrinking—carrying out fits for data in progressively smaller $(T_c - T)$ ranges. Since our direct experimental results are not absolute refractive-index values, but the differential values Δn defined in Eq. (4.1), and since T_r there is not necessarily exactly at T_c, Eq. (2.2) was slightly modified to allow for proper parameter adjustment. The following expression fitted the Δn values:

$$\Delta n = \delta n_c + N_2 t + N_3 t^{1-\alpha} . \tag{4.3}$$

As possible adjustable parameters in this expression we have δn_c, N_2, N_3, T_c, and α. From Eqs. (2.2), (4.1), and

(4.3), one also has the following relationship:

$$\Delta n - \delta n_c = n(T) - [n(T_r) - \delta n_c] = n - n_c = n - N_1 \ . \tag{4.4}$$

In the analysis of the data, we carried out several nonlinear least-squares fits for the Δn results given in Tables I and II. For the fitting we used the well-known FORTRAN nonlinear least-squares program CURFIT.[33] To obtain the best parameter values, the reduced χ^2 function

$$X_v^2 = \frac{1}{N-p} \sum_{j=1}^{N} \frac{(\Delta n^j_{\mathrm{expt}} - \Delta n^j_{\mathrm{calc}})^2}{\mathrm{var}(\Delta n^j)} \tag{4.5}$$

was minimized for N data points. The parameter p gives the number of adjustable parameters in the fitting equation. The variance is given by

$$\mathrm{var}(\Delta n^j) = (\sigma_n^j)^2 + \left[\frac{\partial n^j}{\partial T}\right]^2 (\sigma_T^j)^2 \ . \tag{4.6}$$

Since the critical anomaly in this mixture is very weak and since we had $\sigma_T \approx 0.0005\,^\circ\mathrm{C}$, it turned out that in Eq. (4.6) the second term could be neglected. This resulted in a constant value of 2.3×10^{-12} for the variance of each data point in Eq. (4.5).

In Table III a summary of the fitting results is given. Because of the weak anomaly and many adjustable parameters, it was not practical to leave the critical temperature T_c as a free parameter. Instead, several values for T_c of each run were chosen in a T range allowed by the direct experimental observations. Fit numbers smaller or equal to 5 (see Table III) represent fits for the different runs in which all the data (between 20 °C and T_c) have been used. For fits with numbers above 5, range shrinking was applied and only data between 30 °C and T_c were used. For the different fits the uncertainty on each parameter is not explicitly quoted. For one standard deviation, however, the uncertainty in the parameter is usually a few units in the last digit. From the results in Table III one can observe that there is reasonable agreement between the parameter values obtained for the two different samples and the different runs. Range shrinking did not appreciably change the parameters, indicating that Eq. (4.3) is sufficient for describing the data. One can, however, notice a certain correlation between the coefficient N_3 and the value of the critical exponent α. For large α

TABLE II. Experimental values for the refractive-index changes as a function of temperature for sample *B* of a critical microemulsion of AOT-water-decane.

T (°C)	$10^3\Delta n$	T (°C)	$10^3\Delta n$	T (°C)	$10^3\Delta n$
Run III		Run IV		Run V	
20.0000	7.5633	20.0010	7.5633	21.0000	7.0843
20.3690	7.3868	20.0780	7.5255	21.3040	6.9425
20.6430	7.2576	20.1740	7.4782	21.5110	6.8416
20.8910	7.1379	20.5110	7.3206	21.7920	6.7061
21.0010	7.0874	20.8270	7.1662	21.9990	6.6084
21.3200	6.9330	21.4780	6.8574	22.4390	6.3973
21.6110	6.7944	22.1170	6.5517	22.8770	6.1893
22.1120	6.5549	22.3790	6.4256	23.2620	6.0065
22.5210	6.3626	22.7580	6.2460	23.7410	5.7796
23.0190	6.1231	23.1340	6.0695	24.1980	5.5590
23.2470	6.0128	23.4590	5.9151	24.5500	5.3888
23.6280	5.8332	23.8300	5.7355	25.1880	5.0895
23.8710	5.7166	24.0510	5.6315	25.6770	4.8531
24.0190	5.6441	24.3280	5.4991	26.2500	4.5852
24.4210	5.4550	24.5990	5.3699	26.7790	4.3300
24.6800	5.3321	25.3430	5.0170	27.3010	4.0812
24.8290	5.2628	26.0660	4.6735	27.6890	3.9014
25.0170	5.1714	26.4700	4.4812	28.0110	3.7470
25.8550	4.7712	26.8010	4.3237	28.3190	3.6051
26.1570	4.6293	27.1730	4.1472	28.8310	3.3625
26.4890	4.4718	27.6210	3.9360	29.4640	3.0537
26.7180	4.3646	27.9800	3.7627	30.1080	2.7513
26.9130	4.2701	28.2320	3.6430	30.5190	2.5589
27.1700	4.1503	28.5010	3.5169	30.9290	2.3666
28.6450	3.4476	28.7910	3.3782	31.8390	1.9381
28.9400	3.3089	29.1670	3.1986	32.1110	1.8089
29.3090	3.1356	29.4510	3.0663	32.6340	1.5630
29.6100	2.9906	29.6890	2.9560	33.1520	1.3204
29.8210	2.8929	29.9020	2.8551	33.6190	1.1029
30.0280	2.7921	30.2130	2.7070	34.5480	0.6649
30.2100	2.7070	30.5110	2.5652	34.7140	0.5893
30.6530	2.4990	30.8120	2.4202	34.8133	0.5451

TABLE II. (*Continued*).

T (°C)	$10^3\Delta n$	T (°C)	$10^3\Delta n$	T (°C)	$10^3\Delta n$
Run III		Run IV		Run V	
30.9300	2.3666	31.3190	2.1839	34.8777	0.5105
31.3100	2.1870	31.6900	2.0074	35.0041	0.4538
32.2320	1.7553	32.0380	1.8435	35.1656	0.3781
32.4400	1.6544	32.6900	1.5378	35.2201	0.3529
32.9830	1.3992	33.3310	1.2384	35.3109	0.3151
33.4420	1.1913	33.6490	1.0872	35.4244	0.2584
33.8100	1.0115	34.0990	0.8760	35.4480	0.2458
34.0020	0.9233	34.5420	0.6712	35.5028	0.2205
34.2210	0.8193	35.1091	0.4065	35.5878	0.1827
34.4500	0.7122	35.2102	0.3592	35.7406	0.1134
34.6330	0.6302	35.3304	0.3056	35.7971	0.0882
34.7090	0.5921	35.4119	0.2617	35.8448	0.0693
34.9510	0.4821	35.5038	0.2269	35.8901	0.0472
35.0011	0.4569	35.6104	0.1761	35.9214	0.0346
35.1092	0.4065	35.7098	0.1292	35.9509	0.0189
35.2103	0.3592	35.8188	0.0819	35.9617	0.0157
35.3206	0.3119	35.9001	0.0441	35.9701	0.0126
35.4171	0.2647	35.9050	0.0409	35.9753	0.0091
35.5002	0.2269	35.9111	0.0378	35.9809	0.0063
35.5510	0.2018	35.9169	0.0378	35.9901	0.0031
35.6091	0.1764	35.9207	0.0346	35.9932	0.0031
35.6513	0.1575	35.9268	0.0315	35.9969	0.0000
35.7194	0.1260	35.9301	0.0293		
35.7631	0.1071	35.9362	0.0252		
35.7981	0.0913	35.9401	0.0252		
35.8142	0.0819	35.9469	0.0220		
35.8622	0.0630	35.9503	0.0189		
35.8909	0.0501	35.9613	0.0157		
35.9091	0.0409	35.9700	0.0126		
35.9494	0.0220	35.9809	0.0091		
35.9701	0.0126	35.9851	0.0063		
35.9804	0.0094	35.9901	0.0031		
35.9901	0.0031	35.9932	0.0031		
35.9994	0.0000	35.9981	0.0000		

values, N_3 tends to be on the small side, and vice versa. The differences in parameter values between the different fits probably give a realistic estimate for the uncertainty on a given parameter. From looking at the obtained values for the critical exponent α, it is immediately clear that, within an uncertainty of about 0.03, this refractive-index anomaly is consistent with an Ising value for the critical exponent α. On the basis of the results of Table III, we arrive at the following best values for N_2 and N_3:

$$N_2=0.161\pm0.005 \; , \tag{4.7}$$

$$N_3=-0.011\pm0.002 \; . \tag{4.8}$$

Now the question arises whether N_3, and thus the critical part of the refractive index, is entirely due to a density anomaly, or contains also an intrinsic singular contribution. In order to find out, one has to compare calculated values for R_3 in Eq. (2.1) and R_3' in Eq. (2.8). Since no direct experimental results for the density are available, one has to use an indirect way to obtain R_3 via Eq. (2.5). It is not possible to use Eq. (2.4) because also heat-capacity values are lacking. Provided one assumes two-scale-factor universality, all parameters are available in literature except dT_c/dP. In order to get this value for our microemulsion, we carried out the experiment described in Sec. III B. In Fig. 7 the results for the change of the critical temperature with pressure are given. In that figure $P_0=1$ atm. The data for three different runs fall on a straight line with a slope

$$\frac{dT_c}{dP}=(-14.3\pm0.2)\times10^{-8}\ \text{K/Pa} \; . \tag{4.9}$$

In the calculation of R_3 with Eq. (2.5) we use the Ising values[28,34] $\alpha=0.11$ and $X=1.97\times10^{-2}$. From light scattering, Huang and Kim[8] derived results for the correlation length in a microemulsion with the same composition. Although they stated that their results in the homogeneous phase were consistent with an Ising value $\nu_I=0.63$, a better fit was obtained with $\nu=0.75$ and $\xi_0=12.2$ Å in the power-law expression

$$\xi=\xi_0 t^{-\nu} \; . \tag{4.10}$$

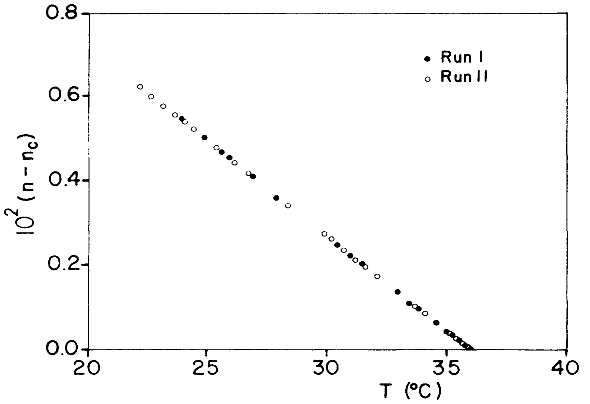

FIG. 4. Refractive-index difference $(n-n_c)$ as a function of temperature in the one-phase region below the critical point of an AOT-water-decane microemulsion. Data for the two runs of sample A are given.

By imposing the Ising value $\nu_I=0.63$, we observed that their experimental results could be represented reasonably well provided $\xi_0=23$ Å was used in Eq. (4.10). We used this value also in Eq. (2.5) because their Ising exponent values have to be imposed consistently. Using the above information we obtain

$$R_3=-(0.033\times10^{-3})\rho_c \ . \qquad (4.11)$$

We do not have an exact value for ρ_c but that is not important because it can be eliminated (see below) in a comparison with R'_3. Since, however, most of the mixture is decane with about 5% water ρ_c will be close to 0.8 g per cm^3.

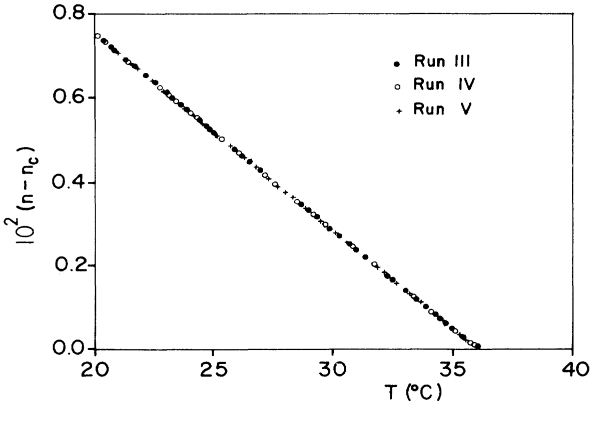

FIG. 5. Refractive-index difference $(n-n_c)$ as a function of temperature in the one-phase region below the critical point of an AOT-water-decane microemulsion. Data for the three runs of sample B are given.

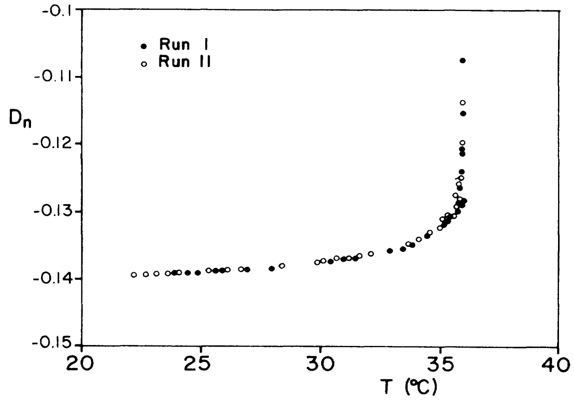

FIG. 6. Temperature dependence of the quantity D_n, defined in Eq. (4.2), for run I and run II of sample A.

For the calculation of R'_3 with Eq. (2.8) a value for $(\partial\rho/\partial n)$ is needed. As pointed out in Sec. II one can use the Lorentz-Lorenz formula for this purpose. One needs, however, absolute values of the refractive index for that calculation. We have for that purpose supplemented our high-resolution differential measurements with lower-resolution absolute values of the refractive index obtained by using an Abbe refractometer. The results for the two different samples are given in Table IV. From these data we arrive via Eq. (2.9) and (2.10) at the result

$$\frac{1}{\rho}\left[\frac{\partial\rho}{\partial n}\right]=2.27\pm0.02 \ . \qquad (4.12)$$

Using Eq. (2.8) and the result (4.8) we obtain

$$R'_3=-(0.026\pm0.006)\rho_c \ . \qquad (4.13)$$

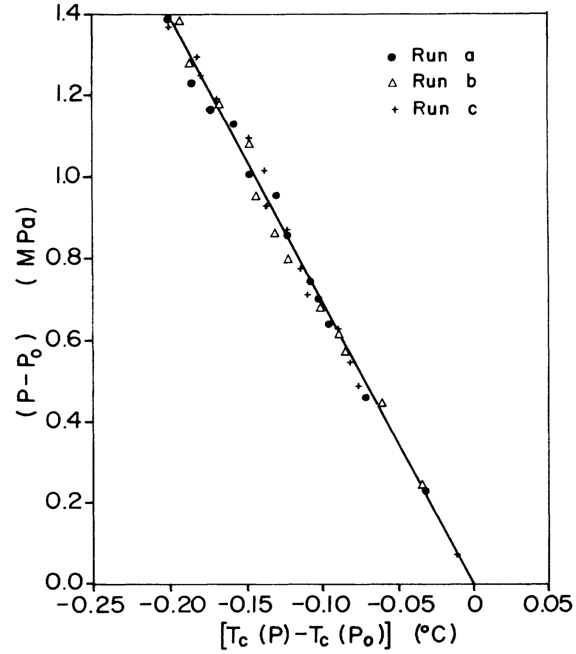

FIG. 7. Variation of the critical temperature with pressure for a microemulsion of AOT-water-decane. P_0 is a pressure of AOT-water-decane. Data for three different runs are given.

TABLE III. Values for the parameters in Eq. (4.1) from fits to the data of the different runs in Tables I and II.

Run-fit	T_C (°C)	$10^6\delta n_c$	α	N_2	N_3	χ^2_ν
I-1	(36.0025)	−0.4	0.124	0.1580	−0.0125	0.4784
I-2	(36.0020)	−0.3	0.119	0.1588	−0.0132	0.4751
I-3	(36.0018)	−0.2	0.118	0.1591	−0.0135	0.4747
I-4	(36.0015)	−0.2	0.115	0.1604	−0.0147	0.4777
I-5	(36.0010)	0.0	0.111	0.1615	−0.0158	0.4981
I-6	(36.0025)	−0.3	0.138	0.1560	−0.0107	0.4867
I-7	(36.0018)	−0.2	0.121	0.1584	−0.0129	0.4763
I-8	(36.0010)	−0.1	0.108	0.1609	−0.0152	0.4768
II-1	(36.0035)	0.6	0.114	0.1606	−0.0148	0.5393
II-2	(36.0030)	0.8	0.113	0.1607	−0.0149	0.5399
II-3	(36.0025)	1.0	0.112	0.1609	−0.0151	0.5404
II-4	(36.0020)	1.2	0.111	0.1611	−0.0152	0.5413
II-5	(36.0015)	1.4	0.110	0.1613	−0.0155	0.5421
III-1	(36.9980)	1.4	0.080	0.1653	−0.0151	0.6790
III-2	(35.9990)	0.9	0.084	0.1641	−0.0140	0.6171
III-3	(35.9995)	0.6	0.086	0.1636	−0.0135	0.6095
III-4	(36.0000)	0.4	0.087	0.1634	−0.0134	0.6092
III-5	(36.0005)	0.2	0.087	0.1634	−0.0133	0.6090
IV-1	(35.9980)	0.1	0.084	0.1633	−0.0134	0.7467
IV-2	(35.9985)	−0.1	0.088	0.1625	−0.0126	0.7422
IV-3	(35.9990)	−0.2	0.091	0.1621	−0.0122	0.7407
IV-4	(35.9995)	−0.4	0.094	0.1615	−0.0116	0.7414
IV-5	(35.0000)	−0.7	0.095	0.1613	−0.0114	0.7623
IV-6	(35.9980)	0.0	0.074	0.1657	−0.0157	0.7482
IV-7	(35.9985)	−0.1	0.078	0.1648	−0.0148	0.7437
IV-8	(35.9990)	−0.3	0.081	0.1641	−0.0141	0.7424
IV-9	(35.9995)	−0.5	0.084	0.1634	−0.0135	0.7431
IV-10	(36.0000)	−0.7	0.085	0.1631	−0.0132	0.7443
V-1	(35.9970)	−0.2	0.117	0.1580	−0.0087	1.5319
V-2	(35.9975)	−0.2	0.123	0.1580	−0.0083	1.5230
V-3	(35.9980)	−0.3	0.129	0.1580	−0.0077	1.5232
V-4	(35.9985)	−0.5	0.133	0.1571	−0.0074	1.5253
V-5	(35.9990)	−0.6	0.136	0.1568	−0.0071	1.5292
V-6	(35.9970)	−0.1	0.121	0.1581	−0.0084	1.5279
V-7	(35.9975)	−0.3	0.121	0.1581	−0.0084	1.5231
V-8	(35.9980)	−0.4	0.121	0.1582	−0.0084	1.5239
V-9	(35.9985)	−0.6	0.121	0.1583	−0.0085	1.5270
V-10	(35.9990)	−0.8	0.120	0.1584	−0.0086	1.5326

TABLE IV. Absolute values for the refractive index.

T (°C)	n (sample A)	n (sample B)
20	1.4109	1.4102
21	1.4104	1.4097
22	1.4100	1.4092
23	1.4095	1.4088
24	1.4091	1.4083
25	1.4085	1.4078
26	1.4080	1.4074
27	1.4076	1.4069
28	1.4072	1.4065
29	1.4067	1.4062
30	1.4064	1.4058
31	1.4060	1.4054
32	1.4056	1.4050
33	1.4052	1.4046
34	1.4049	1.4043
35	1.4046	1.4040

If we make the ratio between R_3' and R_3 the density ρ_c drops out and we get

$$\frac{R_3'}{R_3}=790\ . \tag{4.14}$$

This means that the anomaly in the refractive index is almost three orders of magnitude larger than the anomaly expected in the density on the basis of two-scale-factor universality from correlation-length results and the slope of the critical line. However, if we take Huang and Kim's original $\xi_0=12.2$ Å (admittedly with an inconsistent ν) R_3'/R_3 is reduced by about a factor 8 to around 100. This shows that the anomaly in the refractive index still remains almost two orders of magnitude larger than the anomaly expected in the density.

V. SUMMARY AND CONCLUSIONS

In this paper we have presented new experimental data for the refractive index as a function of temperature for a critical microemulsion of AOT-water-decane in the homogeneous phase below the critical point. In total, five different runs for two different samples were measured for the temperature range between 20 °C and the critical temperature at 36 °C. The effect of pressure on the critical temperature was also experimentally investigated.

Theoretically,[20] it is expected for consolute points belonging to the Ising universality class, that the leading contributions from dT_c/dP and dT_c/dE^2 both have a $t^{1-\alpha}$ temperature dependence. The first one is related to the density anomaly, while the second one is an instrinsic refractive-index (or dielectric constant) effect. Although it has been maintained by some authors[23] that the critical anomaly in the refractive index is only due to the density effect, we have recently[24] shown that in the case of triethylamine-water the contribution due to dT_c/dE^2 is of the same order as the contribution of the density and of opposite sign. In the analysis of our experimental data in Sec. IV we have addressed these questions in detail.

From a power-law analysis of the data it was found that the critical anomaly observed in the refractive index could be described by means of a $t^{1-\alpha}$ contribution with the Ising value of 0.11 for the critical exponent α.

Assuming two-scale-factor universality and combining our dT_c/dP results with the correlation-length amplitude ξ_0 from literature,[8] it was possible to calculate via Eqs. (2.5) and (2.8), the density contribution to the refractive-index anomaly. The result obtained in (4.14) shows that the experimentally obtained anomaly in the refractive index is almost three orders of magnitude larger than expected on the basis of the calculated density effect. This microemulsion thus represents a case in which the intrinsic effect in the refractive index is by far the dominant one.

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[1] D. Roux and A. M. Bellocq, Phys. Rev. Lett. **52**, 1895 (1984), and references therein.

[2] A. M. Bellocq, P. Honorat, and D. Roux, J. Phys. (Paris) **46**, 743 (1985), and references therein.

[3] M. Corti, V. Degiorgio, and M. Zulauf, Phys. Rev. Lett. **48**, 1617 (1982).

[4] M. Corti, C. Minero, and V. Degiorgio, J. Phys. Chem. **88**, 309 (1984).

[5] V. Degiorgio, R. Piazza, M. Corti, and C. Minero, J. Chem. Phys. **82**, 1025 (1985).

[6] M. Corti and V. Degiorgio, Phys. Rev. Lett. **55**, 2005 (1985).

[7] S. H. Chen, Ann. Rev. Phys. Chem. **37**, 351 (1986).

[8] J. S. Huang and M. W. Kim, Phys. Rev. Lett. **47**, 1462 (1981).

[9] M. W. Kim and J. S. Huang, Phys. Rev. B **26**, 2703 (1982).

[10] M. Kotlarchyk, S. H. Chen, and J. S. Huang, Phys. Rev. A **28**, 508 (1983).

[11] M. Kotlarchyk, S. H. Chen, J. S. Huang, and M. W. Kim, Phys. Rev. A **29**, 2054 (1984).

[12] M. W. Kim, J. Bock, and J. S. Huang, Phys. Rev. Lett. **54**, 46 (1985).

[13] P. Honorat, D. Roux, and A. M. Bellocq, J. Phys. Lett. (Paris) **45**, 961 (1984).

[14] S. C. Greer and M. R. Moldover, Ann. Rev. Phys. Chem. **32**, 233 (1981).

[15] A. Kumar, H. R. Krishnamurthy, and E. S. R. Gopal, Phys. Rep. **98**, 57 (1983).

[16] J. P. Wilcoxon and E. W. Kalor, J. Chem. Phys. **86**, 4684 (1987).

[17] K. Hamano, N. Kuwahara, T. Koyama, and S. Harada, Phys. Rev. A **32**, 3168 (1985).

[18] M. E. Fisher, Phys. Rev. Lett. **57**, 1911 (1986).

[19] G. Dietler and D. S. Cannell, Phys. Rev. Lett. **60**, 1852 (1988).

[20] J. V. Sengers, D. Bedeaux, P. Mazur, and S. C. Greer, Physica A **104**, 573 (1980).

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

[22] P. C. Hohenberg, A. Aharony, B. I. Halperin, and E. D. Siggia, Phys. Rev. B **13**, 2986 (1976).

[23] D. Beysens, in *Phase Transitions: Cargese 1980*, edited by M. Levy, J.-C. LeGuillou, and J. Zinn-Justin (Plenum, New York, 1982), and references therein.

[24] C. Pépin, T. K. Bose, and J. Thoen, Phys. Rev. Lett. **60**, 2507 (1988).

[25] J. Thoen, R. Kindt, and W. Van Dael, Phys. Lett. **A76**, 445 (1980); **A87**, 73 (1981); B. C. Miller, E. A. Clercke, and S. C. Greer, J. Phys. Chem. **87**, 1063 (1983); D. T. Jacobs and S. C. Greer, Phys. Rev. A **24**, 2075 (1981); R. H. Cohn and S. C. Greer, J. Phys. Chem. **90**, 4163 (1986); J. L. Tveekrem, S. C. Greer, and D. T. Jacobs, Macromolecules **21**, 147 (1988), and references therein.

[26] P. Dorion, J. R. Lalanne, B. Pouligny, S. Imaizumi, and C. W. Garland, J. Chem. Phys. **87**, 578 (1987).

[27] N. Rebbouh, J. Buchert, and J. R. Lalanne, Europhys. Lett. **4**, 447 (1987).

[28] J. C. LeGuillou and J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980); J. Phys. Lett. **46**, L137 (1985).

[29] J. Thoen, E. Bloemen, and W. Van Dael, J. Chem. Phys. **68**, 735 (1978); E. Bloemen, J. Thoen, and W. Van Dael, *ibid.* **73**, 4628 (1980).

[30] R. B. Griffiths and J. C. Wheeler, Phys. Rev. A **2**, 1047 (1970).

[31] D. Beysens and P. Calmettes, J. Chem. Phys. **66**, 766 (1977).

[32] F. J. Wegner, Phys. Rev. B **5**, 4529 (1972).

[33] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).

[34] C. Bervillier and C. Godrèche, Phys. Rev. B **21**, 5427 (1980).