novation Industries, 3 Fieldstone Drive, Woburn, Mass. 01801.
[15]The less general solution with $C(z \pm t) = 1$ was given by Swami (Ref. 13).
[16]See, in particular, Eq. (7.5) in H. Takeno, Scientific Report of the Research Institute of Theoretical Physics (Hiroshima Univ., Takehara, Hiroshima-Ken., Japan, 1961), Vol. 1.
[17]H. Bondi, F. A. E. Pirani, and I. Robinson, Proc. Roy. Soc. London, Ser. A 251, 519 (1959).

Critical Anomaly in the Dielectric Constant of a Nonpolar Pure Fluid

R. Hocken, M. A. Horowitz, and S. C. Greer
Institute for Basic Standards, National Bureau of Standards, Washington, D. C. 20234
(Received 14 June 1976)

We report measurements of changes in the dielectric constant ϵ of SF_6 along a near critical isochore. We find an anomalous increase in ϵ. The amplitude of the anomaly is about 10 times larger than the one predicted by current theories, which assume a constant polarizability.

Near a critical point in a fluid, the critical fluctuations can be expected to distort the local fields seen by the individual molecules. For a fluid in the critical region, such a phenomenon can lead to an anomaly in the dielectric constant $\epsilon(\omega)$ or, equivalently, in the refractive index $n(\omega)$, since $n^2(\omega) = \epsilon(\omega)$. If such an anomaly is present, it must be accounted for in the analysis of measurements of the refractive index and dielectric constant in the critical region. Since such measurements provide powerful tools for probing critical behavior in fluids, it is imperative that we understand this anomaly.

We have measured the dielectric constant at 647 Hz along a near-critical isochore in SF_6. We find that for $T > T_c$, the anomaly reaches a magnitude at $T - T_c = 0.001$ of about 0.1% of the background. The anomaly which we observe is larger by a factor of 10 in magnitude, more strongly divergent, and more complex in its temperature dependence than recent theoretical computations have predicted.

Many theories for the interaction of electromagnetic radiation with nonpolar pure fluids[1-5] have been used as the basis for calculations of the dielectric constant in the critical region.[5-8] These computations fall into two groups. The first group[6-9] is based on expansions in powers of the polarizability. Stell and Høye[8] (SH) have the most highly developed of these theories and they predict that, along the critical isochore,

$$\epsilon(\omega) - \epsilon_{CM} = A\theta^2\omega^2 f(k, \xi) + B\theta^3 t^{1-\alpha}. \quad (1)$$

Here ϵ_{CM} is the Clausius-Mossotti contribution to $\epsilon(\omega)$, θ the molecular polarizability, $\alpha(\sim 0.12)$ the critical exponent for the divergence of the specific heat at constant volume,[10] ξ the correlation length, $t = (T - T_c)/T_c$, and $k = \omega/c$. B is not known in closed form, A is a complicated quantity, and $f(k, \xi)$ is a complicated function which is simple only in certain limits. Thus it is difficult to make quantitative predictions from Eq. (1).

The second type of theory, developed by Bedeaux and Mazur[5] (BM) is an expansion in terms of the density correlation functions. Including all two-body correlations and using an Ornstein-Zernike correlation function, they find

$$\epsilon(\omega) - \epsilon_{CM} = C\omega^2\psi(k, \xi) + D\xi^{-1}. \quad (2)$$

The critical exponent for the divergence of ξ is $\nu(\sim 0.64)$.[10] In Eq. (2), C and D are easy to calculate and $\psi(k, \xi)$ is a function given in Ref. 5. The frequency-dependent terms of (1) and (2) are essentially equivalent.[11] For the frequency-independent terms, SH find a divergence as $t^{1-\alpha}$ and BM as t^{ν}; the difference is due to the assumption by BM of an Ornstein-Zernike form for the correlation function.[11] Both theories assume a constant polarizability, θ.

Neither of the above theories agrees well with the only existing measurement of the index-of-refraction critical anomaly in a pure fluid. Hocken[12] measured the real part of the refractive index of Xe along a near-critical isochore. He found that, although his data agreed qualitatively with the Hocken-Stell theory,[7] which is the same as the first term in Eq. (1), the coefficient A obtained experimentally was about ten times larger than the A calculated from the theory. Subsequent attempts to fit these data with the proposed forms (1) and (2) failed,[13] because neither form is singular enough to represent the observed anomaly.

Refractive-index measurements near a liquid-liquid critical point[14] also show an anomaly, which recent calculations by Bedeaux[11] show to be larger than the theory[15] would predict.

We decided to measure this critical anomaly in $\epsilon(\omega)$ at a low frequency in a nonpolar pure fluid so that only the frequency-independent term would be important, resulting in a simpler analysis of the data.

The capacitance cell was adapted from the optical pressure cell described by Hocken *et al.*[16] A Kovar[17] wire was put through each sapphire window and sealed with solder glass and epoxy. The internal surfaces of the windows were lapped flat to two waves/inch and capacitor plates (successive layers of Pt, Cr, and Au) deposited in $\frac{1}{2}$-in. diam disks. The Kovar spacer was about 0.94 mm thick and its sides were parallel to about 20 sec of arc. During the measurements, the cell was held with the capacitor plates normal to the acceleration of gravity.

The cell was filled with SF_6 obtained commercially with a specified purity of 99.99%. Visual observation of meniscus disappearance at half the cell height was used as the criterion to fill to within 0.2% of the critical density.

The temperature of the cell was controlled with a two-stage thermostat and was stable to within ± 0.2 mK. Temperature gradients were, at the very worst, 0.1 mK across the sample. The temperature of the sample was monitored with a quartz crystal thermometer on a "laboratory" temperature scale.

We measured the capacitance of the cell with a General Radio bridge (model 1615-A) operated at 647 Hz. The cell body, spacer ring, and inner thermostat block were at ground potential. Since the capacitance cell did not have guard rings, fringe fields were present. Fringe fields should give smooth contributions to the background, but complications might arise when gravitational stratification occurs. The effects of fringe fields are expected to be small, since our measurement of the dielectric constant of SF_6 at critical density yielded $\epsilon = 1.28$, in good agreement with Weiner's value of 1.26 at 10 kHz.[18]

During the course of the experiment, we noted a drift in the filled cell capacitance C, which we attribute to the outgassing and dissolving of impurities (perhaps the epoxy). Reproducible data could be obtained by measuring the temperature derivative of the capacitance ($\Delta C/\Delta T$), rather than C itself. The derivative data were obtained by measuring the change in capacitance for a finite change in temperature; $\Delta C/\Delta T$ was considered as a function of the mean temperature during the temperature step. The derivative data were quite reproducible in measurements made either by heating or by cooling the sample and taken in various runs over a period of several months. We also attempted to measure the conductance of the sample near T_c and found it to be smaller than our bridge could resolve $[10^{-6}\ (\mu\Omega)^{-1}]$.

The qualitative measurements showed an increase in ϵ near T_c of the order of 10^{-3} of the background—an anomaly 10 times larger than predicted by Eq. (2). Measurements of $\Delta C/\Delta T$ were made from 0.069°C below T_c to 0.47°C above T_c. The data below T_c are not considered in this analysis because they are less reproducible and more difficult to interpret.

We express the data in terms of the dimensionless variable x where $x = (T_c/C_c)(\Delta C/\Delta T)$, which is the same as $(T_c/\epsilon_c)(\Delta\epsilon/\Delta T)$. The subscript c refers to the critical value. The SH theory predicts that at low frequency

$$x_{\rm SH} = [-(1-\alpha)B\theta^3/\epsilon_c]\,t^{-\alpha}, \qquad (3)$$

where the coefficient has not been estimated but is expected by Stell[11] to be of the same size as that of the coefficient of the leading term in the BM theory, the predictions of which are more concrete. In the BM theory,

$$x_{\rm BM} \simeq -\frac{2\nu}{27}\frac{(\epsilon_c-1)^3}{\epsilon_c^{\,2}}\frac{(\epsilon_c+2)^2}{\xi_0}A_{\rm OZ}t^{\nu-1}$$
$$\approx -2\times10^{-3}t^{\nu-1}, \qquad (4)$$

where $A_{\rm OZ}$, the scale factor in the Orstein-Zernike correlation function, is obtained from thermodynamic and light-scattering data.[18-21]

In Fig. 1 we present a log-log plot of the experimental x as a function of t. (The inset is a linear plot of the data.) The value of T_c used for this plot was taken as the experimental point at which the sign of $\Delta C/\Delta T$ changed, which was determined with a precision better than 1 mK.

We make the following observations on Fig. 1: (a) Even outside the gravity-rounded region, x is much larger than expected. (b) The data do not fall on a straight line, indicating that a simple power-law divergence is not present. In the range $10^{-5} < t < 2.5\times10^{-4}$, the temperature dependence of x can be described within the error by either the BM or SH theory, as can be seen by comparing the slopes shown in the legend. (c) The slope of the log-log plot *increases* in the region where we expect a *decrease* due to gravity ef-

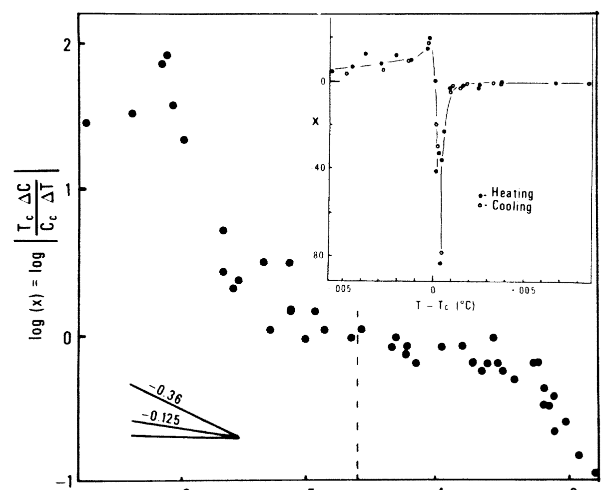

FIG. 1. Inset: The measurements of $x=(T_c/C_c)(\Delta C/\Delta T)$ very near T_c. T_c was taken as the point at which the sign of $\Delta C/\Delta T$ changed. The negative peak occurs somewhat above T_c because for the four points nearest T_c, the temperature interval ΔT spanned T_c and thus the peak is "rounded." Solid circles indicate points taken while heating; open circles, cooling. Main figure: The $\ln|x|$ as a function of t above T_c, where $x=(T_c/C_c)(\Delta C/\Delta T)$ and $t=(T-T_c)/T_c$. The region to the left of the dashed line is expected to be affected by gravity. At $\ln t=-4.5$, Bedeaux and Mazur (Ref. 5) predict $\ln|x|=-1.1$. Bedeaux and Mazur predict a slope of -0.36; and Stell and Høye (Ref. 9), -0.125. The "rounding" very near T_c is a result of the fact that the temperature interval ΔT spanned T_c for those few points.

fects, indicating a *stronger* divergence as T_c is approached.

Random errors were assessed by making nine runs over a 3 month period; and they are best represented by the scatter apparent in Fig. 1. We have investigated several sources of systematic errors. The effects of nonequilibrium were included in the random error by taking measurements both ways, by heating and by cooling; the fact that no differences were discerned was taken as evidence of equilibrium.

The density gradient induced by gravity is a source of several systematic errors. First, the anomaly is averaged over the sample height and thereby rounded, while the maximum in C is shifted upwards from T_c.[7] Correcting for these effects *sharpens* the anomaly. Second, the capacitance is decreased when the fluid becomes stratified. The contribution to C in the range $10^{-5}<t<10^{-4}$ is about 10% of the observed anomaly; correcting for it would *increase* the anomaly. Third, the inhomogeneity of the dielectric requires that the asymmetries of the capacitor itself be considered. A cell asymmetry of 1% will be combined with a 10% density gradient to contribute an error of only 0.007% in C. Thus, while gravity effects complicate the analysis of the experiment, correcting for such effects seems to strengthen the evidence for a significant anomaly.

Impurities have been shown to have a negligible effect on critical exponents.[20] Just as in the case for gravity, we believe that any inhomogeneity of an impurity would round an anomaly and not sharpen it.

We investigated the frequency dependence of the anomaly by taking data at 6 kHz and found no difference in the results. We have considered the effects of the electric field energy on critical-region thermodynamics.[22] Our calculations indicate that, while such an effect would indeed sharpen the anomaly, the effect is negligible in our experiment. When we varied the voltage on the cell from 10Vrms to 1V rms, we found no observable change in the data.

In conclusion, we see an anomaly in the dielectric constant of a pure fluid near its critical point which is larger than values predicted by current published calculations. Ours is the third report of such an anomaly, the others being refractive-index measurements.[12,14] All these experiments can, of course, be improved. In particular, in all three cases the measurements are made with a background drift. If the experiments are correct, then the results suggest the presence of a real, frequency-independent term in the refractive index which has thus far escaped attention. Stell and Høye have[8] suggested that perhaps the polarizability itself has a critical anomaly. Stell[11] has also suggested that the hole-particle symmetry effectively assumed in these theories may have masked other terms. We hope our work will stimulate both experimentalists and theoreticians to resolve this discrepancy.

We thank R. Mountain, D. Bedeaux, and G. Stell for helpful discussions. NATO Research Grant No. 1065 enabled D. Bedeaux to visit us.

[1] J. Yvon, *Recherches sur la Théorie Cinetique des Liquides* (Herman and Cie, Paris, 1937).

[2] H. Hoek, thesis, University of Leiden, 1939 (unpublished).

[3] L. Rosenfeld, *Theory of Electrons* (North-Holland, Amsterdam, 1951).

[4] P. Mazur and M. Mandel, Physica (Utrecht) 22, 299 (1956).

[5]D. Bedeaux and P. Mazur, Physica (Utrecht) 67, 23 (1973).
[6]S. Y. Larson, R. D. Mountain, and R. Zwanzig, J. Chem. Phys. 42, 2187 (1965).
[7]R. Hocken and G. Stell, Phys. Rev. A 8, 887 (1973).
[8]G. Stell and J. S. Høye, Phys. Rev. Lett. 33, 1268 (1974).
[9]L. Mistura, J. Chem. Phys. 59, 4563 (1973). Mistura uses thermodynamic arguments to predict that although ϵ remains finite, its temperature derivative diverges weakly.
[10]H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, Oxford, England, 1971).
[11]D. Bedeaux and G. Stell, private communications.
[12]R. Hocken, thesis, State University of New York at Stony Brook, 1973 (unpublished); R. Hocken and L. R. Wilcox, Bull. Am. Phys. Soc. 17, 614 (1972). Earlier measurements of the refractive index of Xe showed no anomaly; see J. A. Chapman, P. C. Finnimore, and B. L. Smith, Phys. Rev. Lett. 21, 1306 (1968); D. H. Garside, H. V. Mølgaard, and B. L. Smith, J. Phys. B 1, 449 (1968).
[13]R. Hocken and D. Bedeaux, private communication.
[14]C. L. Hartley, D. T. Jacobs, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 33, 1129 (1974).
[15]S. K. Kim and P. Mazur, Physica (Utrecht) 71, 579 (1974).
[16]R. Hocken, M. R. Moldover, E. Muth, and S. Gerner, Rev. Rev. Sci. Instrum. 46, 1699 (1975).
[17]Commercial names are used only for completeness and do not signify an endorsement by the National Bureau of Standards.
[18]J. Weiner, thesis, University of Massachusetts, 1974 (unpublished).
[19]J. M. H. Levelt Sengers, W. L. Greer, and J. V. Sengers, J. Chem. Phys. Ref. Data 5, 1 (1976).
[20]R. Hocken and M. R. Moldover, Phys. Rev. Lett. 37, 29 (1976).
[21]D. S. Cannell, Phys. Rev. A 12, 225 (1975).
[22]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960), p. 83.

Inclusive Reactions $p + n \to p + X$ and $\pi^+ + n \to p + X$ at 100 GeV/c

J. Hanlon, A. Brody, R. Engelmann, T. Kafka, and H. Wahl*
State University of New York at Strony Brook, Stony Brook, New York 11794†

and

A. A. Seidl, W. S. Toothacker, and J. C. Vander Velde
University of Michigan, Ann Arbor, Michigan 48104‡

and

M. Binkley, J. E. A. Lys, and C. T. Murphy
Fermi National Accelerator Laboratory, Batavia, Illinois 60510‡

and

S. Dado, A. Engler, G. Keyes, R. W. Kraemer, and G. Yekutieli§
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213‡

(Received 24 February 1976; revised manuscript received 11 August 1976)

We have measured the inclusive cross section for the reactions $p+n\to p+X$ and $\pi^++n\to p+X$ at 100 GeV/c in the kinematic region $|t|< 1.0$ GeV^2. The data were obtained from an exposure of the Fermilab 30-in. deuterium-filled bubble chamber to a tagged positively charged beam. The differential cross sections for these reactions are observed to scale in the ratio of the pn and π^+n total cross sections and to be consistent with the predictions of a Reggeized one-pion-exchange model.

We present a study of the reactions

$$p+n\to p+X \qquad (1)$$

and

$$\pi^++n\to p+X \qquad (2)$$

from an analysis of 41 000 pictures of interactions in the Fermilab 30-in. deuterium-filled bubble chamber exposed to an unseparated beam of 100-GeV/c positive particles. A tagging system[1] allowed the identification of individual beam parti-