tion $v_0/v = 0.74$ along with the experimental melting density of solid helium yields a hard-sphere diameter $a = 3.32$ *A*, which is unreasonably large. Therefore we can only take the above comparison of α values as an indication that condensate-fraction estimates may be quite sensitive to the shape of $f(r)$ assumed in JWF which adequately represents ^{4}He.

In conclusion, we have estimated the condensate fraction α_2 for ground-state ^{4}He solid using the JWF of Ref. 3, obtaining a value orders of magnitude larger than estimates[5] using experimental data for ^{3}He. If no JWF can provide a *qualitatively* adequate description of solid ^{4}He,[8] then α_2 could conceivably be zero (no Bose–Einstein condensation in the solid). Otherwise, our value $\alpha_2 \approx 0.01$ may still be significantly conditioned by the shape of $f(r)$ used in the JWF.

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PVT Surface of He^4 near Its Critical Point[*]

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High-resolution measurements of the pressure coefficient $(\partial P/\partial T)_\rho$ of He^4 are reported in both the one-phase and two-phase regions close to the critical point. The data consist of 29 isochores covering the density range $-0.2 < \Delta\rho < 0.2$ and the temperature range $-0.020 < t < 0.032$, where $\Delta\rho = (\rho - \rho_c)/\rho_c$ and $t = (T - T_c)/T_c$. The intersections of the isochores with the coexistence curve locate 28 points on the coexistence curve. These points fit the equation $|\Delta\rho| = (1.395 \pm 0.020)t^\beta$, with $\beta = 0.3554 \pm 0.0028$ and $\rho_c = 69.580 \pm 0.020$ mg/cm^3. Parameters are reported for the best fit of the data to the "linear model" of Schofield, Litster, and Ho, in which the critical exponents have the values $\alpha = 0.115 \pm 0.006$ and $\gamma = 1.1743 \pm 0.0005$, and to a more accurate parametric model in which $\alpha = 0.067 \pm 0.006$ and $\gamma = 1.2223 \pm 0.0017$. The more accurate model does not have the symmetry required by the scaling hypothesis.

I. INTRODUCTION

Recent advances in the theory of critical phenomena have emphasized the need for high-quality experimental data and, through the scaling hypothesis of Widom,[1] Griffiths,[2] Kadanoff,[3] and others,[4] have provided a means for analyzing the data in a simple fashion. The scaling hypothesis assumes that sufficiently close to its critical point the chemical potential of a fluid can be written

$$\mu(T, \rho) \equiv \mu_c(T) + \Delta\mu \ , \qquad (1)$$

$$\Delta\mu = \Delta\rho \, |\Delta\rho|^{\delta - 1} h(x) \ , \qquad (2)$$

where the chemical potential μ_c on the critical isochore is assumed to be an analytic function of tem-

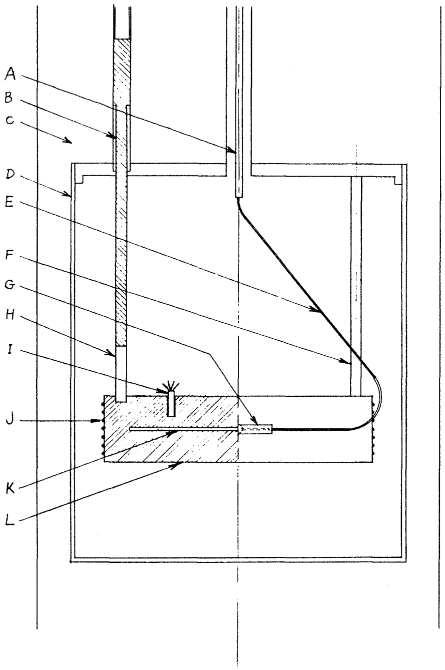

FIG. 1. Critical-point cell, shown in half-section. (A) 0.8-mm-i.d. ×2.1-mm-o.d. Cu vacuum-jacketed pressure-sensing tube; (B) heat-switch rod, oxygen-free-high-conductivity (OFHC) Cu; (C) liquid-He bath; (D) brass vacuum can; (E) 0.3-mm-i.d. ×0.5-mm-o.d. 30% Cu-Ni capillary; (F) and (H) 3.2-mm-o.d. ×0.25-mm wall stainless-steel support tubes; (G) brass fitting for pressure-sensing capillary, at midplane of sample space; (I) germanium resistance thermometer; (J) manganin wire heater, 2000 Ω; (K) sample space 1.0 mm high, 5.2027 cm^3 volume at 5 K; (L) OFHC Cu cell 10.2 cm o.d. × 2.9 cm high.

perature; $h(x)$ is an analytic function of the single variable

$$x = t/|\Delta\rho|^{1/\beta}\ , \tag{3}$$

with t and $\Delta\rho$, the scaled temperature and density, given by

$$t = (T - T_c)/T_c\ , \tag{4}$$

$$\Delta\rho = (\rho - \rho_c)/\rho_c\ ; \tag{5}$$

and δ is a critical exponent.

In an earlier paper[5] on the critical isochore of He^4, we presented evidence that μ_c is an analytic function of temperature and that the pressure on the critical isochore has the sort of anomaly required by Eq. (2). However, measurements at the critical density can only verify (or contradict) certain consequences of scaling. A detailed check of the scaling law and determination of the form of $h(x)$ requires accurate measurements of some thermodynamic property over a range of both density and temperature. Available data on the thermodynamic properties of He^4 fall short of satisfying this need.

The pioneering *PVT* measurements of Roach[6] lacked sufficient resolution in pressure and temperature, and they were subject to an unknown and possibly large gravity error.[7] The heat-capacity measurements of Moldover[8] had insufficient density resolution and suffered from thermometer drifts and spurious heat leaks. Both experiments used ill-defined temperature scales above the critical temperature. Therefore we have measured the pressure coefficient $(\partial P/\partial T)_\rho$ along 29 isochores in the density range $-0.2 < \Delta\rho < 0.2$ and the temperature range $-0.020 < t < 0.032$.

II. EXPERIMENTAL

The apparatus and experimental techniques were the same as were used in the author's study of the critical isochore[5]; therefore they will be described only briefly here.

A diagram of the low-temperature part of the apparatus is shown in Fig. 1. It is designed to minimize gravitational effects, assure good thermal equilibrium, and maintain a short thermal time constant.

Pressure differences were measured with a differential fused-quartz Bourdon gauge[9] of 300-Torr range and 10^{-3}-Torr resolution. Its reference capsule was maintained at a constant absolute pressure which was monitored by an absolute fused-quartz Bourdon gauge[10] of 2500-Torr range. This gauge could detect a change of 10^{-3} Torr, although its absolute accuracy was about 0.1 Torr. For this reason, the derivatives $(\partial P/\partial T)_\rho$ are considerably more accurate than the absolute pressures. A set of internally consistent pressures can, of course, be obtained by integration using our previously reported[5] critical pressure, 1706.12 ± 0.10 Torr, as an integration constant. The random error in $(\partial P/\partial T)_\rho$ caused by the resolution of the pressure gauge was about 0.1%. There may also be a systematic error of the order of 0.2% associated with the temperature scale (see below), which would affect all points about equally.

For each of the three cooling runs included in this experiment, the initial density was determined by measuring the He^4 gas condensed into the cell. Subsequent changes in density were made by withdrawing gas into a volumetric micrometer. The resolution of the volumetric micrometer was 2×10^{-5} mg/cm^3, much better than was needed. The over-all accuracy of the density measurements was about 0.02%. Because the amount of helium gas in the dead volume increased with pressure, no two experimental points were measured at exactly the same density. No attempt has been made to correct the data to standard isochores.

Temperatures were measured with a pair of germanium resistance thermometers which had been used for our measurements of the critical isochore[5] and were then calibrated by the National Bureau of Standards on the NBS Provisional Scale 2–20 K (1965)[11] (the acoustical thermometer scale). Vapor-pressure measurements indicated the calibration of the thermometers had changed by about 0.5 mK between the two experiments. The magnitude of the shift was independent of temperature within the temperature range of this experiment. Therefore all temperatures measured in this experiment were corrected in order to make the critical temperature (determined from the coexistence curve) agree with that previously reported.[5] The validity of this correction is confirmed by the agreement between the pressure-coefficient measurements in the two experiments (see below). The two thermometers agreed with each other within 0.2 mK before and after the NBS calibration. The temperature resolution was 0.3 μK.

The principal source of error in the temperature measurement was the NBS calibration. Calibration points were at about 1 K intervals and their error was stated to be ± 2 mK relative to the NBS scale. Hence the error in temperature intervals could be of the order of 0.2%, but is probably much smaller since most sources of error are not strongly temperature dependent. All temperatures and temperature derivatives reported in this paper refer to the NBS Provisional Scale 2–20 K (1965). The deviation of this scale from the thermodynamic scale is not known at present. Advantages of this temperature scale for He^4 critical-point work have been discussed in an earlier paper.[5]

III. EFFECT OF GRAVITY

The sample space was 1.0 mm high and of uniform horizontal cross section, and the pressure-sensing tube was arranged to measure the pressure at the midplane. The total hydrostatic-pressure difference across the cell was 5×10^{-3} Torr (3×10^{-6} times the critical pressure) at the critical density and 6×10^{-3} Torr at the largest density.

If h is the height of the cell, g is the acceleration of gravity, and μ_1, μ_2, and μ_3 are the chemical potentials at the top, center, and bottom of the cell, we have

$$\mu_3 - \mu_2 = \mu_2 - \mu_1 = \tfrac{1}{2} g h \ . \tag{6}$$

In a cell of uniform cross section, the difference in pressure between the bottom and top of the cell is given by

$$P_3 - P_1 = \rho_a g h \ , \tag{7}$$

where ρ_a is the mean density in the cell (mass of sample divided by total volume). The pressure and density at the midplane, P_2 and ρ_2, must be obtained by inverting the equation of state, subject to the conditions (6) and (7). By standard thermodynamic techniques it can be shown that the pressure coefficient at constant mean density is given by

$$\left(\frac{\partial P_2}{\partial T}\right)_{\rho_a} = s_2 - \frac{\rho_2(s_3 - s_1)}{\rho_3 - \rho_1} \ , \tag{8}$$

where ρ_1, ρ_2, ρ_3 and s_1, s_2, s_3 are the densities and entropies per unit volume at the top, center, and bottom of the cell. Note that in the limit of small h, Eq. (8) reduces to the Clapeyron equation if ρ_a is in the two-phase region and to the Maxwell relation

$$\left(\frac{\partial P}{\partial T}\right)_{\rho} = \left(\frac{\partial S}{\partial V}\right)_{T} \tag{9}$$

if ρ_a is in the one-phase region.

If pressures are measured at the midplane, the gravity correction is extremely small when $\Delta\rho_a = 0$ because the compressibility is very nearly symmetric in $\Delta\rho$. It is also small when $\Delta\rho_a$ is large, since then the compressibility is small. At values of $\Delta\rho_a$ where the correction may be large, there is no simple expansion of Eq. (8) which can be used to estimate the magnitude of the effect. Therefore we have done numerical calculations by methods similar to those of Hohenberg and Barmatz[12] for various values of t and $\Delta\rho_a$. These calculations show that the gravity error in the pressure coefficient does not exceed 10^{-3} for any of the points reported here.

IV. PRESSURE COEFFICIENT

Measurements of the pressure coefficient $(\partial P/\partial T)_\rho$, the temperature $t = (T - T_c)/T_c$, and the density $\Delta\rho = (\rho - \rho_c)/\rho_c$ are plotted in dimensionless form in Figs. 2 and 3. The units for the pressure coefficient and temperature are those reported in our earlier paper[5]: $P_c/T_c = 328.209$ Torr/K and $T_c = 5.19828$ K (NBS). The densities are reduced using the critical density determined in this experiment: $\rho_c = 69.580$ mg/cm^3. Tables of the data are available from National Auxiliary Publication Service.[13]

V. COEXISTENCE CURVE

The temperature at which each isochore crossed the coexistence curve was determined from the discontinuity of the pressure coefficient in the following way. On the two-phase part of the isochore the pressure was represented by an integrated form of the vapor-pressure equation reported in our earlier paper [Eq. (9) of Ref. 5]; on the one-phase part the pressure was represented by a cubic equation in t fitted by least squares to pressure measurements close to the crossing. The

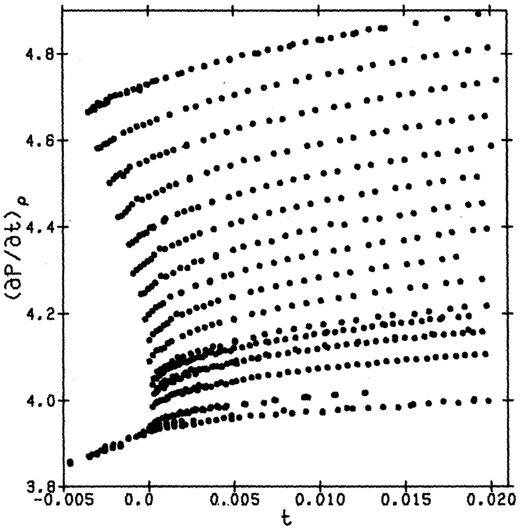

FIG. 2. Pressure coefficient $(\partial P/\partial T)_\rho$ of He^4 in units of $P_c/T_c = 328.209$ Torr/K. The values of $\Delta\rho$ for the isochores shown are, from top to bottom: 0.1993, 0.1844, 0.1696, 0.1546, 0.1400, 0.1265, 0.1127, 0.0994, 0.0858, 0.0720, 0.0571, 0.0532, 0.0437, 0.0305, 0.0114, and 0.0015. The isochore for $\Delta\rho = 0.0114$ is one reported in Ref. 5.

temperature of intersection of the two curves was determined by Newton–Raphson iteration. The corresponding density was taken from the point closest to the intersection, since the variation in density from point to point was very small. These data are presented in Table I.

They were fitted by the method of least squares to the equation

$$(T_c - T)/T_c = x_0 \left| (\rho - \rho_c)/\rho_c \right|^{1/\beta} , \tag{10}$$

with the weighting factor $\Delta\rho^2$. The best values of the fitting parameters were found to be

$$\beta = 0.3554 \pm 0.0028 , \tag{11}$$

TABLE I. Coexistence curve of He^4. Densities and temperatures have been reduced using $\rho_c = 69.580$ mg/cm^3, $T_c = 5.19828$ K.

$\Delta\rho$	$10^3 t$
−0.195 319	−3.9440
−0.181 091	−3.2223
−0.167 007	−2.5613
−0.152 491	−1.9810
−0.138 551	−1.4823
−0.124 897	−1.1287
−0.111 244	−0.8178
−0.097 734	−0.5549
−0.083 937	−0.4131
−0.070 284	−0.1796
−0.055 481	−0.1353
−0.041 828	−0.0276
−0.027 887	0.0686
0.030 463	−0.1349
0.043 541	−0.0414
0.043 828	−0.0828
0.053 170	−0.0968
0.057 051	−0.1223
0.071 997	−0.2390
0.085 794	−0.4065
0.099 448	−0.5888
0.112 670	−0.8393
0.126 467	−1.1674
0.139 976	−1.5448
0.154 636	−2.0518
0.169 582	−2.6481
0.184 385	−3.3809
0.199 332	−4.1968

$$\rho_c = 69.580 \pm 0.014 \text{ mg/cm}^3 , \tag{12}$$

$$x_0 = 0.392 \pm 0.013 . \tag{13}$$

If Eq. (10) is expressed in the more usual form

$$|\Delta\rho| = B(-t)^\beta , \tag{14}$$

the constant B has the value

$$B = 1.395 \pm 0.020 . \tag{15}$$

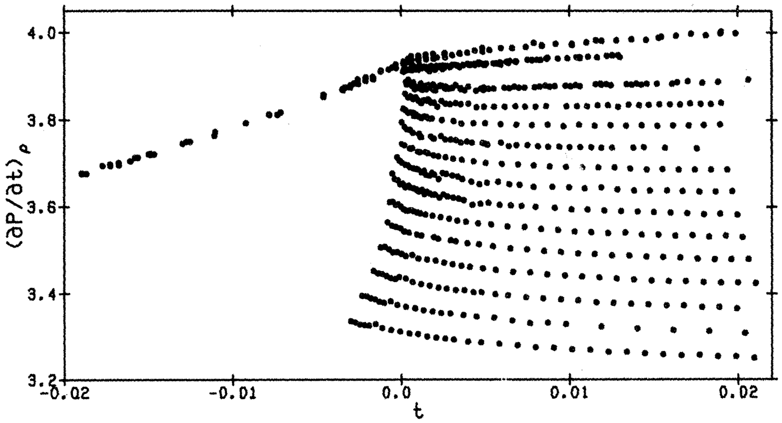

FIG. 3. Pressure coefficient $(\partial P/\partial T)_\rho$ of He^4 in units of $P_c/T_c = 328.209$ Torr/K. The values of $\Delta\rho$ for the isochores shown are, from top to bottom: 0.0015, −0.0094, −0.0279, −0.0418, −0.0555, −0.0703, −0.0839, −0.0977, −0.1112, −0.1249, −0.1386, −0.1525, −0.1670, −0.1811, and −0.1953. The isochore for $\Delta\rho = -0.0094$ is one reported in Ref. 5.

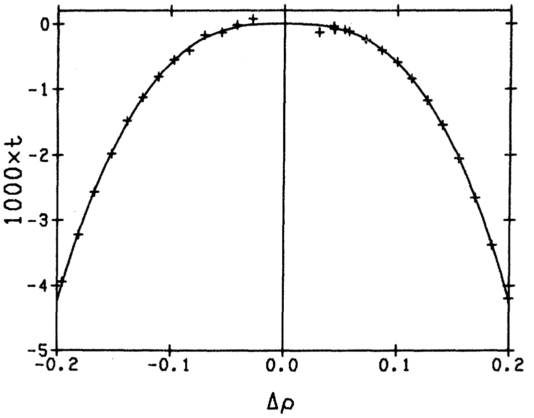

FIG. 4. Coexistence curve of He^4. The curve is calculated from Eqs. (10)–(12).

The data were taken in two cooling runs subsequent to the NBS calibration of the thermometer. Since the calibration of the thermometer may have changed each time it was warmed to room temperature, T_c in Eq. (10) was fitted separately for the two runs, but the other parameters were constrained to be the same. The values of T_c were found to be 0.530 ± 0.085 and 0.600 ± 0.081 mK larger than the value we reported previously.[5] All temperatures in this experiment were corrected so that the critical temperature would agree with that of the earlier work.

The standard deviations given in Eqs. (11)–(15) are those of the least-squares fit and reflect the internal consistency only. If allowance is made for errors in gas measurement and cell volume, we have

$$\rho_c = 69.580 \pm 0.020 \text{ mg/cm}^3 . \tag{16}$$

This is more accurate and slightly smaller than our earlier value[5] (69.64 ± 0.07) and agrees exactly with Moldover's value[8] (69.58 ± 0.07). It is consistent with that of el Hadi, Durieux, and van Dijk[14] (69.76 ± 0.20), but not with those of Edwards[15] (69.451 ± 0.069) and of Roach[6] (69.0). The values of B and β given above are consistent with those of Edwards[15] (1.4166 ± 0.0032 and 0.3598 ± 0.0007) and of Roach[6] (1.42 and 0.354 ± 0.010). Edwards's $\Delta\rho$'s are 0.001–0.002 smaller in magnitude than ours, whereas Roach's are 0.002–0.005 larger.

Agreement of our measurements with Eq. (14) is shown in Figs. 4 and 5. The greater errors for small values of $\Delta\rho$ result from the fact that the discontinuity in $(\partial P/\partial T)_\rho$ approaches zero as $\Delta\rho$ approaches zero. It was for this reason that we used a weighting factor of $\Delta\rho^2$.

We tested the effect of allowing for the slope of the rectilinear diameter by fitting the equation

$$\Delta\rho = \frac{T - T_c}{\rho_c}\frac{d\rho_d}{dT} \pm B(-t)^\beta , \tag{17}$$

where $d\rho_d/dT$ is the slope of the rectilinear diameter, for which we used the value $-0.0214\rho_c$ K^{-1} calculated from Edwards and Woodbury's[16] refractive-index measurements. The fit to Eq. (17) was slightly worse than to Eq. (14), and the parameters were not significantly changed except that ρ_c was 0.04 mg/cm^3 smaller. If, as is suggested by the measurements of el Hadi *et al.*,[14] $d\rho_d/dT$ becomes smaller in magnitude near T_c, then the effect would be even smaller. In view of this and of the complications that would otherwise occur in the equation of state, we will assume the coexistence curve to be symmetric over the temperature range of these experiments.

V. PARAMETRIC OF EQUATION OF STATE

The scaling hypothesis very much simplifies the task of finding an equation which adequately represents the pressure as a function of the two independent variables, density, and temperature. The parametric equations proposed by Schofield[17] are particularly attractive because: (i) they satisfy the scaling law; (ii) they are manifestly analytic everywhere in the one-phase region except at the critical point, and the singularity is confined to the one variable r, which is always positive; and (iii) the equations for the common thermodynamic functions all have a particularly simple form.

Schofield proposed the transformation

$$t = r(1 - b^2\theta^2) , \tag{18}$$

$$\Delta\mu \equiv \mu - \mu_c = ar^{\gamma+\beta}\theta(1-\theta^2) , \tag{19}$$

where μ_c is the chemical potential on the critical isochore, a and b are constants, β and γ are the

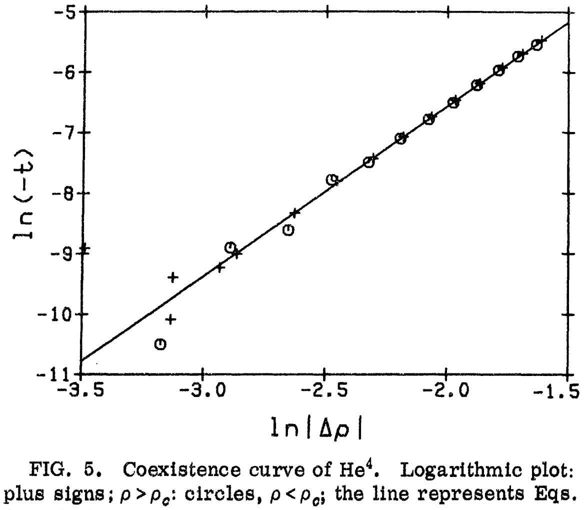

FIG. 5. Coexistence curve of He^4. Logarithmic plot: plus signs; $\rho > \rho_c$: circles, $\rho < \rho_c$; the line represents Eqs. (10)–(12).

critical exponents,[18] and r and θ are new independent variables replacing $\Delta\mu$ and t. In these variables the critical point is represented by $r=0$, the critical isochore by $\theta=0$, the critical isotherm by $\theta=\pm 1/b$, and the coexistence curve by $\theta=\pm 1$. In the one-phase region, r and θ are confined to the intervals $r \geqslant 0$ and $-1 \leqslant \theta \leqslant 1$. Schofield then proposed the equation of state

$$\Delta\rho = r^{\beta}\theta g(\theta) , \tag{20}$$

with $g(\theta)$ an analytic function of θ which is to be chosen to fit the experimental data. Schofield, Litster, and Ho[19] found that if $g(\theta)$ is taken to be a constant, very good fits are obtained with experimental data for the critical point of He^4 and the Curie point of CrBr$_3$, especially if the constant b is chosen to satisfy the equation

$$b^2 = (\gamma - 2\beta)/\gamma(1-2\beta) . \tag{21}$$

They call this particular choice for $g(\theta)$ and b the "linear model." Barmatz and Hohenberg[12,20] use the term linear model and the abbreviation LM to refer to any model satisfying Eqs. (18)–(20) in which $g(\theta)$ is constant, regardless of the value of b. We will use the same convention. They refer to Eq. (21) as the "minimization condition." We will call it "condition M."

To the theoretical physicist, μ and t are a natural pair of independent variables in terms of which the transformation to r and θ can be defined. From the point of view of the experimental physicist, it is inconvenient to use as an independent variable a property (μ) which cannot be measured. Therefore we will define the transformation by the equations

$$t = r(1 - b^2\theta^2) , \tag{22}$$

$$\Delta\rho = m\theta r^{\beta} \tag{23}$$

and write for the chemical potential

$$\Delta\mu = a r^{\gamma+\beta}\theta(1-\theta^2) f(\theta) , \tag{24}$$

with $f(\theta)$ to be determined by experiment. The factor $\theta(1-\theta^2)$ is necessary to make $\Delta\mu$ vanish on the coexistence curve and the critical isochore. The linear model is characterized by $f(\theta)=1$.

If $f(\theta)$ is an even function ($\Delta\mu$ antisymmetric in $\Delta\rho$), Eq. (24) can be integrated with respect to ρ to obtain an analytic expression for the Helmholtz free energy, from which all the common thermodynamic functions are obtained by differentiation. If $f(\theta)$ is not an even function, the free energy, the pressure, the entropy, and the heat capacity can generally only be obtained as series expansions.

Since our model [Eqs. (22)–(24)] satisfies the scaling hypothesis, only two of the critical exponents[18] α, β, γ, and δ are independent. We have determined β from the coexistence curve and choose γ to fit our pressure-coefficient data. We regard α and δ as *defined* by the scaling relations

$$\alpha \equiv 2 - \gamma - 2\beta , \tag{25}$$

$$\delta \equiv (\gamma/\beta) + 1 . \tag{26}$$

We will make use of α where it simplifies our expressions, but we will have no need for δ.

In view of the success of Schofield, Litster, and Ho[19] in fitting Roach's[6] *PVT* data with the linear model and of Barmatz and Hohenberg[20] in fitting Moldover's[8] C_v data and Barmatz's[21] sound-velocity data with the same model, we first tried to fit our pressure coefficients to the linear model. In the linear model, the pressure is given by

$$P = -A_0(t) + a\theta(1-\theta^2) r^{\gamma+\beta} + (am/2b^4)(L_1 + L_2\theta^2 + L_3\theta^4) r^{\gamma+2\beta} , \tag{27}$$

where

$$L_1 = \frac{\gamma - 2\beta - b^2\alpha\gamma}{\alpha(1-\alpha)(2-\alpha)} , \tag{28}$$

$$L_2 = \frac{b^4\alpha(3-2\beta-2\alpha) - b^2(\gamma-2\beta)}{\alpha(1-\alpha)} , \tag{29}$$

$$L_3 = \frac{b^4(1-2\beta-2\alpha)}{\alpha} . \tag{30}$$

In Eq. (27) $A_0(t)$ is the nonsingular part of the Helmholtz free energy per unit volume and is an analytic function of the temperature. The pressure coefficient in the one-phase region is given by

$$\left(\frac{\partial P}{\partial T}\right)_{\rho} = -A_0'(t) + a\theta(1+m\theta r^{\beta})\left(\frac{\gamma-(\gamma-2\beta)\theta^2}{1-(1-2\beta)b^2\theta^2}\right) r^{\gamma+\beta-1} + \frac{am}{2b^4\alpha}\left(\frac{\gamma-2\beta-b^2\alpha\gamma}{1-\alpha} - b^2(\gamma-2\beta)\theta^2\right) r^{\gamma+2\beta-1} \tag{31}$$

and in the two-phase region by

$$\frac{dP_v}{dT} = -A_0'(t) + \frac{am[\gamma-2\beta-b^2(1-2\beta)(\gamma+2\beta)] r^{\gamma+2\beta-1}}{2b^4\alpha(1-\alpha)} . \tag{32}$$

Here $A_0'(t)$ is the derivative of $A_0(t)$. It can be adequately represented by a quadratic function of t:

$$-A_0'(t) = c_1 + c_2 t + c_3 t^2 . \tag{33}$$

Comparing Eqs. (22) and (23), remembering that $|\theta| = 1$ on the coexistence curve, we find that m is given by

$$m = B(b^2-1)^{\beta} . \tag{34}$$

Since B and β are already determined from the coexistence curve and α is defined in terms of γ by Eq. (25), Eqs. (31) and (32) have six adjustable parameters: γ, a, b, and the three c's. They were fitted by the method of least squares with all the

TABLE II. Parameters of the model equations.

Parameter	Value	Parameter	Value
	Coexistence curve [Eqs. (10) and (14)]:		
ρ_c	69.580 ± 0.20 mg/cm^3	x_0	0.392 ± 0.013
β	0.3554 ± 0.0028	B	1.395 ± 0.020
	Linear model [Eqs. (27), (33), and (34)]:		
γ	1.1743 ± 0.0005	a	6.053 ± 0.016
b	1.1683 ± 0.0042	c_1	3.93125 ± 0.00015
α	0.1148 ± 0.0056	c_2	-3.448 ± 0.062
m	0.975 ± 0.018	c_3	-16.9 ± 1.7
	Best parametric model [Eqs. (33)–(40)]:		
γ	1.2223 ± 0.0017	G_1	6.921 ± 0.317
b	1.2030 ± 0.0051	G_2	-17.232 ± 0.863
α	0.0668 ± 0.0058	G_3	11.235 ± 0.719
m	1.048 ± 0.020	G_4	2.052 ± 0.571
F_1	9.053 ± 0.119	G_5	-0.676 ± 0.288
F_2	0.514 ± 0.029	c_1	3.93023 ± 0.00020
H_1	-4.291 ± 0.188	c_2	-14.03 ± 0.74
H_2	-1.248 ± 0.053	c_3	-5.1 ± 2.7

points equally weighted. The best-fit values of the parameters are given in Table II and the deviations from the fitted equation are plotted in Figs. 6 and 7. The standard deviation σ of the fit is about 1.5 times the experimental error. It depends only weakly on b but is a minimum for the value of b given by condition M using the fitted value for γ.

Inspection of Figs. 6 and 7 shows that the fit is generally good, but there are systematic deviations, and the deviations are not symmetric in $\Delta\rho$. Because of these asymmetries, it is not possible to improve the fit by substituting various even functions for $f(\theta)$ in Eq. (24). On the other hand, if $f(\theta)$ is not even, it is impossible to derive an expression for the pressure in closed form. Therefore to obtain a better fit it is necessary to abandon Eq. (24) and construct a trial equation similar to Eq. (27) with more general functions of θ;

$$P = -A_0(t) + \theta(1-\theta^2)\,F(\theta)\,r^{\gamma+\beta} + [G(\theta^2) + \theta(1-\theta^2)\,H(\theta^2)]\,r^{\gamma+2\beta}\ . \tag{35}$$

Since at constant temperature

$$dP = (1+\Delta\rho)\,d\mu\ , \tag{36}$$

it is easily shown that the singular term of lowest order in r must be the same in $\Delta\mu$ as in P. Hence

$$\Delta\mu = \theta(1-\theta^2)\,F(\theta)\,r^{\gamma+\beta} + O(r^{\gamma+2\beta})\ . \tag{37}$$

The factor $\theta(1-\theta^2)$ is needed here for the same reason it is needed in Eq. (24). The factor $1-\theta^2$ multiplying $\theta H(\theta^2)$ is needed to make the pressure single-valued on the coexistence curve (when $\theta = \pm 1$).

After trying various functions for F, G, and H, we obtained a good fit with the polynomials;

$$F(\theta) = F_1 + F_2\,\theta\ , \tag{38}$$

$$G(\theta^2) = G_1 + G_2\,\theta^2 + G_3\,\theta^4 + G_4\,\theta^6 + G_5\,\theta^8\ , \tag{39}$$

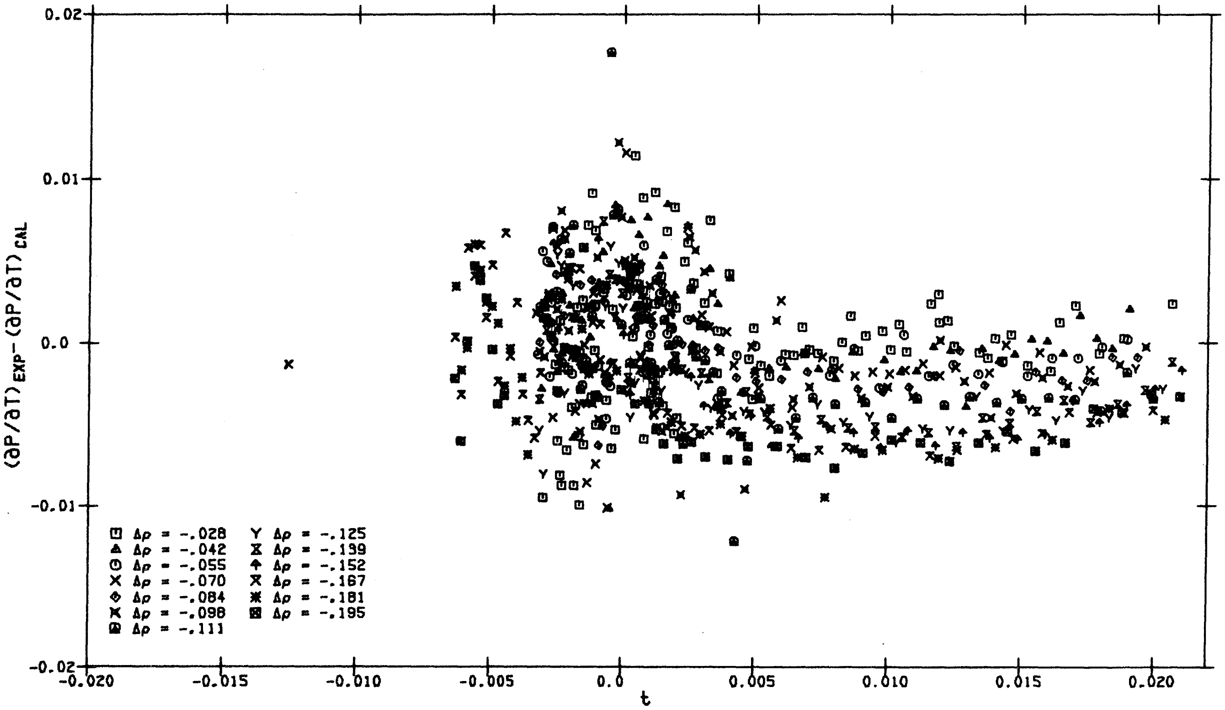

FIG. 6. Deviations from the linear model [Eqs. (27), (33), and (34)] for $\Delta\rho < 0$, in units of P_c/T_c.

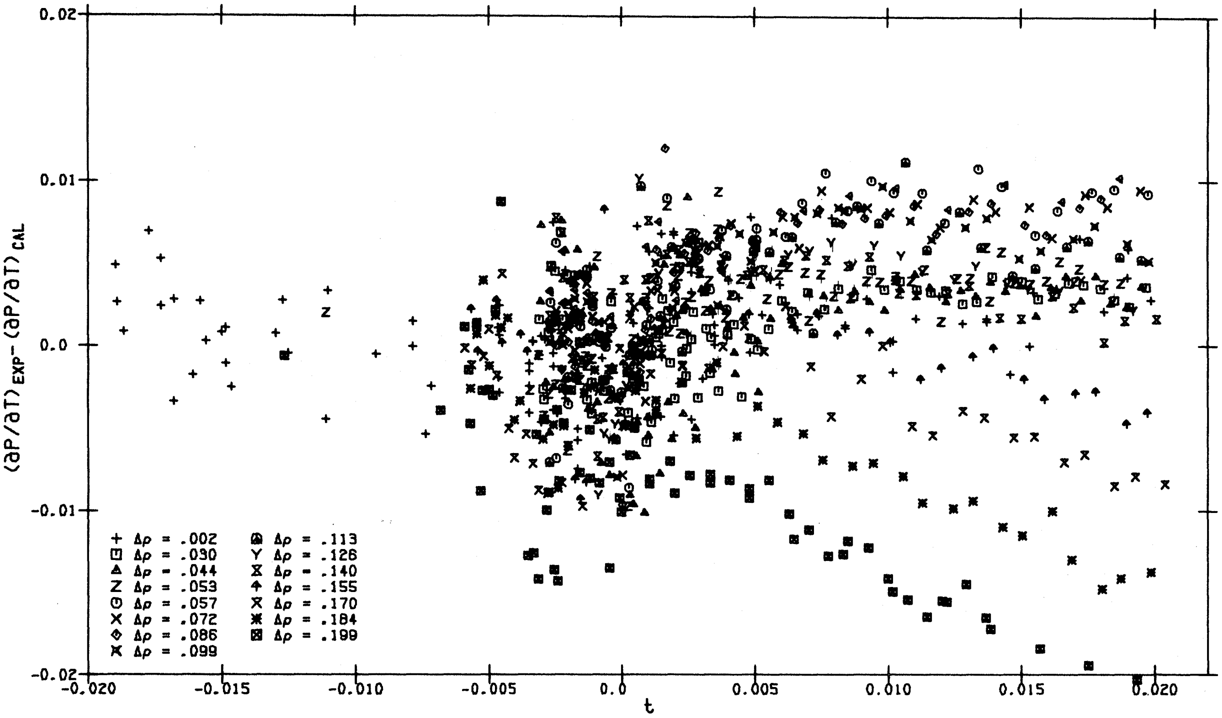

FIG. 7. Deviations from the linear model [Eqs. (27), (33), and (34)] for $\Delta\rho > 0$, in units of P_c/T_c.

$$H(\theta^2) = H_1 + H_2\,\theta^2 \,. \qquad (40)$$

$A_0'(t)$ was fitted by a quadratic as before. Best values of the 14 parameters are given in Table II, and deviations from the fitted equation are plotted in Figs. 8 and 9. Again, the best value for b is

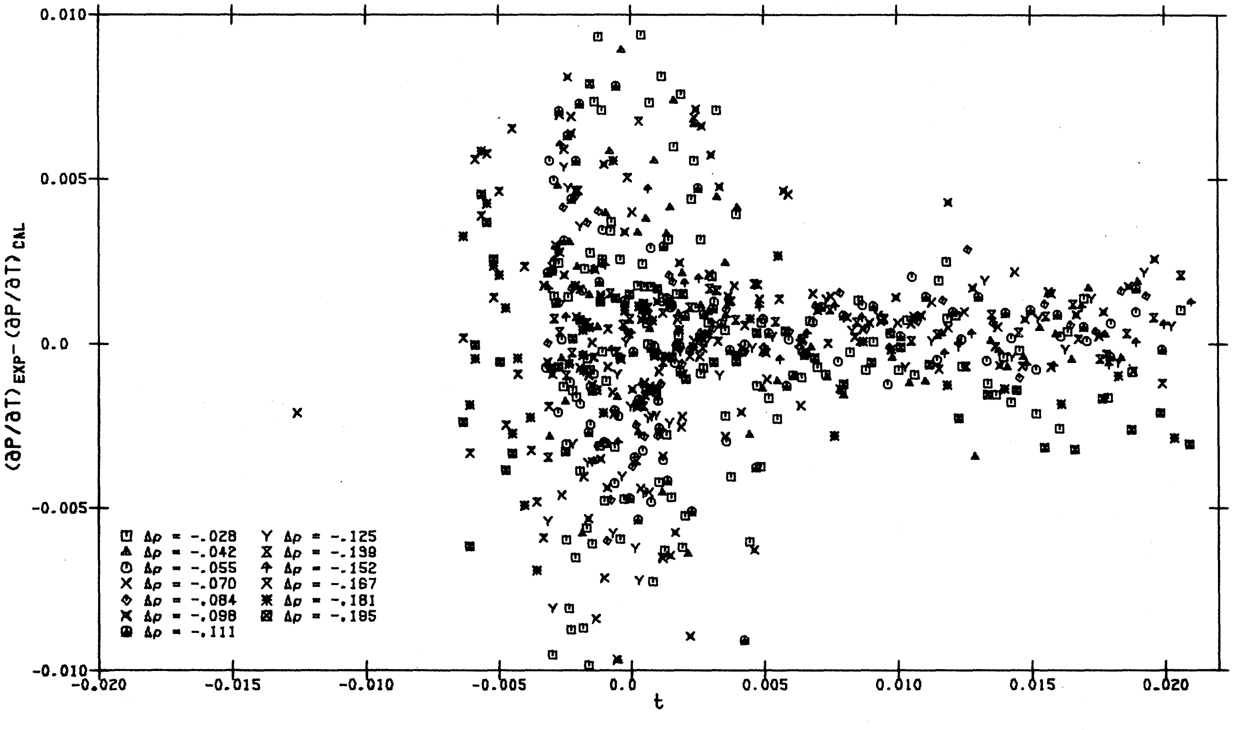

FIG. 8. Deviations from the best parametric model [Eqs. (33)–(40)] for $\Delta\rho < 0$, in units of P_c/T_c.

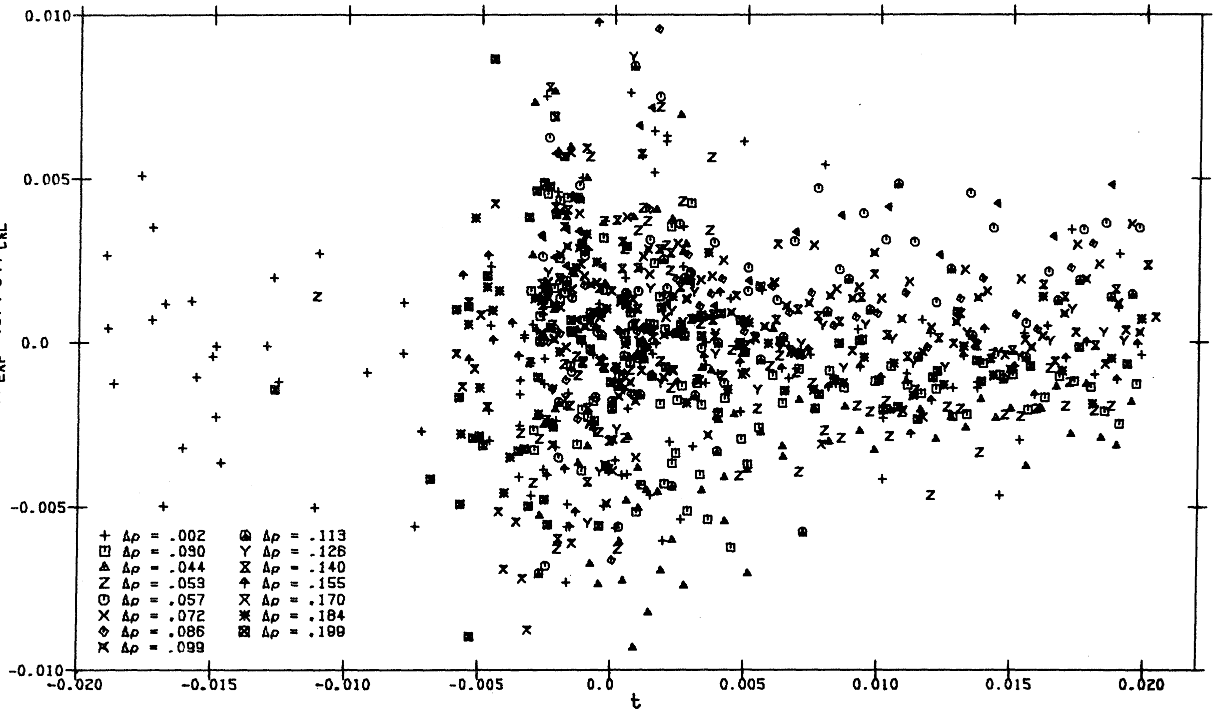

FIG. 9. Deviations from the best parametric model [Eqs. (33)–(40)] for $\Delta\rho > 0$, in units of P_c/T_c.

that given by condition M. The standard deviation is about equal to the experimental error, so no significantly better fit can be obtained by adding more terms. In fact, nearly as good a fit can be obtained without the two highest terms in G and the highest term in H. The improvement in fit over that for the linear model is due principally to the term in $F_2\theta$ in Eq. (38). Because of this term, the chemical potential and the pressure are not antisymmetric in $\Delta\rho$ even very close to the critical point. In this respect, the model does not obey the scaling hypothesis.

The value of the exponent α calculated from this fit (0.067 ± 0.006) agrees very well with that obtained by Barmatz and Hohenberg[20] (0.07 ± 0.005) directly from the heat-capacity data. The value of α derived from our linear model fit (0.115 ± 0.006) is nearly twice as large, and this difference illustrates the fact that the values of critical exponents derived from experimental data are model dependent.[22]

VI. COMPARISON WITH EARLIER MEASUREMENTS

Using Eq. (35) and its temperature derivative together with the constants in Table II to represent the measurements reported here, we can compare these measurements with other PVT data. In Fig. 10 are plotted the deviations from Eq. (35) of the three isochores reported earlier[5] by us, showing the good agreement between the two experiments. Figure 11 is a similar plot of Roach's pressure measurements,[6] using only those data which are within the density and temperature limits of our experiment. In order to minimize the effect of systematic errors, the pressures, temperatures, and densities have been reduced using Roach's critical constants ($\rho_c = 69.0$ mg/cm^3, $T_c = 5.189$ K, $P_c = 1705.0$ Torr), which are slightly different from ours. Aside from using Roach's

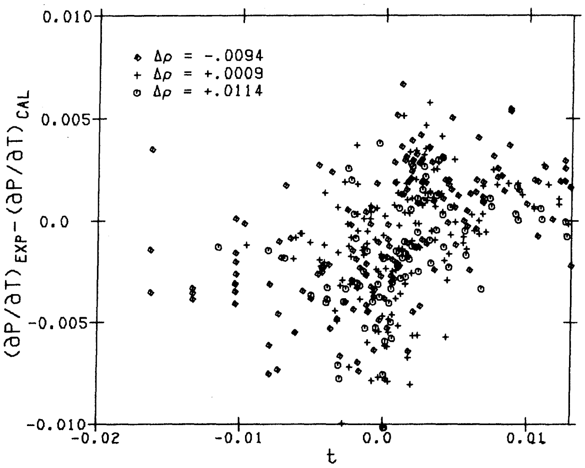

FIG. 10. Deviations from the best parametric model of the pressure-coefficient measurements of Kierstead (Ref. 5), in units of P_c/T_c.

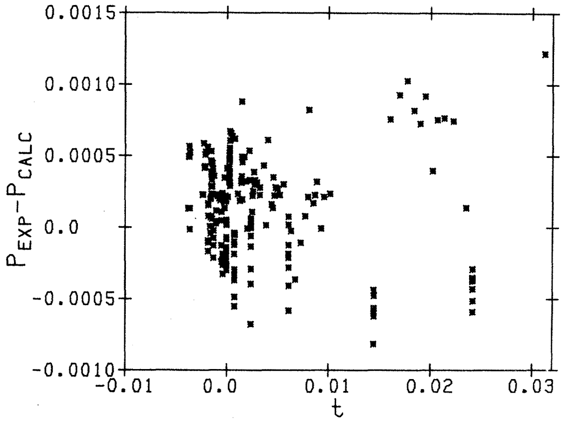

FIG. 11. Deviations from the best parametric model of the pressure measurements of Roach (Ref. 6), in units of P_c.

T_c, we have not tried to correct his temperature scale, since it is not well defined above T_c. Figure 11 shows that there is not any large systematic deviation between his measurements and ours.

VII. CONCLUSIONS

We have presented a set of high-resolution measurements of the pressure coefficient of He^4 covering the critical region. They are of sufficient accuracy to provide a sensitive test of any proposed equation of state, and they are referred to a well-defined temperature scale. We have also presented a set of values of temperature and density on the coexistence curve which are consistent with the pressure-coefficient measurements, and we have obtained from them a new value for the critical exponent β (0.3554 ± 0.0028).

The linear model of Schofield, Litster, and Ho[19] fits the data well enough for applications not requiring the very highest accuracy. However, the values of the critical exponents γ (1.1743 ± 0.0005) and α (0.115 ± 0.006) associated with this model probably do not represent the true limiting behavior.

We have proposed a more elaborate parametric model which fits the data well enough for the most exacting applications. This model is not entirely in accord with the scaling hypothesis, but the deviation is not large enough, compared to the experimental error, to warrant a firm conclusion regarding the validity of scaling. In this model γ is 1.2223 ± 0.0017 and α 0.067 ± 0.006.

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