Static and dynamic light-scattering study of a critical ternary mixture: Renormalization of the critical exponents

J. Rouch, A. Safouane, and P. Tartaglia*

*Centre de Physique Moléculaire Optique et Hertzienne, Université de Bordeaux I,
351 Cours de la Libération, 33405 Talence Cédex, France*

S. H. Chen

Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 26 January 1988)

Extensive dynamical light-scattering experiments have been performed on the critical ternary system water, benzene, and ethanol close to its 25 °C plait point. The experimental results show the theoretically expected renormalization of the critical exponents. Furthermore, the critical slowing down of concentration fluctuations is very well accounted for by the Kawasaki mode-coupling theory including background effects.

Renormalization of the critical exponents γ and ν which characterize, respectively, the divergence of the osmotic compressibility X and of the correlation length ξ, i.e., $X = X_0 \varepsilon^{-\gamma}$, $\xi = \xi_0 \varepsilon^{-\nu}$, where $\varepsilon = (T - T_c)/T_c$ has been predicted by Widom[1] and Fisher[2] for a binary critical mixture in which an impurity has been added (renormalization by hidden variables). When the mass fraction of the impurity is large, the exponents are fully renormalized and take their limit values $\gamma^* = \gamma/(1-\alpha)$ and $\nu^* = \nu/(1-\alpha)$, where $\alpha = 0.110$ is the constant-volume specific-heat-anomaly exponent. Extensive studies have been published in pure and binary fluids, but only a few works[3-6] have been devoted to critical ternary mixtures, leading to some discrepancies between the experimental results. In this paper we wish to summarize new extensive dynamical light-scattering measurements, including scattered intensity, turbidity, linewidth, and viscosity, on a critical ternary mixture water-benzene-ethanol (WBE) close to its plait point at 25 °C. The sample containing 10.33 wt. % of water, 52.05 wt. % of benzene, and 37.62 wt. % of ethanol has a critical temperature of (24.971 ± 0.003) °C. In this case, we consider ethanol as the impurity, since it favors the mutual solubility of the two otherwise immiscible components, water and benzene. In this way, the ternary system can be treated effectively as a binary one with renormalized critical exponents.

The experimental setup was described in detail elsewhere.[7] The light from a very low-power, intensity-stabilized, He-Ne laser is focused on the sample whose temperature is kept constant to within 1 mK for periods of several hours. The transmitted beam impinges on a calibrated photocell in order to deduce the turbidity. The light scattered at an angle θ, corresponding to a wave vector

$$q = (4\pi/\lambda)n \sin(\theta/2) ,$$

where $n = 1.435$ is the refractive index of the sample at the laser wavelength $\lambda = 0.6328$ μm, and is collected by a very-low-noise-level ITT FW130 phototube. After amplification and discrimination, the output pulses feed a

100-channel clipped-real-time correlator designed by one of us.[8] To account for possible very-long-time drifts, the laser intensity was monitored using a photodiode. Both diodes and the correlator are connected to an on-line PDP-11/23 computer.

The experimental results are as follows. The scattered intensity I_s has been accurately measured at low q, far from the plait point, in order to deduce a precise value of γ^*, since in this regime I_s varies as $\varepsilon^{-\gamma^*}(1+\varepsilon)$. We obtain $\gamma^* = 1.49 \pm 0.03$ as is apparent from the log-log plot of Fig. 1. This value of γ^* is definitely larger than that of 1.2402 predicted by a renormalization-group calculation for pure or binary fluids. On the other hand, this value is in very good agreement with the findings of Goldburg and co-workers[3,4] and of Chu and Lin,[5] respectively, 1.50 ± 0.08 and 1.50 ± 0.03 for different ternary systems. However, our values are slightly larger than the theoretical estimate $\gamma^* = \gamma/(1-\alpha) = 1.40$ and the experimental result of Ohbayashi and Chu,[6] $\gamma^* = 1.40 \pm 0.02$. A plausible explanation of the above slight discrepancies may be found in the fact that the actual values of the critical exponents dramatically depend on the path used to approach the plait point.[9]

When close to the critical plait point, I_s becomes q-dependent and reads

$$I_s \sim \varepsilon^{-\gamma^*}(1+\varepsilon)G(X) ,$$

where $G(X)$ is the Fourier transform of the pair correlation function and $X = q\xi$. In the Ornstein-Zernike-Fisher approximation, $G(X)$ can be written as

$$G(X) = (1+X^2)^{-1+\eta/2} .$$

In this regime, the loss of intensity due to scattering of the laser beam when crossing the sample is no longer negligible. The turbidity τ expressing the rate of loss of the intensity is given by

$$\tau = \tau_0 \varepsilon^{-\gamma^*} G'(X_\pi)(1+\varepsilon) ,$$

where τ_0 is a constant and $G'(X_\pi)$ is the integral of the Ornstein-Zernike function over the whole solid angle. If we assume that $\eta \sim 0$, $G(X_\pi)$ can be expressed as
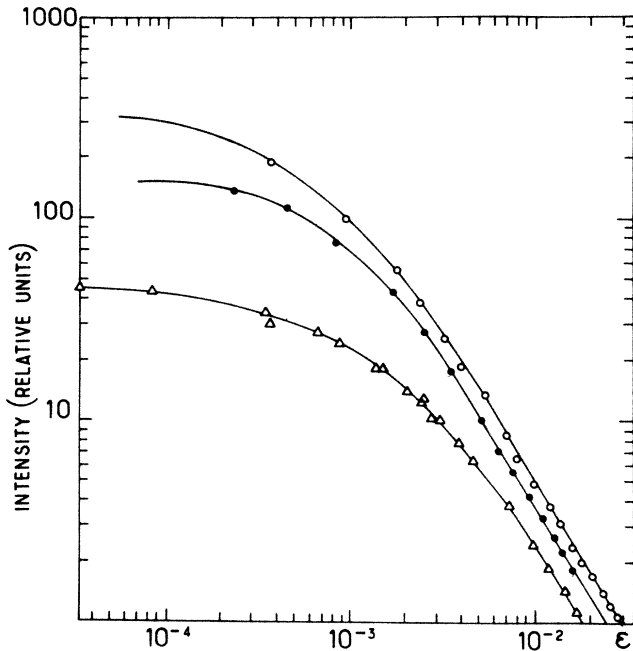
FIG. 1. Intensity as a function of $\varepsilon = (T - T_c)/T_c$ for various q values. $\triangle$, $q = 2.68 \times 10^5$ cm^{-1}; $\circ$, $q = 2.02 \times 10^4$ cm^{-1}; $\bullet$, $q = 9.04 \times 10^4$ cm^{-1}. The lines correspond to the theory described in the text.

$$G'(X_\pi) = \frac{4\pi}{X_\pi^6} [(X_\pi^4 + X_\pi^2 + 2) \ln(1 + X_\pi^2)$$

$$- X_\pi^2 (X_\pi^2 + 2)] , \qquad (1)$$

where X_π is the value of X for backscattering. Combining turbidity and intensity measurements at large-q values, it is possible to infer the value of ξ_0, the short-range correlation length. We found that $\xi_0 = (2.6 \pm 0.2)$ Å. the above value of ξ_0 is in the range usually obtained in fluid systems.[10]

As was shown by Kawasaki[11] from mode-coupling theories, the inverse Γ_c of the decay time of the critical-concentration fluctuations can be written as

$$\Gamma_c = q^2 D_C \frac{K(X)}{X^2} , \quad D_c = R \frac{k_B T}{6\pi\eta\xi} , \qquad (2)$$

where $K(X)$ is the universal Kawasaki function

$$K(X) = \frac{3}{4} \left[1 + X^2 + \left(X^3 - \frac{1}{X} \right) \arctan X \right] , \qquad (3)$$

R is a universal amplitude equal to 1.027,[7] and η is the shear viscosity, the other notations being the usual ones. In order to fit the experimental results both in pure fluids and in binary mixtures, it has been shown that one must take into account background effects.[7,12] The value Γ of the linewidth appears as the sum of two terms Γ_c and Γ_B. The first one, Γ_c, is given by Eq. (2), whereas the second one can be calculated if the behavior of the viscos-

ity is well known, using the Oxtoby and Gelbart approach.[13] In this procedure, the shear viscosity η is given by a multiplicative regular, or background part, η_B, which follows the usual Arrhenius law, and by a critical, diverging part, $\eta_c = \eta_B[(q_D\xi)^\phi - 1]$, where q_D is a Debye cutoff parameter and ϕ is a universal exponent equal to 0.054. To the lowest order of approximation, Γ_B can be written

$$\Gamma_B = R \frac{k_B T}{6\pi\eta} \frac{0.675}{q_D} \frac{q^4}{1 - \Phi \ln(q_D\xi)} \left[\frac{1}{X^2} + 1 \right] . \qquad (4)$$

From an extensive set of measurements of the viscosity taken by one of us,[14] it is possible to infer the value of the background viscosity and then the Debye cutoff, $q_D^{-1} = (7.0 \pm 1.0) \times 10^8$ cm. Furthermore, assuming the validity of the scaling law $\gamma^* = (2 - \eta)v^*$, we deduce that $v^* = 0.76 \pm 0.02$.

In Fig. 2, we plot, as a function of X, on a log-log scale, the reduced universal linewidth

$$\Gamma_c^*(\text{theor}) = R \frac{K(X)}{X^3}$$

calculated from the Kawasaki mode-coupling theory and the corresponding experimental one

$$\Gamma_c^*(\text{expt}) = \frac{6\pi\eta}{k_B T} \frac{(\Gamma - \Gamma_B)}{q^3} ,$$

Γ_B being obtained from Eq. (4). The agreement between the theoretical and the experimental results is very good in the full range of X values, including both the hydro-
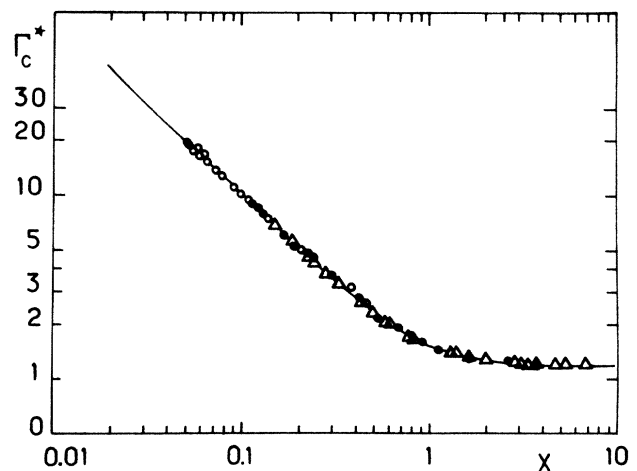

FIG. 2. Reduced linewidth Γ_c^*(expt) after background subtraction as a function of X for various q values. The symbols are the same as those in Fig. 1. The solid line is the theoretical results Γ_c^*(theor).

dynamical and the critical regimes. This fact shows the importance of the background correction. Indeed, background effects which account for more than 10% of the linewidth in the hydrodynamic regime could be the reason for the systematic deviation from the Kawasaki plot observed by Goldburg and Pusey.[4]

*Permanent address: Dipartimento di Fisica, Università degli Studi di Roma, "La Sapienza," Piazzale Aldo Moro 2, I-00185 Roma, Italy.

[1] B. Widom, J. Chem. Phys. 46, 3324 (1967).

[2] M. E. Fisher, Phys. Rev. 176, 257 (1968); M. E. Fisher and P. E. Sceney, Phys. Rev. A 2, 825 (1970).

[3] C. S. Bak, W. I. Goldburg, and P. N. Pusey, Phys. Rev. Lett. 25, 1420 (1970).

[4] W. I. Goldburg and P. N. Pusey, J. Phys. (Paris) Colloq. 1, C-33 (1972); 1, C-111 (1972).

[5] B. Chu and F. L. Lin, J. Chem. Phys. 61, 5132 (1974); F. Lin, D. Thiel, and B. Chu, Phys. Lett. 47A, 479 (1974).

[6] K. Obayashi and B. Chu, J. Chem. Phys. 68, 5066 (1978).

[7] S. H. Chen, C. C. Lai, J. Rouch, and P. Tartaglia, Phys. Rev. A 27, 1086 (1983).

[8] S. H. Chen, C. C. Lai, and W. Weldkampf, Rev. Sci. Instrum. 46, 1356 (1975).

[9] J. Rouch, P. Tartaglia, and S. H. Chen, Phys. Rev. A 37, 3046 (1988).

[10] See, for instance, Proceedings of the International Conference on Phase Transition, Cargese, 1980, edited by M. Levy et al. (Plenum, New York 1982).

[11] K. Kawasaki, in Phase Transition and Critical Phenomena, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5A, p. 165.

[12] H. C. Burstyn, J. V. Sengers, and P. Esfandiari, Phys. Rev. A 25, 948 (1982).

[13] D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. 61, 2957 (1974).

[14] L. Guidoni, V. Viti, G. D'Arrigo, L. Mistura, and P. Tartaglia, Phys. Rev. Lett. 31, 1973 (1973); G. D'Arrigo, L. Mistura, and P. Tartaglia, J. Chem. Phys. 66, 74 (1977).