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PHYSICAL REVIEW A VOLUME 2, NUMBER 6 DECEMBER 1970

Density and Compressibility of Oxygen in the Critical Region*

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(Received 26 June 1970)

Density-versus-height profiles have been measured in the critical region of oxygen by means of capacitance techniques. Results are given for the liquid and vapor densities at coexistence, for compressibilities along the coexistence curve to within $t \equiv (T - T_c)/T_c = -6 \times 10^{-5}$, for compressibilities along the critical isotherm to within $(\rho - \rho_c)/\rho_c = 5 \times 10^{-2}$, and for compressibilities along the critical isochore to within $t = 2 \times 10^{-4}$. The data are analyzed in terms of power-law descriptions and are shown to be in excellent agreement with recent scaling-law analyses of data for other fluids.

I. INTRODUCTION

The behavior of fluids in the critical region is generally described by power laws, which are expected to hold in the limit as the critical point is approached. Experimental data are analyzed in terms of a set of coefficients and exponents in the following relationships[1]: for $\rho = \rho_c$, $T > T_c$,

$$\rho_c^2 K_T = \Gamma t^{-\gamma}, \tag{1}$$

$$C_v = A t^{-\alpha}; \tag{2}$$

for $\rho = \rho_c$, $T < T_c$,

$$C_v = A(-t)^{-\alpha'}; \tag{3}$$

for $T = T_c$,

$$p(\rho, T_c) - p(\rho_c, T_c) \sim \mu(\rho, T_c) - \mu(\rho_c, T_c) = D\,\Delta\rho\,|\Delta\rho|^{\delta-1}; \tag{4}$$

coexistence curve,

$$\Delta\rho = B(-t)^{\beta}, \tag{5}$$

$$\rho^2 K_T = \Gamma'(-t)^{-\gamma'}, \tag{6}$$

where $\Delta\rho = (\rho - \rho_c)/\rho_c$, $t = (T - T_c)/T_c$, K_T is the isothermal compressibility, and μ is the chemical potential.

The failure of the classical, or mean-field, theories to yield the correct values for the exponents and coefficients in the above equations has been demonstrated many times experimentally. Calculations based on the Ising model, or its lattice-gas analog, agree more closely with the existing body of experimental evidence although significant differences still exist.

The scaling-law equation of state, proposed by Widom,[2] Griffiths,[3] Kadanoff,[4] and others, is a more phenomenological approach. It offers promise of giving a formulation of the thermodynamic behavior in the critical region which would be in good agreement with the most reliable data available. This equation may be expressed in the following form:

$$\mu(\rho, T) - \mu(\rho_c, T) = \Delta\rho\,|\Delta\rho|^{\delta-1} h(x), \tag{7}$$

with $h(x)$ being a function only of the variable $x = t/|\Delta\rho|^{1/\beta}$, and $x = -x_0$, a constant, on the coexistence boundary. Vicentini-Missoni, Sengers, and Green[5] have applied this equation of state to the experimental data on CO_2, Xe, and He^4 with good success. However, they cite the need for new data and consider their conclusions tentative because of the lack of extensive, precise experimental information.

Equation (7) implies several assumptions about the symmetry of the *PVT* surface in the critical region. Some of these are the following: (a) $\Delta\mu = \mu(\rho, T) - \mu(\rho_c, T)$ is antisymmetric about ρ_c and (b) $\gamma = \gamma' = \beta(\delta - 1)$. Calculations based on the threedimensional Ising model, on the other hand, suggest that γ' may be larger than γ, the former being about $\frac{21}{16}$ and the latter being $\frac{5}{4}$.[6]

This paper provides an experimental test of the correctness of the above assumptions and gives accurate values for some of the exponents and coefficients in Eqs. (1)–(6). Equation (7) indicates that measurements of chemical potential difference as a function of density would be most desirable. Since $(\partial\rho/\partial\mu) = -g^{-1}(d\rho/dz) = \rho^2 K_T$ (where g is the gravitational constant, and z is the coordinate in the vertical direction), this task is most easily accomplished experimentally by making density-versus-height measurements. Such measurements have been carried out previously by optical methods[7–10] and by radioactive tracer techniques.[11] We have chosen to make use of capacitance techniques. Besides measuring changes in $\Delta\mu$ directly, this method is advantageous in that it has a sensitivity which is about two orders of magnitude greater than conventional pressure-versus-density measurements.

Oxygen was chosen as the working substance because of the extensive determination, carried out at this laboratory, of the PVT surface outside of the critical region,[12] and because there also exist measurements of its heat capacity C_V in the critical region.[13]

II. EXPERIMENTAL

One of the most important factors in the design of an apparatus for use in the critical region is the height of the volume in which the measurements are to be made. This consideration dictates the use of horizontal, flat-plate capacitors for measurements on thin layers of fluids. Figure 1 shows the details of the capacitors used here. Gold plated onto fused quartz disks formed the capacitor plates. The spacer is a thin ring of quartz glued onto the upper disk. The spacing is nominally about 0.01 cm, and the plates have an area of 0.49 cm^2, which results in a vacuum capacitance of about 3.5 pF. Most of the remaining surface of the disks is also plated with gold, which is grounded to minimize stray capacitance. A 0.16-cm-diam hole through the middle of each disk facilitates circulation of the fluid.

This apparatus makes use of a stack of five such capacitors, also shown in Fig. 1. The capacitors are separated by quartz cylinders which are also gold plated and grounded. The heights of the capacitors are 10.681, 8.131, 5.580, 4.618, and 2.068 cm, respectively, above a common plane, in this case the bottom of the sample holder.

The disks and cylinders were assembled inside a copper tube and were held in place by a compression spring. Later it was found necessary to glue

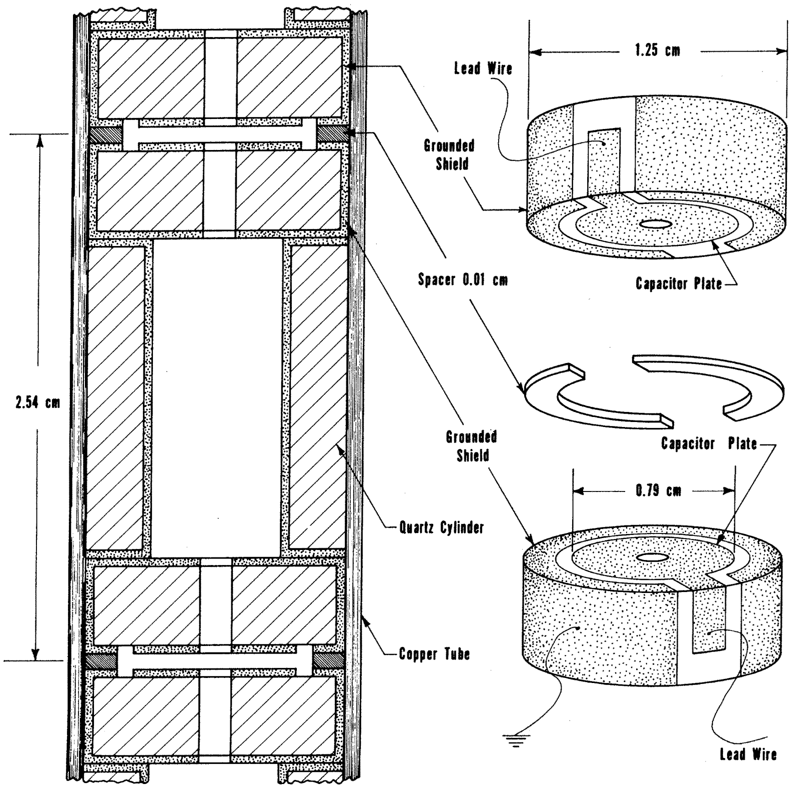

FIG. 1. Details of the capacitors.

the disks together after the fashion of Roach[14] to maintain the required structural stability. The glue was applied to the quartz spacer, thereby ensuring that no solid material would be located between the plates.

The capacitors were mounted inside a heavy-walled copper sample holder equipped with a heater and platinum resistance thermometer. The sample holder is surrounded by an adiabatic shield which is mounted in a cryostat similar to that described by Diller.[15] Samples are introduced into the sample holder by means of a stainless-steel capillary which is wound with a heater. The capillary is terminated by a valve on top of the cryostat to minimize external volumes and facilitate the achievement of equilibrium conditions in the sample holder.

The five capacitors use six electrical leads, one being common. These enter the high-pressure cell through $\frac{1}{16}$-in.-o.d. ceramic insulated steel tubes. The insulating material is powdered magnesium oxide, which is generally permeable to high-pressure gas. To remedy this situation, the ends of the tubes were impregnated with an Epoxy-resin adhesive under pressure. The dielectric constant was measured with a capacitance bridge having a sensitivity of 10^{-5} pF.

After the sample was loaded and a series of capacitances C were measured along a selected path at constant temperature, or over a narrow temperature range, the sample holder was evacuated to obtain the vacuum capacitances $C_0(T)$. Densities were derived from the Clausius-Mossotti equation

$$\rho = \frac{3M}{4\pi\alpha}\,\frac{\epsilon - 1}{\epsilon + 2}\ , \tag{8}$$

where ϵ is the dielectric constant C/C_0, M the molecular weight, and α the molar polarizability. The quantity $(\epsilon - 1)/[(\epsilon + 2)\rho]$ is not exactly constant but varies several tenths of a percent with density in the range of interest here, and possibly somewhat with temperature. In order to obtain more accurate results, this dependence was taken into account. The dielectric constant was first measured at temperatures and pressures outside the critical region, and corresponding densities were obtained from the PVT data of Ref. 12. The resulting curves of $(\epsilon - 1)/[(\epsilon + 2)\rho]$ versus ρ were interpolated to find the one used in the critical region. Thus the capacitors were calibrated against the PVT data taken outside the critical region. Any elastic deformation of the capacitors due to hydrostatic pressure was automatically taken into account by this method.

Equilibrium times varied from about one hour to more than four hours for the data closest to the critical point. In general, the system took longer to reach equilibrium when two phases were present.

III. RESULTS

Measurements were made along the following three paths [$x = \text{const}$, according to Eq. (7)]: along the critical isotherm ($x = 0$), along the critical isochore ($x = \infty$), and along the coexistence boundary ($x = -x_0$). The data were treated by means of the power-law analysis, Eqs. (1)–(6), using computer least-squares techniques. In each case, the data were weighted according to the estimated experimental uncertainties.

The results are presented in the reduced units used by Vicentini-Missoni, Sengers, and Green[5] for ease of comparison. The density is reduced by ρ_c, the temperature by T_c, the pressure by P_c, and the chemical potential by P_c/ρ_c.

A. Densities on Coexistence Boundary

The sample holder was loaded at a temperature about 20 K above the critical and at a pressure corresponding as closely as possible to the critical density. The sample was then cooled into the two-phase region and capacitances were measured at several closely spaced temperatures. This filling procedure generally resulted in placing two capacitors in one phase and three in the other. The average density, determined from the filling conditions and the known PVT surface,[12] was used to calculate the amounts of liquid and vapor at each point. This knowledge, combined with the known geometry of the apparatus, allowed the approximate determination of the height of the meniscus in the sample holder.

When density gradients were observed to exist in each phase (for sufficiently small ΔT's) the measured densities were extrapolated to the calculated height of the meniscus. The compressibilities at coexistence, reported in Sec. III B, were utilized for this purpose. These extrapolations amounted to about 2.5% in density in the worst case.

The densities of coexisting liquid and vapor were measured at 19 temperatures between 150 and 154.566 K ($6\times10^{-5} < t < 3\times10^{-2}$). The results are given in Table I. A preliminary analysis of the data has been given previously.[16] Since the liquid and vapor densities were measured at the same temperatures, a modified form of Eq. (5) was used for the analysis:

$$\frac{\rho_l - \rho_v}{\rho_c} = B\left(\frac{T_c - T}{T_c}\right)^{\beta}\ . \tag{9}$$

This form of the equation has the advantage of being unaffected by the asymmetry of the coexistence boundary. Also, it does not require *a priori* an accurate knowledge of the critical density. Equation (9) has another advantage for analyzing data very close to the critical point where the compressibility becomes quite large. In this region, in spite of careful ex-

TABLE I. Experimental saturation densities of oxygen.

T (K)	ρ, liquid (g/cm^3)	ρ, vapor (g/cm^3)
150.000	0.6753	0.2149
153.000	0.5963	0.2821
153.500	0.5754	0.3011
153.600	0.5705	0.3054
154.000	0.5470	0.3268
154.100	0.5402	0.3341
154.101	0.5396	0.3342
154.200	0.5317	0.3422
154.300	0.5211	0.3518
154.397	0.5096	0.3634
154.490	0.4928	0.3803
154.500	0.4897	0.3809
154.510	0.4877	0.3848
154.523	0.4840	0.3898
154.540	0.4778	0.3948
154.544	0.4758	0.3973
154.546	0.4742	0.3984
154.560	0.4656	0.4029
154.566	0.4617	0.4120
154.566	0.4626	0.4084

perimental techniques, the meniscus becomes very difficult to locate. As a result, the values of the individual saturation densities have rather large uncertainties. However, the quantity $\rho_l - \rho_v$ is unaffected since $d\rho/dz$ is the same in both phases.

The value of T_c was varied arbitrarily to obtain the best fit to the data. The critical parameters were found to be $T_c = 154.576$ K and $\rho_c = 0.4362$ g/cm^3. Fitting all the data with $|t| \leq 0.01$ yielded $B = 3.637 \pm 0.010$ and $\beta = 0.353 \pm 0.0005$. The uncertainties are standard deviations, indicating only the precision of the data, and do not reflect possible systematic errors. The saturation data may be averaged to obtain the rectilinear diameter, $\bar{\rho} = \frac{1}{2}(\rho_l + \rho_v)/\rho_c$,

$$\bar{\rho} = 1 + 0.684(-t), \qquad (10)$$

in reduced units. Equations (9) and (10) may be used to obtain the densities of either phase within the range of the measurements.

B. Compressibilities on Coexistence Boundary

These data, which are closely associated experimentally with the saturation densities of Sec. III A, are probably among the most difficult to obtain accurately. That this is true is obvious from the wide range of values reported for γ' in the literature. One of the problems results from the difficulty of measuring K_T at exactly the density of saturation.

We have attempted to circumvent this difficulty by measuring the compressibility as a function of density on several isotherms, shown in Fig. 2 and in Table II. The data at 154.0 K are PVT results taken from Ref. 12. Figure 2 shows that within the experimental precision the data, and therefore $\Delta\mu$, are antisymmetric about ρ_c for densities within 30% of critical. Only the points at a $\Delta\rho$ of 0.44 show a definite deviation from this antisymmetry. The data in Fig. 2 do not fall on a single curve, and from (7) they would not be expected to do so. The data on each isotherm, however, may be approximated by a straight line over a narrow density interval. Because of the antisymmetry mentioned above, the vapor and liquid data on each isotherm were fitted together, and the compressibilities were extrapolated to the density of the saturated liquid as given by (9) and (10). The results are shown in Fig. 3. Equation (6) was applied to the results and the parameters were found to be, in reduced units, $\Gamma' = (1.18 \pm 0.18) \times 10^{-2}$ and $\gamma' = 1.241 \pm 0.018$ when the PVT point from Ref. 12 was not used, and $\Gamma' = (1.09 \pm 0.22) \times 10^{-2}$, $\gamma' = 1.253 \pm 0.025$ when this point was included. Because of the relatively small number of data and the narrow range of temperature, the values of the parameters are quite sensitive to small changes in the data-fitting process, such as the weighting scheme. It is felt that the standard deviations given above are a good indication of the accuracy.

The extrapolation of the compressibility data to the coexistence boundary [defined by $x = -x_0$ in (7)] may introduce some additional errors. This extrapolation may be avoided; as was pointed out by Edwards,[17] any locus $x = \text{const}$ would serve the same purpose. If the path $x = -0.6x_0$ is chosen

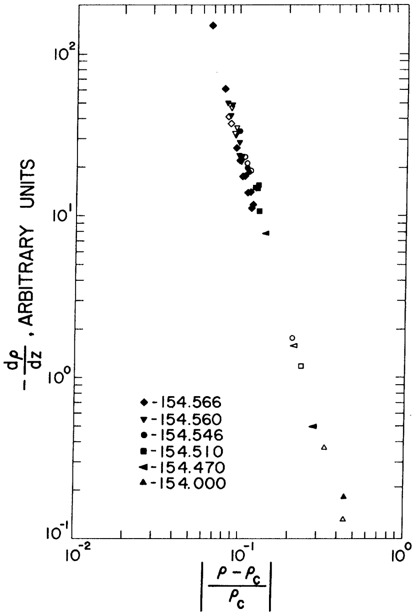

FIG. 2. Compressibilities as a function of density on several isotherms, $T < T_c$. Open symbols: $\rho < \rho_c$, filled symbols: $\rho > \rho_c$.

TABLE II. Density-versus-height data used to calculate compressibilities; T in K, ρ in g/cm^3. [Heights of capacitors, ($h_1, \ldots, h_5$) given in text.]

Data used to obtain compressibilities at coexistence

T	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5
154.330	0.354 36	⋯	0.354 98	0.355 17	0.355 65
154.330	0.519 84	⋯	0.520 11	0.520 32	0.520 54
154.470	0.341 89	0.342 01	0.342 18	0.342 28	0.342 48
154.470	0.496 71	0.497 22	0.498 09	0.498 55	0.499 45
154.470	0.561 37	0.561 39	0.561 44	0.561 64	0.561 63
154.510	0.333 08	0.333 21	0.333 26	0.333 18	0.333 49
154.510	0.331 04	0.331 11	0.331 28	0.331 29	0.331 36
154.510	0.382 06	0.383 47	⋯	0.489 97	0.491 28
154.510	0.487 92	0.489 44	0.490 96	0.491 56	0.492 65
154.546	0.345 56	0.345 80	0.345 90	0.345 88	0.346 18
154.546	0.386 16	0.388 06	0.390 21	0.391 11	⋯
154.546	0.391 01	0.393 45	⋯	0.477 63	0.480 57
154.546	0.476 72	0.480 13	0.482 52	0.483 29	0.485 19
154.560	0.391 72	0.393 93	0.397 50	0.399 30	⋯
154.560	0.395 10	0.398 40	0.467 77	0.471 49	0.476 42
154.560	⋯	0.471 07	0.475 30	0.476 52	0.479 40
154.560	0.469 18	0.474 25	0.477 46	0.478 38	0.480 78
154.566	0.396 88	0.400 67	⋯	0.466 98	0.473 12
154.566	0.398 16	0.402 31	⋯	0.467 42	0.473 53
154.566	0.475 07	0.477 73	0.479 97	0.480 65	0.482 45
154.566	0.483 08	0.484 50	0.485 92	0.486 35	0.487 55

Data used to obtain compressibilities on critical isotherm

T	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5
154.575	0.407 18	0.449 64	0.466 46	0.468 89	0.473 79
154.576	0.394 12	0.396 58	0.399 87	0.401 47	0.409 19
154.576	0.397 41	0.400 92	0.406 57	0.410 38	⋯
154.576	0.349 33	0.349 45	0.349 62	0.349 60	0.349 81
154.576	0.375 34	0.375 89	0.376 54	0.376 68	0.377 47
154.576	0.397 16	0.400 50	0.406 17	0.409 74	⋯
154.576	0.486 26	0.487 42	0.488 42	0.488 72	0.489 71
154.576	⋯	0.464 20	0.470 06	0.471 56	0.475 01
154.576	0.478 60	0.480 47	0.482 17	0.482 75	0.484 17
154.576	0.497 56	0.498 09	0.498 67	0.498 87	0.499 29

Data used to obtain compressibilities on critical isochore

T	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5
154.600	0.410 60	0.421 00	0.443 44	0.450 13	0.461 17
154.609	0.412 82	0.419 79	0.432 04	0.438 71	0.452 34
154.618	0.414 80	0.421 47	0.431 89	0.437 00	0.448 79
154.640	0.418 45	0.423 97	0.431 43	0.434 80	0.443 01
154.641	0.417 24	0.423 01	0.430 68	0.434 28	0.442 65
154.679	0.422 46	0.426 08	0.430 63	0.432 67	0.437 15
154.699	0.427 83	0.431 44	0.435 16	0.436 54	0.440 99
154.820	0.425 54	0.426 96	0.428 67	0.429 30	0.430 99
154.880	0.426 09	0.427 15	0.428 39	0.428 85	0.430 10

the data may be interpolated, and a value of 1.242 ±0.016 is obtained for γ'. The good agreement between the two methods for obtaining γ' supports the assumption of the linearity of the isotherms, in log-log coordinates, right up to the coexistence boundary.

The compressibility at coexistence may also be considered as a function of $\Delta\rho$. The results are illustrated by the filled squares on the right-hand side of Fig. 4. When the data are fitted with Eq. (4), the slope, which we may define by analogy as $(\delta' - 1)$, is 3.52 ± 0.06.

C. Compressibilities on Critical Isotherm

The best value for the critical temperature, found from (9), is 154.576±0.001 K. The sample holder was loaded at this temperature at density about 1.5 ρ_c, and the relative calibration of the capacitors was checked. Then the sample was released slowly in a stepwise fashion, and compressibilities were measured through the critical region. Several hours were required for equilibrium at each step.

A total of thirty measurements were made at 154.576 K and another three at 154.575 K. The results are shown in Fig. 4 and are given in Table II. Here again the data confirm the antisymmetry of $\Delta\mu$ about ρ_c. The antisymmetry is improved somewhat if ρ_c is chosen to be about 0.1% less than the value found from the analysis of the coexistence boundary. This is about the uncertainty with which ρ_c is known. There is apparently no discernible difference between the two isotherms within the density range of the measurements. When the data are analyzed by means of (4), the parameters are found to be $D = 4.04 \pm 0.63$ and $\delta = 4.59 \pm 0.06$. This value of δ is seen to agree quite well with the value found in Sec. III B from the analysis of the data along the coexistence boundary.

D. Compressibilities on Critical Isochore

These data were taken at the same time as the saturation densities in Sec. III A. The sample was merely heated above T_c along the critical isochore. Since there was an appreciable density gradient in the sample holder (as much as 11.6% for $T - T_c = 0.024$ K) care was taken to use in the analysis only the compressibilities measured by the pair of capacitors which bracketed the critical density.

The results are given in Table II and are shown in Fig. 5 along with some results from the *PVT* measurements in Ref. 12. The remarkable thing about Fig. 5 is the apparent change in the slope of the curve at about $t = 10^{-2}$. The limiting value for the slope is larger which is in agreement with the results on Ar and Xe.[18-21] Also shown for the point closest to critical is the effect of the curvature correction, calculated from Eq. (11) below.

When the data are analyzed according to Eq. (1), it is found that the results are very sensitive to the value chosen for T_c. Using 154.576 K for T_c, the data with $t \leq 10^{-2}$ are fit by the parameters $\Gamma = 0.0526 \pm 0.0050$ and $\gamma = 1.247 \pm 0.013$. With $T = 154.575$ K we get $\Gamma = 0.0494$, $\gamma = 1.258 \pm 0.012$. The *PVT* data at $t > 10^{-2}$ correspond to a value for γ of about 1.1.

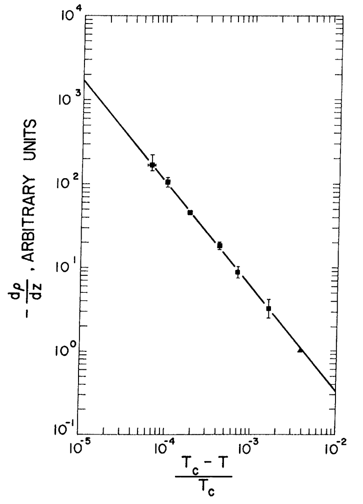

Fig. 3. Compressibilities on the coexistence boundary. ■: dielectric data, ▲: PVT data (Ref. 12).

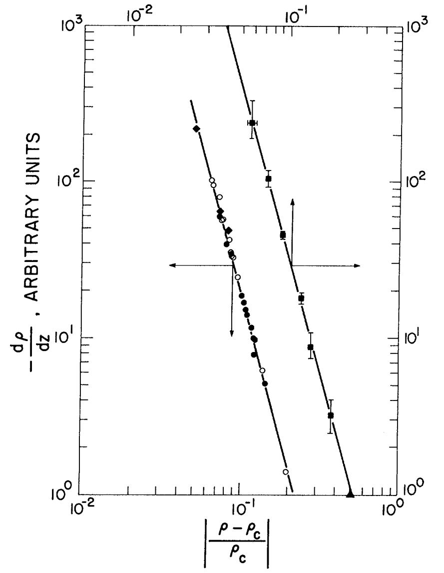

FIG. 4. Compressibilities as a function of density on the critical isotherm and on the coexistence boundary. ●: $\rho > \rho_c$ and ○: $\rho < \rho_c$, $T = 154.576$ K; ◆: $\rho > \rho_c$, $T = 154.575$ K; ▲: Ref. 12; ■: coexistence boundary.

IV. ACCURACY OF RESULTS

There are several sources of error besides the obvious problems of measuring temperature, etc.

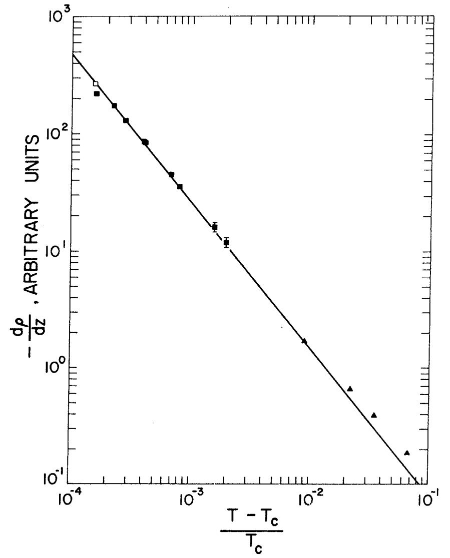

FIG. 5. Compressibilities on the critical isochore, $T > T_c$. ■: dielectric data, □: with curvature correction (see text), ▲: *PVT* data (Ref. 12).

Some of these pertain to this particular apparatus, some to this method of measurement, and others are inherent in any work near the critical point. The capacitors were quite imperfect, i.e., there was a great deal of stray capacitance. This has the effect of decreasing the apparent value of the polarizability without altering its density dependence appreciably. This problem necessitated a separate calibration curve for each capacitor. In addition, the capacitors showed a certain amount of hysteresis with temperature cycling. This effect caused random errors in the density data estimated at 0.05%.

The quantity which was measured, $\Delta\rho/\Delta z$, is equal to $d\rho/dz$ only in the limit of infinitesimal increments in z. In order to correct this situation for a finite Δz, a curvature adjustment must be applied to the data. For this purpose, a preliminary approximation to the *PVT* surface is required. Near the critical point, the surface was assumed to have the form

$$\frac{d\rho}{dz}=\frac{1}{A(\Delta\rho)^4+Bt(\Delta\rho)^2+C(t)^{1.25}}\ , \tag{11}$$

letting $B=C=0$ for $T<T_c$. This correction has a large uncertainty but amounted to less than 1% for most of the data. For a few points the correction was larger (up to 22%), and these were given less weighting. For several points the correction was considerably larger than the measurements themselves, and these data were discarded.

The question of a possible anomaly in the Clausius-Mossotti relationship at the critical point has been considered both theoretically and experimentally by several authors.[22,23] Our results suggest that there is no anomaly, at least in the range of variables considered here, as shown in Fig. 6. The rectilinear diameter calculated from the data in Table I agrees very well with the one found from *PVT* data and extrapolated from lower temperatures. Determining the height of the meniscus proved to be particularly troublesome for the data very close to the critical point. The effect of an estimated 0.5-cm uncertainty in the calculation of the meniscus height is also shown in Fig. 6. This problem has no effect on the fit of (9), however.

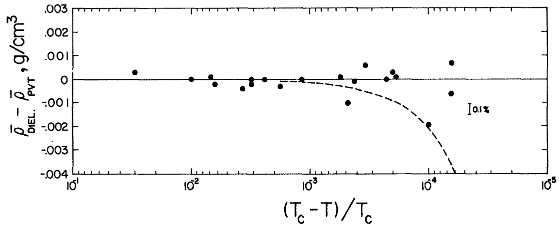

FIG. 6. Comparison of the rectilinear diameter $\bar{\rho}$ from *PVT* data (Ref. 12) and from dielectric data. The dashed curve is the error produced by a ± 0.5-cm error in the assumed height of the meniscus.

The coefficient of electrostriction[24]

$$\frac{1}{\rho}\left(\frac{\partial\rho}{\partial(E^2)}\right)_{\mu,T}=\frac{K_T}{8\pi}\rho\left(\frac{\partial\epsilon}{\partial\rho}\right)_{E,T} \tag{12}$$

raises a more serious problem since the right-hand side of (12) must become infinite as does K_T at the critical point. We may use the compressibility data to estimate this effect in the worst case. Using the following values for the experimental quantities: $E=4150$ V/cm, $\rho(\partial\epsilon/\partial\rho)=1.1$, $K_T\simeq 3\times10^{-3}$ m^2/N (for $T=154.575$ K, $\Delta\rho=0.0311$), we estimate a shift in density of about 0.2%, which is small but appreciable. Application of this adjustment brings the compressibility calculated from this datum into better agreement with the rest of the data on the critical isotherm. The adjustment was considerably smaller for the rest of the data, being generally well within the experimental uncertainty, and therefore it was not applied.

The uncertainties in the curvature adjustment [Eq. (11)], and the electrostriction adjustment [Eq. (12)], place a practical upper limit on the value of the compressibility which can be measured reliably with a given spacing between capacitors. With this apparatus, having a spacing between capacitors of 2.55 cm, this upper limit is about 1×10^{-3} m^2/N. When the pair of capacitors having a spacing of 0.96 cm is used this limit can be extended. Likewise, the reproducibility of the capacitors places a lower limit on the value of the compressibility which can be measured accurately, in this case about 1×10^{-5} m^2/N.

The capacitors were calibrated using *PVT* data[12] which have an estimated uncertainty of 0.1% in density outside the critical region. Relative temperatures were measured and were reproducible to within several tenths of one millidegree. Comparison of vapor pressures measured in this apparatus with values from Ref. 25, however, indicated a systematic difference which is equivalent to 0.01 K. Most of this difference can be accounted for by the specifications of the different thermometers and pressure- and temperature-measurement systems used for the two sets of data. Temperatures are given on the IPTS 1948 temperature scale.

V. DISCUSSION

Because of the limited number of data and the relatively narrow range of the variables, slight variations in the fitting procedures can cause the exponents to vary by amounts approximately equal to the quoted standard deviations. With this in mind, the exponents should be considered equally likely to have any value within this range rather than just the values given in Sec. III. Other uncertainties, due to possible systematic errors, must also be added in if they can be estimated.

Therefore we may say, from this research, that $\beta = 0.353 \pm 0.005$, $\gamma = \gamma' = 1.25 \pm 0.02$, and $\delta = 4.59 \pm 0.10$. Since the exponents have been determined independently they may be used to check some of the exponent relationships which have been postulated. For example, Widom's first conjecture,[26]

$$2(1-\beta) = 1.29 \pm 0.01 \overset{?}{=} \gamma\ , \tag{13}$$

appears to lie just outside the possible range for γ. Widom's second conjecture,

$$\gamma'/\beta = 3.54 \pm 0.08 \overset{?}{=} (\delta - 1)\ , \tag{14}$$

appears to be easily satisfied. Rushbrook's inequality,[27]

$$2\beta + \gamma' \geq 2 - \alpha', \tag{15}$$

will be satisfied if $\alpha' \geq 0.044 \pm 0.022$. The information available, while not very definitive, indicates that α' might easily satisfy this condition. Use of Griffiths's inequality,[28]

$$\beta(1+\delta) \geq 2 - \alpha'\ , \tag{16}$$

leads to $\alpha' \geq 0.027 \pm 0.035$, which does not rule out a logarithmic infinity in the specific heat.

The results are compared with a few of the many measurements which have appeared in the last few years. In making these comparisons, extensive use has been made of the review article by Heller.[29] All data were treated by the usual power-law analysis (1)–(6).

Measured values of β appearing in the literature have generally run from about 0.34 to 0.365 for all fluids examined. There does not appear to be a correlation between β and the quantum parameter Λ^*, and most of the variation between the results would seem to be due to experimental circumstances. For example, failure to measure densities at the height of the meniscus could lead to a broadening of the vapor-liquid dome, which would become more pronounced neared T_c, and which would lead to an apparent value of β which is too low. Temperature-scale irregularities may also play a part. The value of β has also been noticed to vary a little with the range of $|t|$ of the fitted data. In our results, β varied from 0.351 for a $|t|_{\max} = 6 \times 10^{-3}$ to 0.357 for a $|t|_{\max} = 10^{-1}$. On the other hand, the coefficient B does vary considerably from one fluid to another. The value of B found here is about the same as that for Xe.[5]

Direct measurements of the shape of the critical isotherm have apparently been limited to CO_2,[7,8] Xe,[10,18] and He.[14,30–32] The values found for δ have varied from 3.4–4.27 for the He isotopes. Wilcox and Balzarini[10] found $\delta = 4$ for Xe. Heller's[29] analysis of the literature yielded $4.2^{+0.6}_{-0.3}$ for Xe, and 5 ± 1 for CO_2. Our value for $\delta(4.59 \pm 0.10)$ agrees with the optical measurements on CO_2 and the work on Xe within their uncertainties (as given by Heller), but it is considerably higher than the results for He. This discrepancy could be due to quantum effects, but, in consideration of the difficulties encountered in this type of work, it may also be due to experimental effects or to the analysis of the data. The isotherms measured by Chase[30] and by Roach[14] were not at the critical temperature. It is the author's experience that even when this fact is taken into account in the analysis by including a term for the temperature effect [such as Eq. (11) with $B = 0$], the resulting value of δ is much too small. Coopersmith[33] reanalyzed Roach's data by a different method and found δ equal to 4.43 and 4.03 for the liquid and vapor sides, respectively. A later reanalysis using the scaling laws[5] gave 4.45 and is compared below.

Other problems, avoided here, are probably inherent in work involving the measurement of pressure versus density: (a) The isotherm is not antisymmetric about ρ_c in these coordinates over an appreciable density range; (b) the hydrostatic corrections to the experimental pressure measurements are difficult to calculate with sufficient accuracy; (c) the extremely small variation of P with density places very stringent requirements on the resolution of the pressure gauge; also P_c must be very accurately known and, if it is derived via an extrapolation of the vapor-pressure curve, the nonanalyticity of this curve should be taken into account.

The bulk of the measurements of the compressibility on the critical isochore also seem to have been performed on the same substances. The analysis of the combined CO_2 data of Lorentzen,[7] Schmidt,[8] and Michels *et al.*[34] yielded a value of 1.35 ± 0.15 for γ. Levelt-Sengers and Vincentini-Missoni[21] have presented an analysis of the data of Michels *et al.*[19,20] on Ar and Xe and of Habgood and Schneider, and of Weinberg and Schneider[18] on Xe. The different sets of data agree very well and seem to indicate a limiting value of $\gamma = 1.4$ for $t \leq 2 \times 10^{-2}$ decreasing gradually to $\gamma \cong 1$ for $t > 0.2$. Preliminary results of Wilcox and Balzarini[10] gave $\gamma = 1.1 \pm 0.2$ for Xe. The various results for He^3 and He^4 reveal values for γ between 1.05 and 1.20. Our results agree qualitatively with the work on Ar and Xe with γ having a limiting value of about 1.25.

Most previously published compressibilities along the coexistence curve lead to values for γ' which have very large uncertainties. The analysis[29] of the work on Xe leads to $\gamma' = 1 \pm 0.5$, and for CO_2 $\gamma' = 1.1 \pm 0.4$, but the data scatter badly. The results of Chase and Zimmerman,[30] Bendiner, Elwell, and Meyer,[31] Sherman,[32] and Roach[14] yield values for He^4 varying between 1.0 and 1.18 with stated uncertainties of about ±0.1. Edwards,[17] on the

TABLE III. Comparison of the results of scaling-law analysis (Ref. 5) for CO_2, Xe, and He^4 with our results for O_2 (in reduced units).

	Ref. 5			This paper
	CO_2	Xe	He^4	O_2
β	0.35	0.35	0.359	0.353
B	4.030	3.603	2.886	3.637 ± 0.010
δ	4.6 ± 0.1	4.6 ± 0.1	4.45 ± 0.10	4.59 ± 0.10
D	2.6 ± 0.1	3.3 ± 0.2	3.2 ± 0.1	4.04 ± 0.63
γ, γ'	1.26 ± 0.02	1.26 ± 0.06	1.24 ± 0.04	1.25 ± 0.02
Γ	5.26×10^{-2}	5.9×10^{-2}	1.30×10^{-1}	$(5.26\pm0.50)\times10^{-2}$
Γ'	1.19×10^{-2}	1.43×10^{-2}	3.59×10^{-2}	$(1.09\pm0.22)\times10^{-2}$
Γ/Γ'	4.4	4.1	3.6	4.8 ± 1.0

other hand, obtained the value $\gamma' = 1.26 \pm 0.10$ for He^4, which is in good agreement with our value of approximately 1.25. The fact that his compressibility measurements were interpolated to constant values of x makes the agreement even more significant. Recent results on Xe by Giglio and Benedek,[35] using light-scattering techniques, gave $\gamma'_{\text{liquid}} = 1.228 \pm 0.028$ and $\gamma'_{\text{vapor}} = 1.244 \pm 0.017$, in good agreement with our results. Their average value for Γ', 0.93×10^{-2} in reduced units, also agrees relatively well with the value 1.09×10^{-2} which we obtain for O_2.

Accurate determination of the exponents γ and γ' may be beset with other difficulties besides the problems of measuring very small pressure differences. If the data are taken too far from T_c the limiting value will not be obtained. The requirement of measuring compressibilities at exactly constant values of x and of applying a curvature correction where necessary are other considerations which become more important as the critical point is approached more closely. Failure to take these points into consideration could lead to values of the compressibility, and of γ and γ', which are too small.

Vincentini-Missoni, Sengers, and Green[5] have reanalyzed much of the data in the literature using the scaling-law equation of state. The agreement of the present work with their results is excellent. It is significant to note that their equation, fitted to data further away from the critical point, yields results which are in agreement with our direct measurements very near the critical point. This agreement implies that the assumptions built into the scaling laws concerning the symmetry in the *PVT* surface are valid, and that the expression which they used for the scaling function, $h(x)$ in Eq. (7), is adequate to describe the behavior of fluids in the critical region. It also demonstrates that the power-law and scaling-law analyses yield the same results when applied under appropriate conditions. Table III compares the results from Ref. 5 for CO_2, Xe, and He^4 with the present results on oxygen. The exponents are nearly the same and, for the classical fluids at least, the coefficients agree relatively well. For comparison, the exponents predicted via the lattice-gas model[36] are $\beta = 0.312$, $\delta = 5.2$, $\gamma = 1.25$, $\gamma' = 1.25$–1.31, and $\Gamma/\Gamma' = 5.2$.

VI. CONCLUSIONS

The stack of horizontal flat-plate capacitors, coupled with a precise temperature-control system, provides a convenient and useful way to study the detailed nature of the *PVT* surface of a fluid near its critical point. The quantity obtained directly from the measurements $\Delta\rho/\Delta z$, is the most desirable one for studying the critical region. The avoidance of the necessity of measuring very small pressure differences accurately is a distinct advantage. The troublesome problem of temperature gradients can be held to a minimum in a well-designed system.

For further studies it would be advantageous to work even closer to the critical point. For this purpose it might be wise to construct an apparatus having spacings between the capacitors which vary from several millimeters up to several centimeters. The curvature correction and the electrostriction correction will, however, become more important as the critical point is approached more closely.

ACKNOWLEDGMENT

The author is grateful to B. A. Younglove for much valuable advice concerning the design of the apparatus and dielectric measurement techniques.

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PHYSICAL REVIEW A VOLUME 2, NUMBER 6 DECEMBER 1970

Relativistic Correction to the Equilibrium Statistical Mechanics of a Dense Electron Gas*

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(Received 19 June 1970)

The grand partition function for a degenerate electron gas with relativistic corrections of order $(v/c)^2$ in ring approximation is given. The technique used is the method of Montroll and Ward; in this problem independent field degrees of freedom are not required. The correlation energy, which represents a generalization of the Gell-Mann–Brueckner result, is obtained. Comparison with the field-theoretic results of Akhiezer and Peletminskii is made, with the same results. However, in view of the absence of independent field degrees of freedom in our treatment, renormalization is not required here (to obtain their result Akhiezer and Peletminskii must resort to charge, mass, and vacuum renormalization).

I. INTRODUCTION

There is considerable interest at present in the properties of charged-particle systems in a regime where relativistic effects must be examined. Some of this interest is generated by possible applications to fusion problems and some by astrophysical situations. This paper deals with the equilibrium statistical mechanics of a dense degenerate electron gas; the main application is therefore concerned with problems of the latter type, although there are also implications for hot classical laboratory plasmas (as will be noted).

Apart from the above, there is some bearing on the fundamental problem of a basis for a relativistic