Light scattering near a double critical point: Evidence for crossover behavior

B. V. Prafulla, T. Narayanan, and A. Kumar*
Department of Physics, Indian Institute of Science, Bangalore 560 012, India
(Received 22 July 1991)

We report measurements of osmotic compressibility in a quasibinary liquid mixture of 3-methylpyridine, water, and heavy water. The measurements probed the lower consolute point (T_L) for samples of varying loop sizes (ΔT). An *exact* doubling of the critical exponent (γ) was observed over the *entire* experimental temperature range ($T_L - T$) for a sample with ΔT as small as 250 mK. For intermediate ΔT's ($22 \geq \Delta T \geq 1$ °C), a smooth crossover from the double (2γ) to the single exponent (γ) was noticed, as t [$=|(T_L-T)/T_L|$]$\rightarrow 0$. The universal value of γ ($=1.24$) was recovered for experimental paths terminating in T_L for any ΔT, provided the field variable used was t_{UL} [$=|(T_U-T)(T_L-T)/T_U T_L|$] instead of t. This field variable (t_{UL}) follows naturally from the geometrical picture as well as the Landau-Ginzburg theory, as applied to the reentrant phase transitions.

PACS number(s): 64.60.Kw, 64.70.Ja

Among the diverse systems exhibiting the phenomenon of reentrant phase transitions (RPT), the quasibinary liquid mixtures are a prime example [1–5]. In these liquid mixtures, reentrance is manifested by a closed-loop miscibility curve with upper and lower consolute points (T_U and T_L), respectively. The two-phase region in these systems is represented by the loop size ($\Delta T = T_U - T_L$) and the double critical point (DCP) is signified by the limit $\Delta T = 0$. When ΔT is sufficiently large, three-dimensional Ising-like behavior near a T_U or T_L is well understood [6–8].

So far, the research efforts concerning RPT (in quasibinary liquid mixtures) were directed at observing an increase [1–5] in the critical exponent (CE) from its Ising value (near T_U or T_L) as ΔT was suppressed. In the vicinity of the DCP ($\Delta T \rightarrow 0$), a near doubling of the Ising-like CE's was noticed [1–3,5]. The doubling of the CE's is the pivotal finding of the lattice-gas calculations [9,10] (for reentrant miscibility) and the geometrical picture of phase transitions [2,11].

In this paper we not only intend to demonstrate an *exact* doubling of the CE but also scrutinize the approach to double criticality. An additional goal is to recover the universal CE for any ΔT, by employing an alternate field variable to the one commonly used i.e., t [$=|(T_C-T)/T_C|$], where T_C is T_L or T_U.

Light-scattering studies were performed [to deduce the osmotic compressibility (χ_T)] in the quasibinary liquid mixture: 3-methylpyridine (MP), water (W), and heavy water (HW). The samples were prepared using appropriate quantities [12] of MP (99% Aldrich), HW (isotopic purity 99.6%, BARC, India) and triple distilled W prepared in an all-quartz distiller. Determination of the correct critical composition x_c of MP (as guided by the equal volume criteria) for any ΔT is of vital consideration in the preparation of these samples. For instance, x_c (referred to T_L) increases from 0.29 ($\Delta T = 77.5$ °C) to 0.32 ($\Delta T = 0.25$ °C). The ratio of quantity of HW in (HW+W), defined as X, controls ΔT. The coordinates [12] of the DCP are $X_D = 0.1715$ and $T_D = 76.65$ °C. In the earlier investigations [1–5], the closeness to the DCP was marked by samples of $\Delta T \geq 1$ °C, which appeared to be the asymptotic limit. The enormous difficulty in preparing samples of $\Delta T < 1$ °C stems from (i) the parabolic nature [2,12] of the reentrant critical line ($X - T$), (ii) increasing difficulty in obtaining the correct x_c, (iii) the temporal instability [12] of ΔT especially in the limit $\Delta T \rightarrow 0$. After exhaustive trials, we have succeeded in securing a ΔT as small as 250 mK, which we believe to be the physically realizable limit of the access to the DCP.

The light-scattering setup [13] comprises a He-Ne laser ($\lambda = 6328$ Å), a photomultiplier tube (RCA 31034), a photon counter and the associated electronics. The scattered intensity (I_E) is collected at an angle (θ) of 90°. The sample cells were mounted in an air thermostat [13] with a temperature stability of ±3 mK over 6–8 h (in the temperature range of 45–80°C). The temperature is measured with an absolute accuracy of ±60 mK employing a ruggedized thermistor. The necessary precautions for minimizing the local heating of the sample (from intense laser beam), the nonlinearity of the detection system, the mechanical instability of the optics, etc. were taken care of [13].

The incident and transmitted power were monitored (using power meters) at temperatures where I_E was measured to account for the changes in the incident intensity and attenuation of the beam due to increase in turbidity (as $T \rightarrow T_L$), respectively. A typical run encompassed the temperature range $1.5 \lesssim (T_L - T) \lesssim 25$°C and it lasted for 42 h yielding about 40–50 data points. At least two detailed runs were done for ΔT's > 650 mK. All the data were taken in one-phase region as T_L was approached. T_L was determined before and after a given run by the vanishing of the transmitted beam. Data acquisition for $(T_L - T) < 1.5$ °C were avoided to minimize the possible contributions to I_E from multiple scattering. Furthermore, for the phenomenon being studied, the relative weight of $(T_L - T)$ vs ΔT is more important than mere approach to T_L.

The I_E after correcting for turbidity (I_S) was given by

TABLE I. Summary of the data reduction of the scattered intensity using Eq. (2). The uncertainties in A_1, A_2, and ξ_0 are $\lesssim 1\%$. Except for the two limiting cases ($\Delta T = 77.5$ and 0.25 °C), the CE $\gamma_E (=1.24\lambda)$ is an "effective" critical exponent, obtained by force fitting the power law to the entire experimental t range.

T_L (°C)	ΔT (°C)	A_1 ($\times 10^{-2}$)	A_2 ($\times 10^{-5}$)	λ	γ_E	ξ_0 Å	χ^2_ν
38.38±0.01	77.5±0.5	11.721	7.34	1.00	1.24	4.43	1.34
65.36±0.01	22.6±0.02	15.143	18.10	1.16	1.44	6.97	1.93
69.64±0.01	14.02±0.02	10.312	11.61	1.36	1.69	5.58	1.32
72.55±0.01	8.20±0.02	4.604	6.86	1.48	1.84	4.30	0.93
74.59±0.01	4.10±0.02	7.083	3.81	1.72	2.13	3.12	4.42
76.00±0.02	1.30±0.04	2.027	1.54	1.90	2.36	2.04	3.90
76.35±0.02	0.65±0.04	3.019	1.85	1.87	2.32	2.23	1.63
76.53±0.05	0.25±0.10	0.997	0.85	2.00	2.48	1.52	2.15

the relation [8,14]

$$\frac{I_s}{T} = \frac{A t^{-\gamma}}{(1+q^2\xi^2)^{1-\eta/2}} + I_B \ , \qquad (1)$$

where A is the critical amplitude, γ is the CE that describes the divergence in χ and its Ising value [7] is 1.241; I_B is any remnant background intensity: ξ is the correlation length ($\xi = \xi_0 t^{-\nu}$), the Ising values [7] of CE's ν and η being 0.63 and 0.03, respectively. The scattering wave vector q is given by $(4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the mixture and λ is the wavelength of the incident light in vacuum. n was computed at 20 °C using the Lorentz-Lorenz relation as applied to a three-component mixture [15]. The temperature variation of n was estimated assuming [1] a linear decrease of 0.02% per °C.

A nonlinear-least-squares fit program (CURFIT) [16] was used to fit the data. The goodness-of-fit is guided [16] by the minimum in χ^2_ν and the random distribution of residuals. The fit was performed using the following expression:

$$\frac{I_s}{T} = \frac{A_1 t^{-1.24\lambda}}{(1+A_2 t^{-1.26\lambda})^{1-\eta/2}} + A_3 \ , \qquad (2)$$

where $A_1 - A_3$ are the fitting parameters. The term A_3 was discarded, since its retention did not improve the fit and it resulted in an unreasonably small value of λ. Similarly, the need for the extended scaling [6,8] term (Δ) was not found to be compelling. The value of λ corresponding to the minimum in χ^2_ν was deduced by varying λ in small steps (0.005) and T_C was held fixed at its experimental value (slight variation from this value did not alter the best fit λ considerably). Table I indicates the fit parameters for samples of varying ΔT's using Eq. (2). A glaring discrepancy in the data reduction with Eq. (2) was the unacceptably large variation (20–30 %) of λ with the t range used in the analysis. In addition, ξ_0 deduced from the fit shows unrealistic sensitivity to ΔT. The values of λ listed in Table I pertain to the entire experimental t range. Nonetheless, the fit was satisfactory for $\Delta T < 1$ °C ($\lambda = 2$) and for the binary mixture (MP+HW, $\Delta T = 77.5$ °C, $\lambda = 1$), as elucidated in Fig. 1. An *exact* doubling of γ is sustained throughout the experimental t range for $\Delta T = 250$ mK.

Figure 2 illustrates the monotonically decreasing slope (γ_E) for intermediate ΔT's. This *crossover* aspect, coupled with some infirmities of the fit to Eq. (2), led us to adopt a new field variable in lieu of t, the overriding consideration being the recovery of the universal critical behavior in RPT. An alternate way [17,18] to analyze RPT is to take into account the simultaneous approach to the conjugate T_U (or T_L) as a given T_L (or T_U) is probed. This idea can be conveniently translated by using t_{UL} $[=|(T_U - T)(T_L - T)/T_U T_L|]$. The data were then fitted to the following expression:

$$\frac{I_s}{T} = \frac{A'_1 t_{UL}^{-1.24\lambda'}}{(1+A'_2 t_{UL}^{-1.26\lambda'})^{1-\eta/2}} \qquad (3)$$

and the results are listed in Table II.

A striking feature of this method of analyzing the data is the invariance of λ' with ΔT. In other words, the universal value of γ $(=1.24)$ is restored (Fig. 3) even as ΔT varies by 2 orders of magnitude (0.25–22.6 °C). Another appealing aspect of this analysis is that ξ_0 alters randomly with ΔT and its total swing is confined to ±15%—in sharp contrast to the situation when t was used (Table I). However, for the binary mixture the

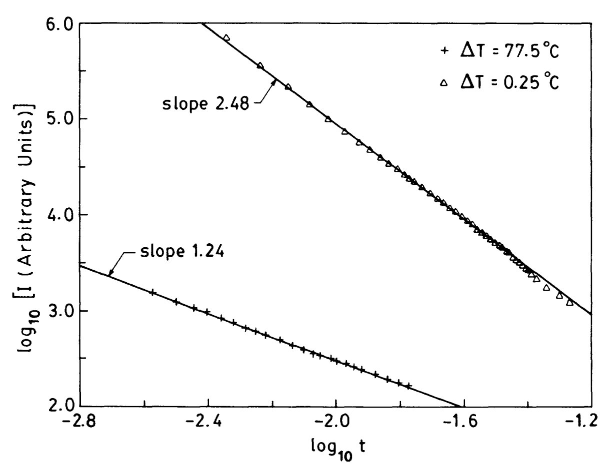

FIG. 1. The normalized scattered intensity (I) vs reduced temperature (t) for the two extreme cases ($\Delta T = 77.5$ and 0.25 °C).

TABLE II. Results of the fitting of the scattered intensity to Eq. (3). The error bars in A'_1, A'_2, and ξ_0 are $\lesssim 1\%$, whereas the uncertainty of $\gamma'_E(=1.24\lambda')$ is assigned by its sensitivity to the t range used in the analysis. A slight lowering of the value of λ' from 1 for some ΔT's could be ascribed to a small off-loading of x_c despite our efforts to correct for it.

T_L (°C)	ΔT (°C)	A'_1 ($\times 10^{-2}$)	A'_2 ($\times 10^{-5}$)	λ'	γ'_E	ξ_0 (Å)	χ^2_ν
38.38±0.01	77.5±0.5	2.247	0.945	0.96±0.01	1.19	1.93	1.46
65.36±0.01	22.6±0.02	1.676	1.450	0.98±0.01	1.22	1.97	0.87
69.64±0.01	14.02±0.02	1.861	1.250	0.99±0.01	1.23	1.83	0.58
72.55±0.01	8.20±0.02	0.929	0.937	1.00±0.01	1.24	1.59	0.53
74.59±0.01	4.10±0.02	3.361	3.813	0.99±0.02	1.23	1.90	2.23
76.00±0.02	1.30±0.04	1.506	1.003	1.00±0.02	1.24	1.64	2.67
76.35±0.02	0.65±0.04	2.597	1.478	0.96±0.01	1.19	1.99	1.52
76.53±0.05	0.25±0.10	0.940	0.778	1.01±0.02	1.25	1.45	2.02

effectiveness of t_{UL} is reduced by the fact that the x_c for T_L differs from that of T_U by about 6%. Thus the experimental path that approached T_L differed considerably from the critical isopleth for T_U. Its consequence was seen in the smaller number (0.96) for λ' (Table II), despite the fact that the fit yielded $\lambda=1$ ($\gamma=1.24$) when analyzed in terms of t (Table I). As in the case of Eq. (2), the fit did not support the inclusion of the extended scaling term (Δ).

The crossover behavior, depicted in Fig. 2, can be rationalized by expanding t_{UL} in terms of t. This provides rich information concerning the approach to double criticality. For instance, $\chi_T=\chi_0 t_{UL}^{-\gamma}$ can be written as

$$\chi_0 t_{UL}^{-\gamma}=\chi_0\frac{T_L}{T_U}\left[t^2+\frac{\Delta T}{T_L}t\right]^{-\gamma}. \qquad (4)$$

It is clear from Eq. (4) that apart from the two limiting cases ($\Delta T=0$ and $\Delta T \gg 1$ °C), both the terms (t and t^2) are important to varying degrees as the relative weights of $|T_C-T|$ and ΔT change. For a given ΔT, the weight of the first term (t^2) recedes with respect to the second term (t) as T_L is approached ($t\to 0$). In a typical experimental t range, a gradual decrease in the CE value to its single limit when *analyzed* in terms of t is expected. Figure 2 emphasizes this behavior. Thus, for moderate ΔT's the phenomenon is essentially a crossover from the doubled CE limit ($t \gg \Delta T$) to a single CE limit ($t \ll \Delta T$).

While the choice of t_{UL} to explain the RPT has been vindicated by the retrieval of the universal CE ($\gamma=1.24$), its genesis can be comprehended both in a fundamental and phenomenological manner. Within the framework of the Landau-Ginzburg theory [17] (as applied to the case of RPT), coefficient a in the free-energy functional transforms from a linear dependence in $|T_C-T|$ to a function of $|(T_U-T)(T_L-T)|$. Moreover, the right-hand side of Eq. (4) can be derived from the geometrical picture of phase transitions [11]. At DCP ($\Delta t=0$), t_{UL} becomes t_D^2, where $t_D=|(T_D-T)/T_D|$. So, the doubled CE persists over any t range [as is also obvious from Eq. (4)]—this special path becomes tangential [2,11] to the parabolic critical line at DCP.

Earlier endeavors [1,19] to recover universal CE's in the RPT invoked the field variables t_D and $|X-X_D|$. However, these variables differed from the actual experimental paths $t_U[=|(T_U-T)/T_U|]$ or t_L

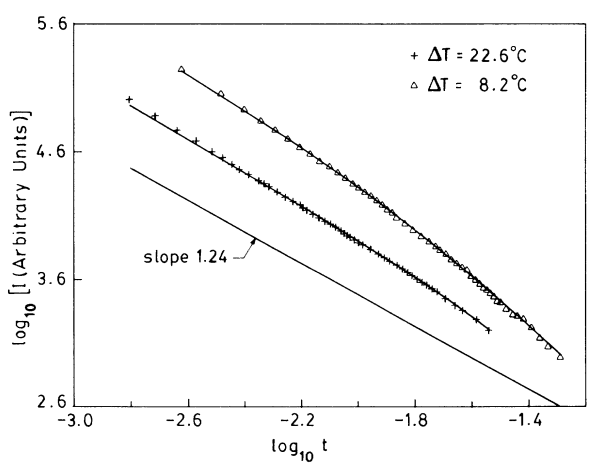

FIG. 2. The crossover feature of critical exponent (γ) for two intermediate loop sizes is displayed. The change of slope of the two curves as ($t\to 0$) is illustrated. The continuous curve is generated by Eq. (3).

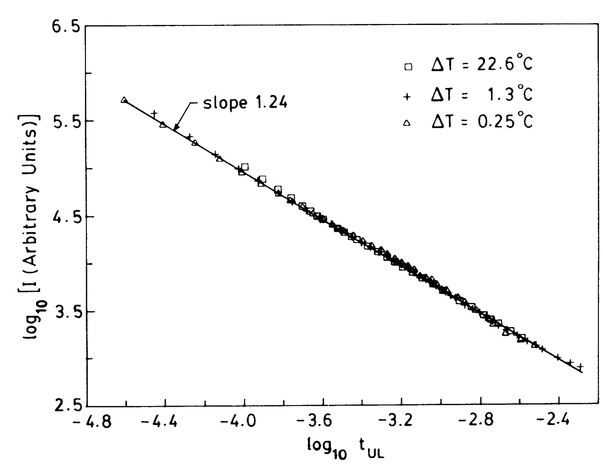

FIG. 3. Double logarithmic plot of the normalized scattered intensity vs t_{UL}, demonstrating the unique and universal critical exponent ($\gamma=1.24$) for three representative loop sizes.

[$=|(T_L-T)/T_L|$] except at the DCP.

The possible breakdown of the quasibinary approximation for this system (MP+W+HW) and the consequent Fisher renormalization [20] of the CE was examined. Based on the analysis of Fisher and Scesney, we estimated [13] the maximum possible enhancement of γ to be less than 0.3% (at least for small t ranges).

To sum up, it is our thesis that the evolution of the critical behavior in a reentrant system ought to be perceived as a crossover from the doubled to single limit of the CE as $t \rightarrow 0$ for a finite ΔT.

We thank E. S. R. Gopal for his keen interest, encouragement, and support for this work. We are grateful to D. Beysens for his invaluable advice in the initial stages of this work. We have benefited from the discussions with E. S. R. Gopal, D. Beysens, P. Guenoun, and A. K. Sood. We also thank P. S. Narayanan and C. K. Subramanian for providing some of the facilities. We are indebted to DAE, IFCPAR, and DRDO for the indispensable financial support for this research. One of us (T.N.) thanks CSIR for support.

*Author to whom correspondence should be addressed.

[1] G. A. Larsen and C. M. Sorensen, Phys. Rev. Lett. **54**, 343 (1985); C. M. Sorensen and G. A. Larsen, J. Chem. Phys. **83**, 1835 (1985).
[2] R. G. Johnston, N. A. Clark, P. Wiltzius, and D. S. Cannell, Phys. Rev. Lett. **54**, 49 (1985), and references cited therein.
[3] V. P. Zaitsev, S. V. Krivokhizha, I. L. Fabelinskii, A. Tsitrovskii, L. L. Chaikov, E. V. Shvets, and P. Yani, Pis'ma Zh. Eksp. Teor. Fiz. **43**, 85 (1986) [JETP Lett **43**, 112 (1986)].
[4] L. A. Davidovich and I. I. Shinder, Zh. Eksp. Teor. Fiz. **95**, 1289 (1989) [Sov. Phys. JETP **68**, 743 (1989)].
[5] T. Narayanan, A. Kumar, and E. S. R. Gopal, Phys. Lett. A **144**, 371 (1990), and references cited therein.
[6] J. V. Sengers and J. M. H. Levelt Sengers, Annu. Rev. Phys. Chem. **37**, 189 (1986); A. Kumar, H. R. Krishnamurthy, and E. S. R. Gopal, Phys. Rep. **98**, 57 (1983).
[7] J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980); J. Phys. (Paris) **50**, 1365 (1989).
[8] W. I. Goldburg, in *Light Scattering near Phase Transitions,* edited by H. Z. Cummins and A. P. Levanyuk (North-Holland, Amsterdam, 1983), p. 531, and references cited therein.
[9] G. R. Andersen and J. C. Wheeler, J. Chem. Phys. **69**, 2082 (1978); **69**, 3403 (1978).
[10] R. E. Goldstein and J. S. Walker, J. Chem. Phys. **78**, 1492 (1983).
[11] A. R. Kortan, H. V. Kanel, R. J. Birgeneau, and J. D. Litster, Phys. Rev. Lett. **47**, 1206 (1981).
[12] T. Narayanan, B. V. Prafulla, A. Kumar, and E. S. R. Gopal, Ber. Bunsenges. Phys. Chem. **95**, 12 (1991).
[13] B. V. Prafulla and A. Kumar (unpublished).
[14] J. Rouch, P. Tartaglia, and S. H. Chen, Phys. Rev. A **37**, 3046 (1988).
[15] D. T. Jacobs, D. J. Anthony, R. C. Mockler, and W. J. O'Sullivan, Chem. Phys. **20**, 219 (1977).
[16] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
[17] A. A. Sobyanin, Usp. Fiz. Nauk **149**, 325 (1986) [Sov. Phys. Usp. **29**, 570 (1986)]; N. P. Malomuzh and B. A. Veytsman, Physica A **168**, 833 (1990).
[18] T. Narayanan, A. Kumar, and E. S. R. Gopal, Phys. Lett. A **155**, 276 (1991).
[19] D. L. Sidebottom and C. M. Sorensen, J. Chem. Phys. **89**, 1608 (1988).
[20] M. E. Fisher and P. E. Scesney, Phys. Rev. A **2**, 825 (1970).