Experimental Critical-Exponent Values for Fluids

Jan V. Sengers · Joseph G. Shanks

Abstract After a review of the history and an assessment of the current status of the subject, we present light-scattering data to determine the critical correlation-function exponents for an aqueous electrolyte solution yielding the experimental values $\gamma = 1.238 \pm 0.012$, $\nu = 0.629 \pm 0.003$, $\eta = 0.032 \pm 0.013$. We conclude the paper with some comments concerning the temperature dependence of non-asymptotic effective critical-exponent values of fluids.

Keywords Critical correlation function · Critical exponents · Gravity effects · Isobutyric acid + water · Light scattering

1 Historic Introduction

This special issue of the Journal of Statistical Physics celebrates fifty years of statistical physics reflected in 100 Statistical Mechanics Conferences under the leadership of Joel Lebowitz. An important development in statistical physics five decades ago was the resurgence of the subject of critical phenomena in condensed matter. For critical phenomena in fluids this renewed interest was stimulated by the experiments of Fairbank, Buckingham, and Kellers [1, 2] in 1957–1961 who found that the isochoric specific heat capacity, C_V, of liquid helium diverges near the lambda transition in a manner reminiscent of Onsager's solution [3] for the specific heat capacity of the two-dimensional Ising model, by the experiments of Voronel and coworkers who observed a divergent behavior of C_V of fluids near the vapor-liquid critical point, first for argon in 1962 [4] and subsequently for oxygen in 1963 [5], and the discovery in 1962 that the thermal conductivity of fluids also diverges at

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the vapor-liquid critical point [6]. The divergent behavior of C_V near the vapor-liquid critical point was subsequently confirmed by Moldover and Little for both He^3 and He^4 [7]. In this paper we shall restrict ourselves to the critical behavior of equilibrium properties in one-component fluids near the vapor-liquid critical point and in nearly incompressible liquid mixtures near a critical point of mixing.

The question arose whether critical phenomena in condensed matter—such as fluids, fluid mixtures, ferro- and anti-ferromagnets—could all be considered from a uniform point of view. To address this issue M.S. Green organized the first conference on critical phenomena in 1965 [8]. At this conference M.E. Fisher [9] explained his nomenclature for the exponents of the asymptotic critical power laws: α for the temperature dependence of the specific heat capacity, β for the temperature dependence of the order parameter along the phase boundary, γ for the temperature dependence of the susceptibility, δ for the dependence of the ordering field on the order parameter at the critical temperature, ν for the temperature dependence of the correlation length, and η to characterize the asymptotic spatial decay of the order-parameter correlation function at the critical point. The asymptotic power laws will be specified in more detail in Sect. 2. At the second conference on critical phenomena, organized by M.S. Green in 1970, L.P. Kadanoff [10] introduced the concept of critical-point universality classes, a concept that would be put on a firm foundation by further development of the renormalization group theory of critical phenomena [11–15]. According to this hypothesis, fluids belong to the universality class of 3-dimensional (3D) Ising-like systems, i.e., systems with short-range interactions and a scalar order parameter.

The early measurements of the critical exponents were reviewed by Heller [16], by Kadanoff et al. [17] in 1967, by Egelstaff and Ring [18] in 1968, by Chu [19] in 1972, and by Anisimov [20] in 1974. From these early reviews it could be concluded that the critical exponents appeared to agree with those of the Ising model to within these exponents were known at the time. However, there was some uncertainty how close to the critical point the asymptotic power laws would be valid. Specifically, an analysis of experimental pressure-density-temperature (P-ρ-T) data, which are more easily affected by gravity than optical experiments, appeared to yield critical exponents that seemed to differ somewhat from those for the Ising model [21–23]. On the other hand Balzarini and Ohnr [24] had observed that β for sulfur hexafluoride tended to decrease on closer approach to the critical temperature. Gravity introduces inhomogeneous density profiles in fluids near the vapor-liquid critical point [25, 26] and it had been realized [27] that such profiles yield the chemical potential μ as a function of the density ρ, precisely the variables for which Widom [28] had formulated the scaling laws for fluids. These profiles could be investigated by optical interferometry [29]. The earlier observation of Balzarini and Ohrn [24] was dramatically confirmed by Hocken and Moldover [30] who found that critical exponents deduced from interferometric measurements of gravitationally induced density profiles very close to the critical temperature for xenon, sulfur hexafluoride, and carbon dioxide were different from those earlier deduced from experimental P-ρ-T data, and they were much closer to the theoretical estimates for the critical exponents of the 3D Ising model [31]. In the mean time Wegner [32] had shown the existence of confluent singularities to the asymptotic scaling laws. When Greer [33] applied a Wegner correction to the coexistence-curve data of liquid mixtures of isobutyric acid + water and of carbon disulfide + nitromethane, she found asymptotic values for the critical exponent β close to the estimated Ising value.

At the same time, we were pursuing light-scattering experiments in our laboratory to determine critical correlation-function exponents. Following a suggestion of McIntyre [34], we had selected a liquid mixture of 3-methylpentane + nitroethane for the purpose. This liquid mixture has the property that the difference between the refractive indices of the two liquid

components is sufficiently small that double-scattering remains negligible even close to the critical temperature, while large enough so that concentration fluctuations dominate light scattering. Moreover, the difference in the density of the two components is small, so that (after stirring) homogeneity of the sample could be maintained for long periods. While we believed our experimental critical exponents to be accurate, we were initially disappointed with the results since they did not agree very well with the then current estimates for the exponents for the 3D Ising model deduced from high-temperature expansions [35]. However, we then noticed that the experimental values [36, 37] were close to the exponent predictions then becoming available from the renormalization group theory [38]. This issue was resolved at the Cargèse conference on phase transitions in 1980 [39]. At this conference, Nickel [40] reported that the exponent values from the high-temperature series expansions for the 3D Ising model had been affected by confluent singularities—as had the early experimental exponent values deduced from P-ρ-T data—and explained the discrepancy between our experimental values and the earlier theoretical estimates. The experimental situation for fluids and fluid mixtures [24, 30, 33, 36, 37, 41–57] was reviewed by Beysens [58], by Moldover [59] and by Sengers [60] at this conference, while Ahlers [61] reviewed the experimental data near the superfluid transition in liquid helium. Consensus was reached at this conference that experimental asymptotic critical exponents of classical fluids and fluids mixtures are in agreement with the exponent values for 3D Ising-like systems, since the cause of the apparent deviations of the series-expansions estimates from experiment [36, 37] and from theory [38, 40] had been found. The conclusion that fluids exhibit Ising-like critical behavior was also supported by the measurements of Anisimov et al. [20, 62–65] in the Soviet Union. Some relevant experimental results were also reviewed by Greer and Moldover after the conference in Cargèse [66].

The hypothesis that all fluids exhibit Ising-like asymptotic critical behavior has been questioned twice. The first objection arose when Degiorgio and coworkers [67–71] reported anomalous critical exponents for some nonionic micellar solutions. Fisher [72] tried to explain the experimental observations in terms of non-asymptotic effective critical exponents, a concept to which we shall return in Sect. 4. However, Dietler and Cannell [73] found that these micellar solutions do exhibit Ising-like asymptotic critical behavior just like molecular fluids, an observation confirmed by Hamano et al. [74, 75] and Rouch et al. [76]. The second objection was raised when Singh and Pitzer [77, 78] reported coexistence-curve data for an ionic solution of triethyl-n-hexylammonium triethyl-n-hexylboride in diphenyl ether which indicated a classical exponent value $\beta = 0.5$, while shortly thereafter Zhang et al. [79, 80] found a classical susceptibility exponent $\gamma = 1.00$ for the same system, suggesting that ionic solutions in which the phase separation is driven by long-range Coulombic forces could exhibit mean-field critical behavior [81, 82]. However, just as in the case of micellar solutions, these experimental results could not be reproduced [83, 84]. Kostko et al. [85] observed long-lived, non-equilibrium, supra-molecular structures in aqueous electrolyte solutions that appeared to be responsible for the apparent mean-field behavior of the susceptibility previously observed in a solution of 3-methylpyridine and sodium bromide [86]. Extensive experimental work of Schröer and coworkers [84, 87–93] and others [94–98] has clearly demonstrated that electrolyte solutions, including ionic micellar solutions [99], satisfy asymptotic power-law behavior with Ising exponents, a conclusion that also has been discussed in detail by Levelt Sengers et al. [100]. However, electrolyte solutions differ from molecular solutions in the nature of their non-asymptotic critical behavior, as will be discussed in Sect. 4.

2 Current Status of Subject

2.1 Theory

The critical behavior of Ising-like systems can be characterized by two independent scaling fields: a "strong" scaling field h_1 (also called ordering field), a "weak" scaling field h_2, and a dependent scaling field h_3, which—asymptotically close to the critical point—becomes a generalized homogeneous function of h_1 and h_2 of the form [11, 12, 14, 101]

$$h_3(h_1, h_2) \approx |h_2|^{2-\alpha} f^{\pm}\left(\frac{h_1}{|h_2|^{2-\alpha-\beta}}\right), \tag{2.1}$$

where, except for two system-dependent amplitudes, $f^{\pm}$ is a universal scaling function with the superscripts $\pm$ referring to $h_2 > 0$ and $h_2 < 0$, respectively. Associated with these scaling fields are two conjugate scaling densities: a strongly fluctuating scaling density φ_1 (order parameter) and a weakly fluctuating scaling density φ_2, such that

$$\varphi_1 = \left(\frac{\partial h_3}{\partial h_1}\right)_{h_2}, \qquad \varphi_2 = \left(\frac{\partial h_3}{\partial h_2}\right)_{h_1}. \tag{2.2}$$

In addition one may define a "strong" susceptibility χ_1 and a "weak" susceptibility χ_2:

$$\chi_1 = \left(\frac{\partial \varphi_1}{\partial h_1}\right)_{h_2}, \qquad \chi_2 = \left(\frac{\partial \varphi_2}{\partial h_2}\right)_{h_1}. \tag{2.3}$$

The definition of the susceptibility χ_1 can be extended to $\chi_1(q) = \chi_1(0)g(q\xi)$ as the spatial Fourier transform of the order-parameter correlation function, where q is the wave number and ξ the correlation length [101, 102]. The scaling laws imply asymptotic power laws along the path $\varphi_1 = 0$ for $h_2 > 0$ and $h_2 < 0$ and along the two sides of the phase boundary $\varphi_1 = \pm\varphi_{\text{cxc}}$ for $h_2 < 0$ as listed in Table 1. The universal critical exponents are related by

$$\gamma = 2 - \alpha - 2\beta, \qquad 3\nu = 2 - \alpha, \qquad \gamma = (2 - \eta)\nu. \tag{2.4}$$

The critical exponents for the 3D Ising universality class have been calculated with considerable accuracy. The available theoretical predictions from high-temperature expansions, Monte Carlo simulations and perturbative field-theoretical methods have been reviewed by Pelissetto and Vicari [104], to whom the reader is referred for details. This body of theoretical work suggests the following values for the critical exponents:

$$\alpha = 0.110 \pm 0.003, \qquad \beta = 0.326 \pm 0.002, \qquad \gamma = 1.239 \pm 0.002,$$
$$\nu = 0.630 \pm 0.002, \qquad \eta = 0.033 \pm 0.004. \tag{2.5}$$

In addition to the asymptotic power laws in Table 1, the renormalization group theory predicts the presence of a correction term proportional $|h_2|^{\Delta_1}$ with $\Delta_1 = 0.52 \pm 0.02$ [104], also referred to as first Wegner correction [32].

The scaling fields are related to the physical fields depending on the type of critical phase transition under consideration. For a one-component fluid near the vapor-liquid critical point, the physical fields are pressure P, temperature T, and chemical potential μ. In the lattice gas [105, 106], a direct theoretical realization of the symmetric Ising model, h_1 is asymptotically proportional to $\Delta\mu = \mu - \mu_c$, h_2 proportional to $\Delta T = T - T_c$, and

Table 1 Universal critical power laws

Critical power law	Thermodynamic path
$\varphi_1 \approx \pm B_0 |h_2|^{\beta}$	$h_2 < 0, \varphi_1 = \pm\varphi_{\text{cxc}}$
$\varphi_2 \approx \frac{A_0^{\pm}}{1-\alpha} h_2 |h_2|^{-\alpha}$	$\varphi_1 = 0$
$\chi_1 \approx \Gamma_0^{+} |h_2|^{-\gamma}$	$h_2 > 0, \varphi_1 = 0$
$\chi_1 \approx \Gamma_0^{-} |h_2|^{-\gamma}$	$h_2 < 0, \varphi_1 = \pm\varphi_{\text{cxc}}$
$\xi \approx \xi_0^{+} |h_2|^{-\nu}$	$h_2 > 0, \varphi_1 = 0$
$\xi \approx \xi_0^{-} |h_2|^{-\nu}$	$h_2 < 0, \varphi_1 = \pm\varphi_{\text{cxc}}$
$g(q\xi \to \infty) \propto (q\xi)^{\eta-2}$	

h_3 proportional to $\Delta P = P - P_c$, where we adopt the usual convention that a subscript c refers to the value of the property at the critical point. Hence, for the lattice gas φ_1 is proportional to $\Delta\rho = \rho - \rho_c$ and φ_2 proportional to $\Delta s = s - s_c$, where ρ is the mass density and s the entropy density. However, as has been pointed out by Fisher and coworkers [107–111], in real fluids all physical fields contribute to the scaling fields, a concept referred to as "complete scaling". Thus for one-component fluids in linear asymptotic approximation [107, 110–113]:

$$h_1 = a_1 \Delta\mu + a_2 \Delta T + a_3 \Delta P, \tag{2.6a}$$

$$h_2 = b_1 \Delta T + b_2 \Delta\mu + b_3 \Delta P, \tag{2.6b}$$

$$h_3 = c_1 \Delta P + c_2 \Delta\mu + c_3 \Delta T, \tag{2.6c}$$

where a_i, b_i and c_i are system-dependent coefficients. For binary fluid mixtures the physical fields are pressure P, temperature T, chemical potential μ_1 of the solvent and chemical-potential difference $\mu_{21} = \mu_2 - \mu_1$, where μ_2 is the chemical potential of the solute. Hence, for a binary liquid mixture near a critical mixing point the scaling fields are [114–116]:

$$h_1 = a_1 \Delta\mu_1 + a_2 \Delta T + a_3 \Delta P + a_4 \Delta\mu_{21}, \tag{2.7a}$$

$$h_2 = b_1 \Delta T + b_2 \Delta\mu_1 + b_3 \Delta P + b_4 \Delta\mu_{21}, \tag{2.7b}$$

$$h_3 = c_1 \Delta P + c_2 \Delta\mu_1 + c_3 \Delta T + c_4 \Delta\mu_{21}, \tag{2.7c}$$

with $\Delta\mu_1 = \mu_1 - \mu_{1c}$ and $\Delta\mu_{21} = \mu_{21} - \mu_{21c}$.

Equations (2.6) imply that the difference between the liquid and vapor densities along the phase boundary below the critical temperature is proportional to $|\Delta T|^{\beta}$, while the average of the vapor-liquid densities, referred to as the coexistence-curve diameter, contains two singular contributions, namely one proportional to $|\Delta T|^{2\beta}$ and another one proportional to $|\Delta T|^{1-\alpha}$ [107, 110–113]. For many years only two physical fields, namely $\Delta\mu$ and ΔT, were considered to contribute to the scaling fields in (2.6a) and (2.6b) leading to a contribution proportional to $|\Delta T|^{1-\alpha}$ in the coexistence-curve diameter. This choice, referred to as "revised scaling" was based on the symmetry properties of various decorated lattice models showing this type of mixing [117–119]. However, to completely account for vapor-liquid asymmetry, all three physical fields must be included in the definition to the scaling fields, as given by (2.6). In a similar manner, complete scaling for binary mixtures in accordance with (2.7) yields contributions proportional to $|\Delta T|^{2\beta}$ and $|\Delta T|^{1-\alpha}$ in the coexistence-curve diameter for the concentration in the two phases in nearly incompressible

liquid mixtures [114–116]. The importance of the presence of a term proportional to $|\Delta T|^{2\beta}$ in the coexistence-curve diameters has only been appreciated rather recently. In the past the presence of a term proportional to $|\Delta T|^{2\beta}$ was considered an artifact due to an "incorrect" choice of the order parameter [66].

2.2 Experimental Information

Subsequent to the experimental results reviewed at the conference in Cargèse [39], many investigators have continued to report experimental values for the exponent α [120–130], the exponent β [120, 131–156], and for the correlation-function exponents γ and ν [126, 133–135, 148, 151, 152, 155, 157–161]. We have quoted here the references available to us, but it would be difficult to give a complete list. Anisimov and Thoen [162] have recently reviewed experimental estimates of the critical exponent α, and they conclude that all experimental data are consistent with the value for α quoted in (2.5).

Experiments in one-component fluids near the vapor-liquid critical point are complicated by gravitationally induced density gradients, but these can be avoided or minimized by optical techniques. In liquid mixtures homogeneity is more easily obtained because the mass diffusion coefficient is very small. In heat-capacity experiments in one-component fluids gravity effects do provide a challenge [46]. To avoid such gravity effects, Haupt and Straub [125] have performed heat-capacity experiments under low-gravity conditions in space. They found $\alpha = 0.1105^{+0.025}_{-0.027}$ for sulfur hexafluoride. This is believed to be the most accurate experimental estimate of the critical exponent α. A review of critical-phenomena experiments in microgravity, and also of experimental ground-based information for He^3, has been recently presented by Barmatz et al. [163].

It would be difficult to quote "best" experimental values for all critical exponents as the values reported in the literature show some spread. Moreover, the accuracy of experimentally determined exponents depends not only on the accuracy of the property measured, but also on assumptions that may have been made to account for corrections mentioned above or for noncritical background effects. The consensus is that all reliable measurements for fluids and fluid mixtures are consistent with asymptotic critical behavior with the exponent values for Ising-like systems in (2.5). This is also true for critical phase separation in polymer solutions [164–172], although in that case an additional crossover from asymptotic Ising behavior to tri-critical theta-point behavior has been observed [173–175].

A few investigators have challenged the hypothesis of universal asymptotic Ising critical behavior in fluids. Shimanskaya and coworkers [176–179] have reported values for the critical exponent β for a number of one-component fluids that vary from 0.341 to 0.355. In view of the complexity of corrections discussed earlier, and results obtained by other investigators [115] for some of the same fluids, we believe that the small error estimates claimed by the authors are unrealistic. Fameli and Balzarini [180] have reported an asymptotic experimental exponent value $\beta = 0.367 \pm 0.006$ for the coexistence curve of a solution of n-heptane in nitrobenzene near the critical point of mixing. The experimental method employed has demonstrated a capability of yielding accurate determinations of the exponent β [24, 51, 132–134]. However, for this mixture the density difference of the two liquid components is substantial and, hence, it is possible that at reduced temperatures smaller than 10^{-4} the experiments may have been affected by gravity effects of the type to be described below. Another possible cause could be the presence of a small impurity. On balance, the experimental evidence for universal Ising-like critical behavior is overwhelming.

2.3 Gravity Effects Near the Vapor-Liquid Critical Point

Wagner and coworkers [181–183] have reported P-ρ-T measurements very close to the critical point of SF_6 and CO_2 with a specially designed multi-cell apparatus. The experiments were conducted with great care and the authors claim that the critical exponents approach classical values at reduced temperatures $t \equiv (T - T_c)/T \leq 10^{-4}$. A similar crossover behavior to classical exponents has been reported for SF_6 by Ivanov and coworkers [184–187]. On the other hand, experiments in microgravity have clearly demonstrated that SF_6 does exhibit asymptotic Ising critical behavior [125, 183, 188]. Hence, the deviations from asymptotic Ising behavior, if real, must be attributed to the presence of the gravitation field in ground-based experiments [189]. A serious problem is that the experimental results of Wagner and coworkers and of Ivanov and coworkers appear to disagree with the results of optical experiments of Cannell [45] and of Hocken and Moldover [30] in the same close vicinity of the critical point, suggesting that the observed deviations may depend on the experimental method employed.

One needs to distinguish between two types of gravity effects. First there is the well-known phenomenon that gravity induces a density gradient, so that experiments measure properties over a range of densities depending on the height of the sample [26, 190]. We refer to such gravity effects on the experimental observations as extrinsic gravity effects. Wagner and coworkers did apply a correction to their measurements for such extrinsic gravity effects. In addition very close to the critical point intrinsic gravity effects will appear, since the inhomogeneity induced by gravity becomes so strong that the growth of the correlation length becomes suppressed [26]. Theoretical estimates [26, 190] suggest that such intrinsic gravity effects would appear at temperatures somewhat closer to the critical temperature than observed by Wagner and coworkers and by Ivanov and coworkers.

Ivanov [187] has suggested an analogy between the effect of gravity near the critical vapor-liquid critical point and the effect of shear on critical liquid-liquid phase separation in binary mixtures. According to Onuki and coworkers [191–193] the renormalization-group theory predicts that application of a strong shear gradient will suppress the critical fluctuations so that the critical power laws become of the classical mean-field type. And indeed classical exponents have been observed experimentally in a binary liquid near the critical mixing point subjected to strong shear by Beysens et al. [194, 195], but with an apparent critical temperature that is lower than the critical temperature in the absence of shear. However, shear is a dynamic field and the crossover to classical critical behavior is governed by a competition between the shear rate and the relaxation time of the critical fluctuations. On the other hand, the gravitational field is a static field that directly couples to the order parameter. Hence, the validity of the analogy is not evident.

A rather detailed analysis of the effects of gravity on the susceptibility and the correlation length near the vapor-liquid critical point has been made by van Leeuwen and Sengers on the basis of a squared-gradient theory [196–201]. They predicted that the susceptibility will increase less rapidly than the theoretical Ising-like power law reaching a *finite* value at the critical temperature. In addition they found a smooth transition from an interfacial density profile to a gravitationally induced density profile above the critical temperature over a (small) range of temperatures, so that in the presence of gravity one no longer can identify a specific temperature associated with the appearance or disappearance of a meniscus. Thus gravity causes a rounding of the critical phase transition as was also noted by Kawasaki et al. [202]. Hence, the implicit experimental assumption of Wagner et al. [181] that the pressure-versus-density isotherm should have a zero slope at the critical temperature needs to be reconsidered. The susceptibility, and hence the compressibility, is expected to

Table 2 Experimental values for the exponent η

Year	Exponent η	Substance	Method[a]	Reference
1971	0.074 ± 0.035	carbon dioxide	L.S.	[203]
1972	0.08 ± 0.01	aniline + cyclohexane	L.S., TUR.	[204]
1972	0.06 ± 0.03	nitrobenzene + hexane	L.S.	[205]
1973	0.06 ± 0.06	helium^4	L.S.	[206]
1974	0.11 ± 0.03	neon	N.S.	[207]
1974	0.055 ± 0.010	nitrobenzene + hexane	L.S.	[208]
1974	0.10 ± 0.05	argon	X.S.	[209]
1975	0.03 ± 0.03	sulfur hexafluoride	L.S.	[45]
1976	0.017 ± 0.014	nitroethane + 3-methylpentane	L.S.	[36, 37]
1977	0.03 ± 0.03	argon	X.S.	[210]
1979	0.045 ± 0.010	nitrobenzene + hexane	L.S.	[64]
1980	0.03 ± 0.02	argon	X.S.	[211]
1980	0.086 ± 0.026	isobutyric acid + D_2O	L.S., N.S.	[212]
1986	0.039 ± 0.009	deuterated isobutyric acid + D_2O	N.S.	[213]
1989	0.03 ± 0.03	perfluoromethyl-cyclohexane + heptane	X.S.	[214]
1989	0.030 ± 0.0015	sodium + ND_3	N.S.	[215, 216]
1998	0.03 ± 0.01	ethylammonium nitrate + deuterated octanol	N.S.	[217]
2004	0.041 ± 0.005	methanol + cyclohexane	TUR.	[161]
1988	0.032 ± 0.013	isobutyric acid + H_2O	L.S.	this paper

[a]L.S. = light scattering, N.S. = neutron scattering, X.S. = X-ray scattering, TUR. = turbidity

be directly related to the slope of the density as a function of height. The temperature dependence of this slope in the presence of gravity is shown in Fig. 4 of Ref. [198]. This slope remains finite at the critical temperature. However, upon further lowering of the temperature the slope, and hence the susceptibility, continues to increase and should become infinite at a temperature where a sharp interface between the vapor and liquid phases will appear. Thus the observation that the susceptibility becomes infinite is in principle not in contradiction with the squared-gradient theory, but it should occur at a temperature somewhat below the thermodynamic critical temperature. For a resolution of this problem additional theoretical studies of the effect of gravity and further careful analysis of the experimental information will be needed.

2.4 Critical Exponent η

The correlation-function exponent η has been the most elusive exponent [101] providing a challenge to experimentalists, in particular, to definitively conclude that $\eta > 0$. A list of reported experimental values is presented in Table 2. Here we give the error estimates quoted by the authors, though they may not always be realistic. In a review of phenomenological scaling functions for critical scattering, Tracy and McCoy [218] concluded in 1975 that *no experiment to date unambiguously and directly establishes that the critical exponent η is greater than zero*. A review of Goldburg in 1983 [219] focused on the results of Cannell [45] and of Chang et al. [36, 37]. As discussed in Sect. 1, by that time a consensus had developed that fluids belong to the universality class of Ising-like systems and should have a non-zero exponent η.

The exponent η, or more precisely the exponent $2 - \eta$, characterizes the shape of the structure factor associated with the order parameter for large values of $q\xi$. Such large values of $q\xi$ can be probed experimentally by small-angle neutron scattering or by small-angle X-ray scattering. However, care must be taken that the experiments are done sufficiently close to T_c so that the correlation length, ξ, has attained its asymptotic power-law behavior. Non-asymptotic behavior in ξ can severely affect the estimated value of η [207, 209–211]. For accurate neutron-scattering experiments, it is imperative that deuterium molecules replace hydrogen molecules. For example, the neutron-scattering measurements of Schneider et al. in isobutyric acid water + D$_2$O [212] revealed behavior of a ternary mixture due to incomplete replacement of H by D [220]. The results of two neutron-scattering experiments deserve special attention. The first is the value $\eta = 0.039 \pm 0.009$ found by Schwahn et al. [213] for deuterated isobutyric acid +D$_2$O and the second is the value $\eta = 0.030 \pm 0.0015$ found by Damay et al. [215, 216] for an exotic mixture of sodium and deuterated ammonia. While it may be difficult to judge the reliability of the error estimates presented, these are clearly the two most accurate experimental values obtained for the exponent η.

With optical experiments it is much more difficult to probe the structure factor for large $q\xi$. Hence, in optical experiments the exponent $2 - \eta$ is primarily obtained from the ratio of the experimental values of γ and ν, making it more difficult to obtain an accuracy that would be competitive with that obtained from reliable neutron-scattering experiments. From the information presented in Table 2 it is difficult to determine the best value of η from optical experiments. Several optical experiments have yielded a value slightly larger than 0.03 [64, 161, 208], while Chang et al. with the light-scattering apparatus in our laboratory found a value slightly smaller than 0.03 [36, 37]. For this reason we continued to pursue accurate measurements of the correlation-function exponents with our light-scattering facility in experiments conducted some time ago [221]. We use this opportunity to report the values of the critical exponents deduced from our measurements, since they have not been previously published.

3 Light-Scattering Experiment for Isobutyric Acid + Water

3.1 Experimental Method

The intensity of scattered light is directly proportional to the isomorphic susceptibility $\chi_1(q)$. Hence, measuring the light scattering intensity as a function of temperature along the critical concentration in the one-phase region, where complete-scaling corrections are not important and the thermal field $h_2 = \Delta T \equiv T - T_c$, provides an excellent method for determining the correlation-function exponents.

In our experiments the intensity of scattered light was measured in a mixture of isobutyric acid + water, with a slightly improved version of the experimental apparatus used previously in our laboratory for studying light scattering in a mixture of trimethylpentane + nitroethane [37]. A schematic representation of the optical arrangement, designed to obtain highly accurate scattering data at a scattering angle $\theta = 90°$, is shown in Fig. 1. The light source is a 5-mW He-Ne laser whose output polarization was perpendicular to the plane determined by the incident beam and the direction in which the scattered light was observed. The incident light, after passing through an intensity stabilizer, was focused at the center of the sample cell. A special provision was made to measure the incident and scattered intensities with the same photodetection system. For this purpose, a few percent of the incident
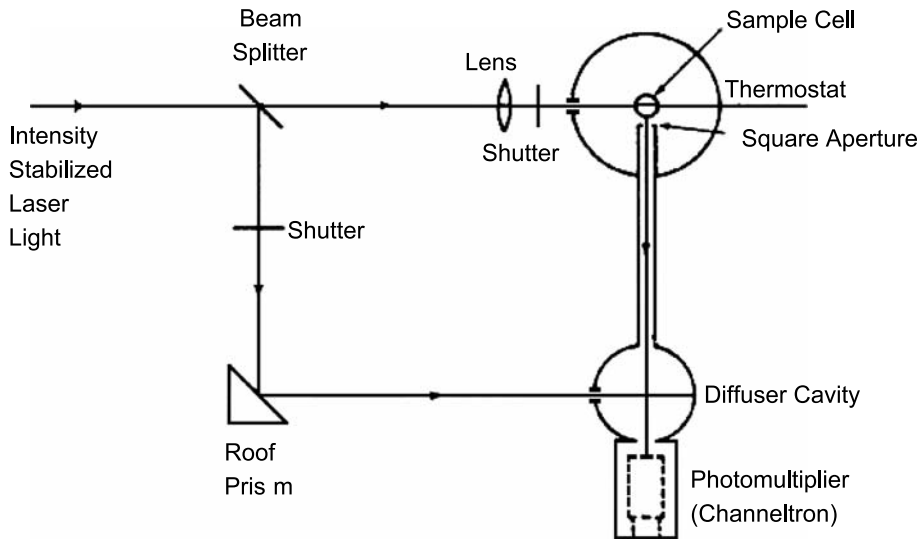
Fig. 1 Schematic representation of optical arrangement [37]

light was reflected at 45° by a beam splitter, whose intensity was further reduced to a level comparable with that of the incident light by having it pass through a diffuser cavity. The correlation functions of the photons received by the photomultiplier tube were analyzed by a photon-counting system that had been built by Burstyn [222]. Optical shutters, installed in both the path of the incident beam and the reference beam, enabled us to measure the scattered and reference light alternately during each experimental run. In addition we also measured the intensity of the transmitted beam relative to the intensity of the reference beam to determine the turbidity of the sample as a function of temperature.

Resolving the asymptotic critical behavior of the scattered intensity requires precise temperature control and measurement. For this purpose the sample was enclosed in an oven with three temperature-controlled "shells". Furthermore, to shield the sample optics and sensitive electronics from temperature variations, the top of the optical table was enclosed in a styrofoam box with the air temperature within the box maintained at about one degree below T_c, so as to provide a constant heat sink for the oven containing the sample. The sample temperature was measured with a Hewlett-Packard quartz crystal thermometer embedded in the inner shell of the sample oven. The temperature could be measured with a resolution of about 10 μK and the temperature stability was about ±20 μK for the duration of a single measurement, lasting between 2 and 8 hours. Further experimental details are provided in the thesis [221].

The optical cell was filled with isobutyric acid and water with the critical concentration of a mole fraction of 0.115 isobutyric acid by the research group of Greer, who had considerable experience with this liquid mixture [33, 223, 224] using a procedure described by Morrison and Knobler [225]. The scattering wave number probed is related to the incident wave number q_0 as $q = 2q_0 \sin(\theta/2)$ with $q_0 = (2\pi/\lambda_0)n$. In our experiment the wavelength of the laser light is $\lambda_0 = 632.8$ nm, while the refractive index n of the isobutyric acid + water mixture can be represented as $n = n(T_c)[1 + B_n \Delta T]$ with $n(T_c) = 1.377$ and $B_n = -1.838 \times 10^{-4}$ K^{-1} [142, 221].

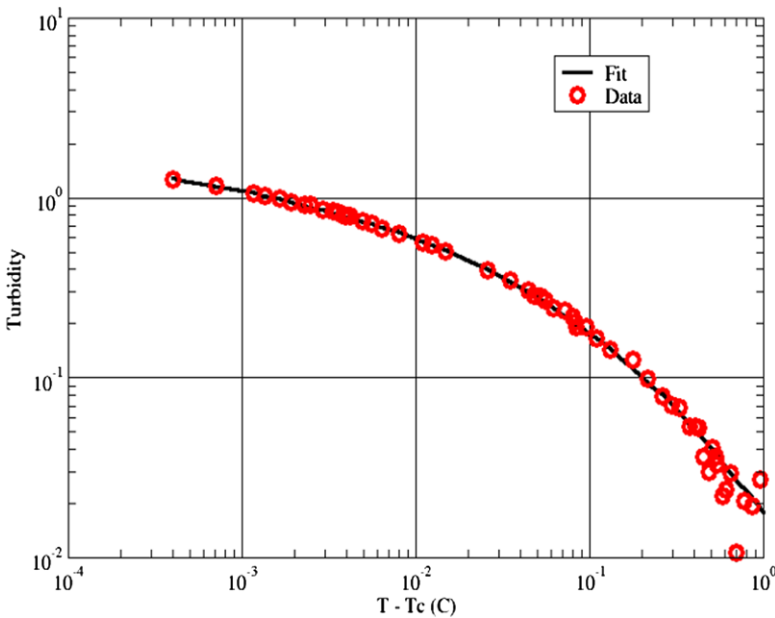**Fig. 2** Turbidity τ of isobutyric + water as a function of $\Delta T = T - T_c$. The *symbols* indicate the experimental data. The *curve* represents the values calculated from (3.2)

3.2 Experimental Results

The original experimental data are contained in a Ph.D. thesis [221]. The analysis of the experimental data to be presented below was completed in 1988, but has not yet been previously published.

3.2.1 Turbidity

In order to correct the light-scattering intensities for turbidity this property was also measured. Our measurements yield relative turbidities as a function of temperature. To convert these relative turbidities into absolute turbidities τ we matched our relative turbidity with the value $\tau = 0.005$ cm^{-1} predicted by Hamano et al. [226] at $T = T_c + 3$ K. The turbidity is sufficiently small at this temperature so that our experimental absolute turbidities are insensitive to this reference choice. The experimental turbidities are plotted as a function of temperature in Fig. 2. In terms of the dimensionless reduced temperature variable

$$t = \frac{T - T_c}{T},\tag{3.1}$$

we represent the turbidity as a function of temperature by an equation of the form:

$$\tau(t) = \frac{8}{3}\pi A[1 + B_x \Delta T]t^{-\gamma} H(q_0 \xi),\tag{3.2}$$

where A is a coefficient to be determined from a fit to the experimental data and where the function $H(z)$ is given by [227]

$$H(z) = \frac{3}{64z^6}[(8z^4 + 4z^2 + 1)\ln(1 + 4z^2) - 4z^2(1 + 2z^2)], \tag{3.3}$$

with the correlation length ξ represented by its asymptotic power law

$$\xi = \xi_0 t^{-\nu}. \tag{3.4}$$

Equation (3.2) differs from the one proposed by Puglieli and Ford [227] in that we have added a correction term $B_x \Delta T$ with $B_x = -0.0111$ K^{-1} to account for a small temperature dependence of the scattering cross-section [221]. Fixing tentatively the exponent values $\gamma = 1.239$ and $\nu = 0.630$, we found that (3.2), with $A = 1.83$ cm^{-1}, $\xi = 0.361$ nm, and

$$T_c = (299.75164 \pm 0.00006) \text{ K}, \tag{3.5}$$

represents the turbidities within experimental accuracy, as shown in Fig. 2.

3.2.2 Light Scattering

The intensity of the scattered light is proportional to $\chi_1(q) = \chi_1(0)g(q\xi)$ which asymptotically close to the critical point becomes

$$\chi_1(q) \approx \Gamma_0 t^{-\gamma} g(q\xi), \tag{3.6}$$

with the asymptotic power law (3.4) for the correlation length ξ. The correlation function $g(y)$ in (3.6) can be represented by an approximant proposed by Fisher and Burford [103]:

$$g(y) \simeq g_{\text{FB}}(y) \equiv \frac{(1 + \psi^2 y^2)^{\eta/2}}{1 + y^2(1 + \frac{\eta}{2}\psi^2)} \tag{3.7}$$

with $\psi = 0.084$ for a cubic lattice. For small values of y (3.7) reduces to the Ornstein-Zernike form

$$g(y) \simeq g_{\text{OZ}}(y) \equiv \frac{1}{1 + y^2}. \tag{3.8}$$

We have measured the (relative) intensity I of the scattered light as a function of temperature from a temperature of 7 K above T_c down to 0.4 mK above T_c with an accuracy of about 0.1%. Figure 3 shows the intensity as a function of $\Delta T = T - T_c$. The experimental light-scattering data are represented by an equation of the form [37]

$$I = I_0 e^{-\tau L}\{(1 + B_x \Delta T)(1 + Re^{-\tau L})t^{-(2-\eta)\nu}(1 + \Gamma_1 t^{\Delta_1})(1 + \widehat{I}^{(2)})g(q\xi) + \Delta I\}, \quad (3.9)$$

where $L = 0.3$ cm is the optical path length, $R = 0.083$ a reflection coefficient, and ΔI a non-critical background contribution to the observed intensity. In this equation we have incorporated a factor $1 + \Gamma_1 t^{\Delta_1}$ with $\Delta_1 = 0.51$ to account for a small correction-to-scaling contribution to the susceptibility at temperatures farther away from T_c. The term $\widehat{I}^{(2)}$ in (3.9) accounts for the intensity from doubly scattered light and is given by (2.12) in a previous publication [228], except that a factor $\sin\theta$ in that equation needs to be deleted as has been noted by Frisken et al. [229]. The validity of our analytic solution for double scattering has been confirmed by computer simulations of multiple scattering [230].

Fig. 3 Light-scattering intensity ($\theta = 90°$) of isobutyric acid + water as a function of $\Delta T = T - T_c$
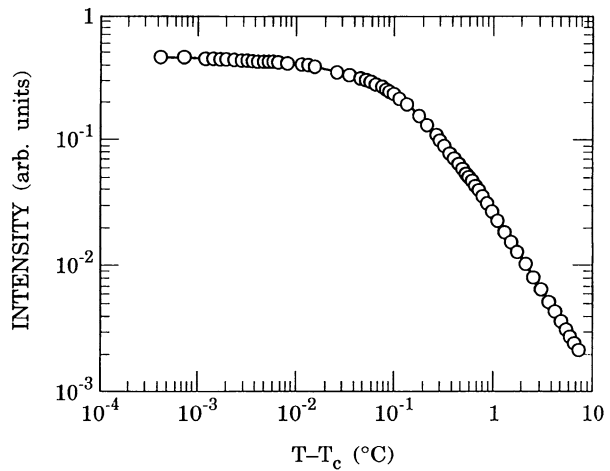

**Table 3** Critical exponents and critical amplitudes for isobutyric acid + water

Parameter	Value	σ
ν	0.629	0.003
η	0.032	0.013
γ	1.238[a]	0.012[a]
ξ_0	0.364 nm	0.007 nm
Γ_1	-0.7	0.5

[a]Deduced from $\gamma = (2 - \eta)\nu$

Equation (3.9) has been used to fit the experimental data with as adjustable parameters the two critical exponents γ and η or, equivalently γ and ν, the two critical amplitudes, ξ_0 and Γ_1, and the two instrumental constants I_0 and ΔI. We could have included an amplitude ξ_1 for a correction-to-scaling contribution to the correlation length, but generally addition of free parameters did not appear to yield significant improvements of the fits. It turns out that the double-scattering contribution increases to about 10% at $\Delta T = 11$ mK. Hence, in the analysis we only included data with $\Delta T > 0.011$ K which correspond to $y < 5.3$. Having determined the value of the critical temperature accurately from the turbidity measurements, we kept T_c fixed in all fits at the value given by (3.5).

In fitting (3.9) we considered both the FB approximant (3.7) and the OZ approximant (3.8) for $g(q\xi)$. However, in the range of $q\xi$ values covered by our experimental data, use of the FB approximant did not yield an improvement of the fit. The values deduced for the critical exponents and the critical amplitudes with their standard deviation σ are presented in Table 3. The errors in the critical exponents are strongly correlated as a result of the exponent relation $\gamma = (2 - \eta)\nu$. To elucidate this correlation we show in Fig. 4 contour plots in the γ versus ν plane corresponding to 68% (σ) and 95% (2σ) confidence intervals around the central values $\gamma = 1.2378$ and $\nu = 0.6291$. Our experimental critical-exponent values are in excellent agreement with the theoretical values (2.5) for Ising-like systems. In Fig. 4 we also show the result when we impose the condition $\gamma = 2\nu$. Our experimental results cannot be reconciled with a zero value for the exponent η. Our value $\xi_0 = (0.364 \pm 0.007)$ nm is in good agreement with the value $\xi_0 = (0.362^5 \pm 0.013)$ nm found by Beysens et al. [57] for isobutyric acid + water. We note that our data imply a negative value for the correction-to-scaling amplitude Γ_1. Negative values for the correction-to-scaling amplitudes have also

Fig. 4 Contour plots corresponding to 68% and 95% confidence intervals around the central values 1.2378 and 0.6291 for the exponents γ and ν
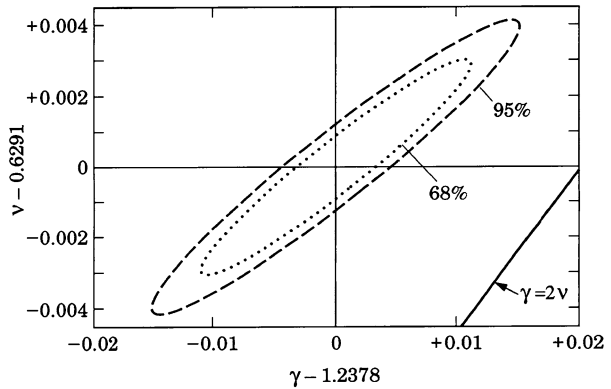
been found by other investigators for aqueous and ionic solutions [54, 145, 146, 231–234]. We now know that this is a general feature for aqueous electrolyte solutions and many other ionic solutions [235], as will be further discussed below.

4 Non-asymptotic Critical Exponents

After Fisher had elucidated the asymptotic critical power laws at the Conference on Critical Phenomena in 1965 [9], Debye [236] made the following remark: *I would like that the theoretical people tell me when I am so and so far away from the critical point, then my curve should look so and so.* In other words, to represent actual experimental data one also needs a theory for non-asymptotic critical behavior. A suitable way to characterize non-asymptotic critical behavior is obtained by considering effective critical exponents. For instance, to represent the non-asymptotic temperature dependence of the susceptibility one introduces an effective susceptibility exponent such that [237]:

$$\gamma_{\text{eff}} \equiv -d \log \chi_1 / d \log t. \tag{4.1}$$

In the Ising critical limit, $\gamma_{\text{eff}} \simeq 1.238$, while $\gamma_{\text{eff}} = 1$ in the mean-field critical limit. A theory for the crossover behavior of effective critical exponents from their Ising value to their mean-field value has been presented by Anisimov et al. [238, 239]. This theory is based on a non-asymptotic theory of critical behavior earlier developed by Chen and coworkers [240, 241]. One starts from the observation that the isomorphic Ising Helmholtz energy $\Phi = -(h_3 - h_1 \varphi_1)$ has, in the classical mean-field limit, an expansion that can be written in the form [116]:

$$\Phi_{\text{cl}} \approx \frac{1}{2} h_2 \varphi_1^2 + \frac{1}{4!} u^* \overline{u} \Lambda \varphi_1^4. \tag{4.2}$$

In (4.2) $\overline{u}$ is a rescaled coupling constant related to the strength and range of the molecular interactions, $u^* = 0.472$ a fixed-point coupling constant for Ising-like systems [241–243], and Λ a dimensionless cutoff wave number for critical fluctuations. Inspired by renormalization-group-theory results of Nicoll et al. [244–246], Chen et al. [241] have formulated a procedure to transform (4.2) into an expression for a renormalized potential Φ_r such that asymptotically close to the critical point Φ_r incorporates asymptotic Ising critical behavior, while away from the critical point Φ_r approaches the classical expansion (4.2). A detailed description of the procedure can be found in several publications
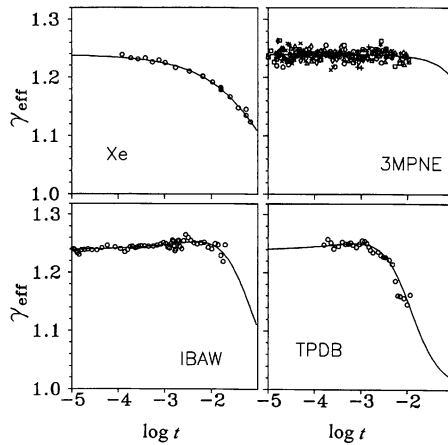
Fig. 5 Effective susceptibility exponent γ_{eff} as a function of the reduced temperature difference t for the one-component fluid Xe, for the molecular liquid mixture 3MPNE, for the aqueous electrolyte solution IBAW, and for the nonaqueous ionic solution TPDB. The *symbols* indicate values obtained by numerical differentiation of the original experimental data for Xe [56], for 3MPNE [37, 221], for IBAW [221], and for TPDB [251]. The *curves* represent values calculated from the theoretical equation for the nonasymptotic critical behavior of the susceptibility. Adapted from Anisimov et al. [250]

[238, 241, 247–249]. The inverse susceptibility χ_1^{-1} is obtained as the second derivative of Φ_r with respect to the order parameter φ_1. Along the critical isochore in the one-phase region of one-component fluids and along the critical isopleth in the one-phase region of partially miscible liquid mixtures, the thermal field h_2 can be approximated by the reduced temperature variable t and one can obtain an explicit non-asymptotic equation for the susceptibility as a function of temperature [249, 250]. Monte Carlo simulations of the susceptibility of the 3D Ising model for various values of the coupling constant $\overline{u}$ have confirmed the validity of the theory for crossover critical behavior [249].

In Fig. 5 we show the effective susceptibility exponent γ_{eff} as a function of temperature along the critical isochore of a one-component fluid (Xe) and along the critical isopleth of three different types of liquid mixtures, namely, the molecular liquid mixture 3-methylpentane + nitroethane (3MPNE), the aqueous electrolyte solution isobutyric acid + water (IBAW), and the nonaqueous ionic solution tetra-*n*-butylammonium picrate + (0.75/0.25) 1, 4-butanediol/1-dodecanol (TPDB), as reported by Anisimov et al. [250]. The symbols indicate the values obtained from a numerical differentiation of the experimental data for Xe [56], for 3MPNE [37, 221], for IBAW[221], and for TPDB [251]. The curves represent the values calculated from the theoretical crossover equation for the susceptibility. The shape of these curves depends on the two physical parameters: Λ and $\overline{u}$. They were deduced from the experimental data, including the experimental data for isobutyric acid + water discussed in Sect. 3.2, with the critical exponents fixed at their theoretical Ising values. The correction-to scaling amplitude Γ_1 is proportional to $1 - \overline{u}$ [242, 248, 249]. For a molecular fluid, like Xe, $\overline{u}$ is smaller than unity: γ_{eff} decreases monotonically with temperature from its limiting Ising value 1.238. The value $\gamma_{eff} = 1$ is never reached in practice, since at the temperatures where critical fluctuations have become insignificant one is also outside the region of asymptotic classical critical behavior. For 3MPNE, $\overline{u} \simeq 1$so that $\Gamma_1 \simeq 0$, and the temperature range of asymptotic Ising critical behavior is large. For the aqueous electrolyte solution IBAW, and for the non-aqueous ionic fluid TPDB, $\overline{u}$ is larger than unity:

the correction-to-scaling amplitude Γ_1 is negative and the crossover behavior becomes non-monotonic. Such non-monotonic crossover behavior has been observed in all aqueous electrolyte solutions and also in many non-aqueous ionic solutions [235]. For molecular fluids the cutoff wave number Λ corresponds to a microscopic length scale of the order of $v_0^{1/3}$, where v_0 is the molecular volume [248]. For polymer solutions Λ is directly related to the inverse of the radius of gyration of the polymer molecules [173, 252]. It appears that in some ionic solutions the cutoff wave number that characterizes the non-asymptotic critical behavior indicates the emergence of a mesoscopic length scale [235]. However, the physical origin of this mesoscopic length scale and the associated supra-molecular structure is not yet clear [85]. To further clarify this issue, additional studies of the non-asymptotic critical behavior of the susceptibility for both solvo-phobic and Coulombic ionic solutions would be desirable [81, 82, 100, 253, 254].

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