

Ising Critical Exponents in Real Fluids: An Experiment

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We report precise optical measurements of the equations of state of Xe, SF₆, and CO₂ very near their critical points ($|T - T_c|/T_c < 5 \times 10^{-5}$). We find that the critical exponents of these fluids in this region are close to the exponents calculated from the three-dimensional Ising model.

Theoretical insight into the critical behavior of fluids has been gained through a combination of phenomenology,^{1,2} model calculations,³ and, more recently, the renormalization-group approach.⁴ Phenomenology and the renormalization-group approach have recently converged to an approximate form for a universal critical equation of state.⁵ Three theoretical approaches^{3,6,7} have resulted in numerically similar values for the critical exponents in this equation of state. In contrast, experiments and recent data correlations⁸ have suggested that although fluid exponents are nearly universal, they differ from the values predicted by theory. It has been speculated that this difference was due to the long-range nature of fluid potentials and might vanish if experiments approached the critical point still more closely.

We have conducted experiments on three fluids, Xe, SF₆, and CO₂, extremely close to their critical points ($-1.5 \times 10^{-5} < \epsilon < 5 \times 10^{-5}$). An analysis of the results *yields*, for all three fluids, exponents and "universal" amplitude ratios⁹ that are close to the predicted Ising values.

In these experiments we used the optical technique developed by Wilcox and co-workers,^{10,11} which is best described by Estler *et al.*¹¹ In this method the Fraunhofer pattern from density profiles in a thin slab of fluid is photographed and analyzed to obtain equation-of-state information. Three quantities are measured: (1) the fringe number, which is closely related to the quantity $\rho - K_T \mu$; (2) the fringe angle, which determines the reduced isothermal compressibility, K_T ; and (3) the temperature. Here μ and ρ are in the customary reduced units.¹¹

All experiments were done with the same cell (thickness = 0.311 cm). It was constructed entirely of sapphire and metal and had a well-defined geometry.¹² We cleaned the disassembled cell using ultrasound and U.S.P. methanol and assembled it immediately under a stream of helium. The cell was then baked (200°C) under vacuum for

24 h. This treatment is essential to avoid slow contamination of the samples by "out-gassing" water from the cell walls. In a separate experiment we monitored this "outgassing" using a residual gas analyzer associated with a National Bureau of Standards (NBS) gas thermometer. After the cell was baked, its valve was opened only during filling.

The gas samples were obtained with specified purity 99.99% or better. They were further purified by freezing and pumping off the residual volatile components. The cell was filled using the apparatus and techniques described by Moldover.¹³ Despite these precautions an apparent drift of the fluid's critical temperature relative to our thermometers was still observed. However, this drift was sufficiently small (for all three substances it was between 5 and 14 nK/min) that we cannot say whether the fluid's critical temperature, our thermometers, or both, were drifting.

The filled cell was enclosed in a seven-stage cylindrical thermostat, two stages of which were active and five passive. The cell was mechanically attached and thermally coupled to the innermost stage (a 25-kg cylinder of copper). This block was passive. Its temperature was controlled by controlling the temperature of the thermally decoupled heater shell which surrounded it. This inner stage was purposely isolated to reduce temperature gradients and integrate temperature oscillations. It has a time constant of six hours with respect to heater-shell temperature changes. The thermal equilibrium of the sample was assessed from the temporal stability of the Fraunhofer pattern. Two isotherms per day were taken far from T_c , but the rate became one per day or less as T_c was approached.

Our primary thermometer was an "aged" thermistor embedded in the inner block. A capsule platinum resistance thermometer calibrated by the NBS Temperature Section was also embedded in the inner block. It was used to calibrate the more sensitive thermistor *in situ* and to check

for long-term drifts. The thermistor bridge was routinely read to $\pm 10 \mu\text{K}$ and the platinum thermometer bridge to $\pm 0.2 \text{ mK}$. No differences between the two thermometers were ever detected during a run.

The fluids studied had critical temperatures above, below, and near ambient. The bridges and thermostat worked equally well throughout this range. We estimate the stability of this system at $\pm 20 \mu\text{K}$ over several days.

The interference patterns were continuously photographed on high-speed film (ASA 400) transported at a rate of about 1 cm/h . The fringe positions were measured with a microdensitometer accurate to $1 \mu\text{m}$. The number of fringes, and the angle at which they appear, are both strong functions of the fluid under study. We have named the parameter which indicates the strength of this dependence the "efficiency," E , of the fluid:

$$E_c \propto \rho_c (n_c^2 - 1)(n_c^2 + 2)/6P_c n_c. \quad (1)$$

It is a measure of the efficiency with which the gravitationally induced density gradients are mapped into refractive index gradients. In our experiment, E directly relates the fringe angle θ to the compressibility with $\theta \propto EgK_T$ ($g = 980 \text{ cm/sec}^2$; n_c and P_c are the critical index of refraction and the critical pressure, respectively). The "efficiency" varies by a factor of 4 among the fluids studied.

The data were analyzed using the Wilcox-Estler (WE) scaled parametric equation of state¹⁴ with two free exponents. This equation has been tested by us on PVT data and gives essentially the same exponents as the linear or cubic models. We used nonlinear least squares routines adapted from Bevington.¹⁵

We choose to characterize the range of our experiment in terms of the distance parameter in the WE model, which is

$$R = (1/K_T)^{1/\gamma}. \quad (2)$$

In a typical case, we could begin to take data at $R \ll 10^{-3}$ and, because of thick cell errors,^{10, 11} were forced to stop at $R \sim 10^{-4}$. Our data are therefore densely clustered in one or at most 1.5 decades of R space ($6 \times 10^3 < K_T < 10^5$). There is no overlap between this range and that of conventional PVT experiments ($R > 10^{-3}$).

Our preliminary results are summarized in Table I. The constants above the dashed line are necessary inputs to the experiment and were not determined internally. The values adopted for these constants affect the coefficients but not the

TABLE I. Summary of equation-of-state parameters. The Ising-model values were taken from Refs. 3 and 9.

Symbol	Xe	SF ₆	CO ₂	SF ₆ + N ₂	Ising Series
P_c MPa.	5.84	3.76	7.37	3.76	-
ρ_c gm/cm ³	1.110	0.730	0.467	0.730	-
n_c	1.138	1.078	1.106	1.078	-
E/E_{xenon}	1.0	0.57	0.25	0.57	-

σ_T	15 μK	20 μK	20 μK	20 μK	-
σ_{K_T}	35.	55.	126.	55.	-
χ^2_{ν}	0.83	0.89	2.11	0.96	-
T_c °C	16.56	45.55	30.99	45.52	-
R_{min}	1.5×10^{-4}	1.5×10^{-4}	1.2×10^{-4}	$2. \times 10^{-4}$	-
R_{max}	1.1×10^{-3}	1.8×10^{-3}	1.3×10^{-3}	$2. \times 10^{-3}$	-
β	0.329	0.321	0.321	0.323	(5/16)
γ	1.23	1.28	1.24	1.266	(5/4)

δ	4.74	4.99	4.85	4.92	5.0
η	0.05	~0	~0	0.01	0.04
α	0.11	0.08	0.10	0.09	(1/8)
β^a	1.48	1.56	1.54	1.59	1.5
Γ/Γ'	4.5	4.9	4.9	4.97	5.03
$Q_1^{-\delta}$	1.59	1.66	1.66	1.73	1.70

^a β , the coexistence curve coefficient, is not one of the universal ratios but appears to be remarkably constant in the Ising models independent of lattice structure (Ref. 3). The compressibility ratio, Γ/Γ' , and $Q_1^{-\delta}$ are universal amplitude ratios (Ref. 9).

exponents or the universal amplitude ratios obtained in this experiment. The constants determined directly by this experiment are in the middle section of the table. The constants presented at the bottom are derived.

Our results and their sensitivity are presented in Figs. 1 and 2. Figure 1 compares our values of β and γ to the best PVT fluid values⁸ and to the theoretical values^{3, 6, 7}. Our results are much closer to the theoretical values. The amplitude ratios are also quite close to the calculated values reported in Ref. 9. Rather than list statistical errors, we include Figure 2 to illustrate our experimental sensitivity to changes in exponents. For xenon the differences between the calculated

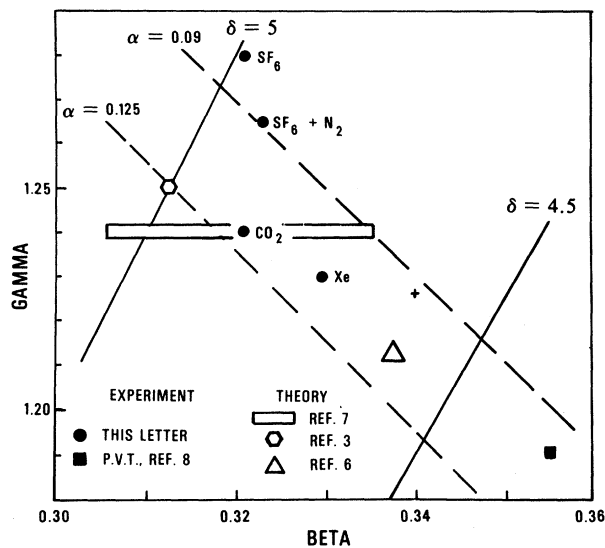


FIG. 1. The values of β and γ from this experiment and a recent, careful correlation of *PVT* values (Ref. 8) are compared to three calculations: (1) series analysis of three-dimensional Ising models (Ref. 3), (2) variational approximations for the renormalization group (Ref. 6), and (3) Padé summation of series derived from the Callan-Symanzik equation (Ref. 7). The point marked + indicates the values of β and γ for xenon used to make Fig. 2 (bottom).

and measured phases are plotted, in units of standard deviations, versus the distance from the critical point R . There are 833 points on 26 isotherms. The upper plot was made with the parameter choice that gives a minimum in χ^2 ($\chi^2 = 0.84$, $\beta = 0.329$, $\gamma = 1.23$). The lower plot was made with the optimized parameters with β fixed at 0.340 ($\chi^2 = 1.33$, $\gamma = 1.226$). The systematic deviations introduced by this small change in β are readily apparent. (For these plots the temperature standard deviation, σ_T , is 15 μK and the reduced compressibility standard deviation, σ_{K_T} , is 35.)

Note that our optimum β value for xenon is consistent with that derived from coexistence-curve data in the same range in Ref. 11, but not with the equation-of-state parameters in the same paper. We think that our improved temperature control and sample geometry have resulted in better data, resolving the inconsistency pointed out in that paper. Our SF_6 data are also consistent with the coexistence-curve data reported by Balzarini and Ohn.¹⁶

Random errors in the dependent variables (K_T and T) were assessed from the reproducibility of angle and temperature measurements within a

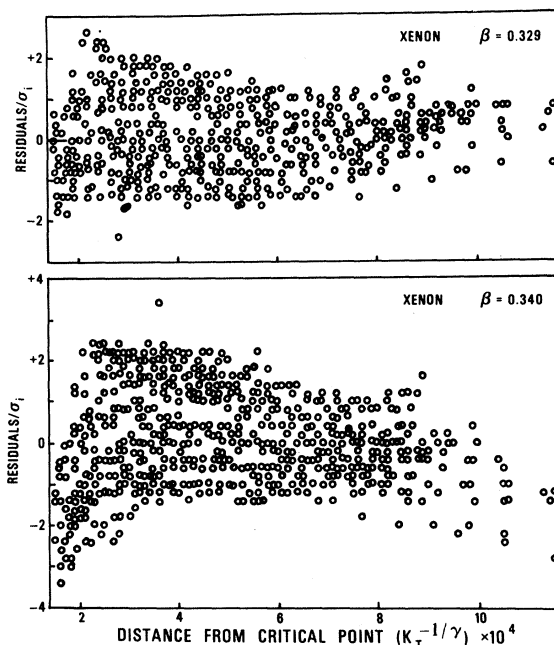


FIG. 2. Deviations between the calculated and measured phase in xenon plotted in units of standard deviations versus the distance from the critical point R . The top graph was made with all the parameters chosen such that χ^2 is at its minimum, 0.83 ($\beta = 0.329$ and $\gamma = 1.23$). For the bottom graph β was fixed at 0.34 and all the other parameters were chosen such that χ^2 is at a minimum ($\gamma = 1.226$, $\chi^2 = 1.33$).

run. To compute χ^2 we estimated our angle error to be approximately 25 μrad , and our temperature error to be about 20 μK . We computed the error in the phase using the chain rule for partial derivatives. We have also investigated possible sources of systematic error. (a) Errors due to finite cell thickness were studied by ray tracing and examining the data for angle (R) dependence. (b) Effects of deviation from the constancy of the Lorentz-Lorenz function¹⁷ were assessed analytically. (c) Errors due to residual impurities were studied in a separate optical experiment. Details will be published in a later paper. We found that (a) by limiting our maximum angle, thick-cell errors could be made smaller than our random error; (b) the refractive-index-anomaly¹⁸ effects are smaller than our random errors since the anomaly is a symmetric function of μ , and to first order, our experiment measures antisymmetric functions of μ ; and (c) the results of the identical experiment on SF_6 with 0.1% N_2 by mass yielded parameters not significantly different from those of pure SF_6 .

We also checked for model dependence by fit-

ting the SF_6 data with the cubic model.⁵ We found no significant change in the resulting exponents. We suspect that the small difference we do observe among the critical exponents of different fluids arises from the effects of nonuniversal corrections to scaling. A test of this conjecture will require a very lengthy analysis of the data because of the complexity of the expressions for $\rho - K_T \mu$ which are suitably parametrized and which contain both scaling and correction-to-scaling terms.

The exponents and coefficient ratios for these quite different pure fluids tend towards the Ising values close to the critical point. We interpret this result to imply that asymptotically the thermodynamic anomalies will be those of the Ising model.

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¹B. Widom, *J. Chem. Phys.* **43**, 3898 (1965).

²L. P. Kadanoff, *Physics (Long Island City, N.Y.)* **2**, 263 (1966).

³A. J. Guttman, *J. Phys. A* **8**, 1236, 1249 (1975); D. S. Gaunt and C. Domb, *J. Phys. C* **3**, 1442 (1970); C. Domb, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1974), Vol. 3, p. 357.

⁴K. G. Wilson and M. E. Fisher, *Phys. Rev. Lett.* **28**, 248 (1972); E. Brézin, J. C. Guillou, and J. Q. Justin, *Phys. Rev. D* **8**, 434 (1973); J. L. Colot, J. A. C. Loodts, and R. Brout, *J. Phys. A* **8**, 594 (1975).

⁵E. Brézin, D. J. Wallace, and K. G. Wilson, *Phys. Rev. Lett.* **29**, 591 (1972); P. Schofield, *Phys. Rev. Lett.* **22**, 606 (1969); J. T. Ho and J. D. Litster, *Phys. Rev. B* **2**, 4523 (1970).

⁶L. P. Kadanoff, A. Houghton, and M. C. Yalabik, *J. Stat. Phys.* **14**, 171 (1976). Figure 1 incorporates revised values for the critical exponents which will be published in an erratum to this paper (L. P. Kadanoff, private communication).

⁷G. A. Baker, Jr., B. G. Nickel, M. S. Green, and D. I. Meiron, *Phys. Rev. Lett.* **36**, 1351 (1976).

⁸J. M. H. Levelt Sengers, *Physica (Utrecht)* **73**, 73 (1974); J. M. H. Levelt Sengers, W. L. Greer, and J. V. Sengers, *J. Phys. Chem. Ref. Data* **5**, 1 (1976); J. M. H. Levelt Sengers and J. V. Sengers, *Phys. Rev. A* **12**, 2622 (1975).

⁹H. B. Tarko and M. E. Fisher, *Phys. Rev. B* **11**, 1217 (1975); A. Aharony and P. C. Hohenberg, *Phys. Rev. B* **13**, 3081 (1976).

¹⁰L. R. Wilcox and D. Balzarini, *J. Chem. Phys.* **48**, 753 (1968); D. Balzarini, Ph.D. thesis, Columbia University, 1968 (unpublished).

¹¹W. T. Estler, R. Hocken, T. Charlton, and L. R. Wilcox, *Phys. Rev. A* **12**, 2118 (1975).

¹²R. Hocken, M. R. Moldover, E. Muth, and S. Gerner, *Rev. Sci. Instrum.* **46**, 1699 (1975).

¹³M. R. Moldover, *J. Chem. Phys.* **61**, 1766 (1974).

¹⁴L. R. Wilcox and W. T. Estler, *J. Phys. (Paris), Colloq.* **32**, C5A-175 (1971).

¹⁵P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).

¹⁶D. Balzarini and K. Ohrn, *Phys. Rev. Lett.* **29**, 840 (1972).

¹⁷R. Hocken and G. Stell, *Phys. Rev. A* **8**, 887 (1973); S. Y. Larsen, R. D. Mountain, and R. Zwanzig, *J. Chem. Phys.* **42**, 2187 (1965).

¹⁸R. Hocken, thesis, State University of New York at Stony Brook, 1973 (unpublished).

Unexplained Superconductivity in the Metallic-Semiconducting NbGe₂-Ge System*

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We have observed superconductivity to 16°K in mixtures of metallic NbGe₂ and semiconducting Ge, and we show that both constituents are necessary. We show that the superconductivity is associated with the NbGe₂, although by itself, it is not a superconductor above 2.5°K. Various explanations are considered.

Anomalous high superconducting critical temperatures are observed for rf-sputtered samples of niobium-germanium in the 95-65 at.% germanium

concentration range; the samples consist of a mixture of metallic NbGe₂ and semiconducting Ge. In this paper we present our results on these