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# Study of the Specific-Heat Singularity of $He^3$ near Its Critical Point*

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We present measurements of the specific heat $C_v$ of $He^3$ with an impurity of 250-ppm $He^4$ near its critical point, characterized by its density $\rho_c$ and temperature $T_c$. The sample cell had a vertical height of 0.5 mm to reduce the effect of gravity on the singularity. Data were taken along five isochores within the density range $-0.17 < \Delta\rho < +0.11$, where $\Delta\rho = (\rho - \rho_c)/\rho_c$, and in the temperature range $3\times 10^{-5} < |t| < 10^{-1}$, where $t = (T - T_c)/T_c$. The data are compared with previous $P$-$V$-$T$ measurements on this system and good consistency is shown between the two sets of data. An adequate description of the data along the critical isochore is found to be given by the extended scaling formulation of Green, Cooper, and Sengers, based on a generalized parametric equation of state. Within experimental error, the critical exponent describing the divergence of $C_v$ is the same for $t > 0$ and $t < 0$ and its value is $\alpha = 0.105 \pm 0.015$. Scaled behavior of the specific heat as a function of temperature and density is exhibited by the data. This scaling is then related to the linear model of Schofield, Litster, and Ho. Good agreement is found between the calculated and the experimentally measured parameters for the linear model. Small systematic deviations will be discussed. We also present an account of the calorimeter relaxation times encountered in the vicinity of $T_c$. In the two-phase region, these relaxation times are much longer than in the one-phase region and diverge as the transition temperature is approached. This behavior is empirically described and tentatively attributed to processes at the boundary between the phases.

## I. INTRODUCTION

The specific heat of single-component fluids near their critical points plays an important role in assessing the validity of the scaling hypothesis.[1] The experimental difficulties encountered in making measurements of $C_v$ sufficiently precise for a detailed evaluation in terms of scaling ideas are considerable. In recent years improvement in thermometry and temperature control have made such measurements increasingly accurate, and recent $C_v$ data have been reported by Moldover[2] on $He^4$ and Edwards, Lipa, and Buckingham[3,4] on Xe and $CO_2$.

The research described below consists of precision measurements of the specific heat at constant volume along five isochores in the vicinity of the critical point of $He^3$. This work is complementary to previous work on $He^3$ in this laboratory.[5,6] Recent research in other institutions on this system includes that of Kerr and Sherman,[7] Chase and Zimmerman (CZ),[8] Moldover and Little,[9,10] as well as previous work by them.[11–13] Dahl and Moldover[14] have recently made measurements of $C_v$ in $He^3$, but with emphasis on metastable states.

The $He^3$ sample used in this study contained 250-ppm impurity of $He^4$, and the densities involved have $|\Delta\rho| \leq 0.17$, where $\Delta\rho = (\rho - \rho_c)/\rho_c$. On each isochore, specific-heat measurements were made in the reduced temperature range $3.0\times 10^{-5} \leq |t| \leq 10^{-1}$, where $t = (T - T_c)/T_c$. The critical parameters, $T_c$ and $\rho_c$, are, respectively, $\approx 3.31$ K and $\approx 4.15\times 10^{-2}$ g/cm$^3$, as determined from previous research.[6,8,13] The work to be described has been reported in a preliminary way.[15]

The dominant effect of the 250-ppm $He^4$ impurity in our sample is to shift the critical temperature upwards by approximately 0.5 mK from the value it would have for a pure sample of $He^3$. This estimate is made by assuming a linear dependence of $T_c$ on the concentration $X_4$ of $He^4$. This assumption is justified from experiments[6(d)] giving $T_c$ for several concentrations $X_4$. Subsequent to the measurements reported in this paper we have measured the specific heat in a $He^3$-$He^4$ mixture containing 20 at.% $He^4$, to be reported at a later date. If we suppose, as a rough approximation, that $C_v$ at constant $t$ along the critical isochores varies linearly with $X_4$, we may estimate from this data that the impurity of 250-ppm $He^4$ introduces a relative change in $C_v$ of ~ 0.02% at $|t| = 10^{-3}$. Since this difference is always small compared to the scatter in our data (~3% at $|t| = 10^{-3}$), we believe we are justified in treating our samples as a one-component system.

The specific heat along the critical isochore is discussed separately in Sec. IV and is compared with the extended scaling expression given by Green, Cooper, and Sengers (GCS).[16] The data along all of the various isochores are then used in Sec. V to make extensive comparisons with $P$-$V$-$T$ measurements on this system by Wallace and Meyer (WM),[6] since these data were readily available to us. The data are then compared with the thermodynamic scaling given by Missoni, Sengers, and Green (MSG)[17] and analysed in terms of the linear model of the parametric equation of state of Schofield and co-workers.[18,19] Our presentation of this analysis differs from a recent one by Huang and Ho.[20] In Sec. V some comments on critical coefficients in several fluids are given.

## II. EXPERIMENTAL

### A. Description of the Apparatus

The calorimeter was designed to operate over a temperature range between about 1.2 and 5 K and made use of a simple heat switch. Special care was taken to minimize the distortion of the specific-heat peak in the critical region, caused by gravity. To this end the sample cavity within the calorimeter had the shape of a flat disk, the height being 0.5 mm with a diameter of approximately 3.5 cm, and the chamber was suspended horizontally. A schematic view of the calorimeter is given in Fig. 1.

The sample cavity was filled via a horizontal stainless steel capillary of inner diameter 0.019 cm connecting the cavity and a low-temperature valve, the latter thermally anchored to the outside He$^4$ bath at 4.2 K. The fill capillary was thermally anchored to the thermal shield (kept at the temperature of the He$^4$ pot) at the midpoint of its length. The valve used was a commercial Hoke model modified in this laboratory in order to reduce the volume below the valve seat. The space beneath the low-temperature valve seat and the interior of the fill capillary constituted together approximately 1% of the total volume of the cell.

The sample chamber was constructed of two parts, both of oxygen-free electrolytic copper, soldered together at the midline. This was suspended horizontally by means of a nylon thread from a stainless-steel rod. The rod could be mechanically raised and lowered to bring the chamber into thermal contact with the He$^4$ pot via three prongs of copper tipped with indium. With repeated cycling of the heat switch at room temperature it was found that the chamber always returned to within 0.5° of tilt from the horizontal position when the heat switch was opened.

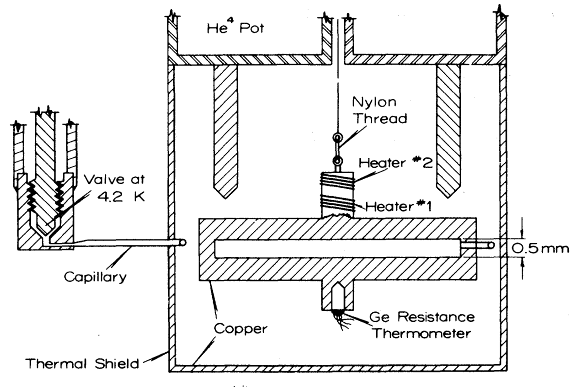

FIG. 1. Schematic diagram of calorimeter.

The temperature of the He$^4$ pot was electronically regulated, and was stable to within 20 $\mu$K for periods of several hours. During data taking, with the heat switch open, the pot was normally regulated to a temperature 50–150 mK below that of the calorimeter. So long as the resultant heat leak was reasonably compensated (see below) there was no perceptible dependence of the measured specific heat on this temperature difference.

The sample chamber was supplied with two noninductively wound heaters, one of which was used to provide measured heat amounts for the calorimetric measurements. The other auxiliary heater was used to counteract the negative heat leak from the He$^4$ pot to the sample chamber. The main thermometer was a specially doped germanium resistor provided as a gift by CryoCal, Inc., and was inserted into a hole in the bottom of the sample chamber. The main heater and thermometer both had superconducting leads. Thermal contact between the copper and the resistor was insured by the use of Apiezon-J oil. This resistor along with a wire-wound standard resistance kept at 4.2 K formed two arms of a two-terminal ac bridge detection system. The other two arms of the bridge were formed by a commercial ratio transformer, which gave a direct reading of the ratio $R_{\mathrm{Ge}}/(R_{\mathrm{Ge}}+R_{\mathrm{stan}})$ to seven digits. Here $R_{\mathrm{Ge}}$ and $R_{\mathrm{stan}}$ are the resistances, respectively, of the germanium thermometer and the standard resistor. The temperature detection system was capable of resolving temperature differences of 0.5 $\mu$K for a heat input of 0.5 erg/sec into the thermometer. The temperature resolution was never an important source of error in making the specific-heat measurements.

The time it took the filled calorimeter to come to thermal equilibrium was less than a few seconds for $|t| > 10^{-3}$, but became as long as 30 min for $(-t) \lesssim 10^{-4}$ in the two-phase region. This increase in the time to reach thermal equilibrium is examined in more detail in Sec. III. The heat leak to the He$^4$ pot was also strongly temperature dependent very near $T_c$. This was apparently due to the anomalous thermal conductivity of the fluid near the critical point,[21,22] and increased convection in the fill capillary at these temperatures. This caused some changes with time and temperature in the temperature drift rate of the calorimeter. The combination of long relaxation times and temperature-dependent heat leak was the principal source of random error in the determination of $C_v$ for $|t^*| \lesssim 10^{-3}$. Here $t^* = (T - T_{\mathrm{tr}})/T_{\mathrm{tr}}$, where

$T_{tr}$ (tr for "transition") is the temperature at which an isochore intersects the coexistence curve; thus $T_{tr} \leq T_c$. For $T > T_{tr}$ the relaxation time was too small to be measured even for the points closest to the transition. The temperature-dependent heat leak was still not negligible in this region, and could require longer waiting times for the establishment of a reliable extrapolation to the final temperature. For larger values of $|t^*|$ the principal source of systematic error was uncertainty in the measurement of the heat pulse, typically about 0.1% of $C_v$. Scatter in this region was of the order of (0.1–0.3)%.

### B. Calibration and Addenda

The germanium resistor was calibrated in the empty calorimeter by first bringing it into contact with the $He^4$ pot by the mechanical heat switch. Calibration tables of the ratio given by the ratio transformer against the vapor pressure of $He^4$ were obtained. Approximately 45 points were taken in the interval 3.0–3.6 K. The vapor pressure was measured over a bulb containing liquid $He^4$ that was submerged in the liquid of the $He^4$ pot. A good thermal connection between the bulb and the liquid in the pot was ensured by means of numerous fine copper wires soldered into the base of the bulb and extending throughout the volume of the pot. Corrections for hydrostatic head and corrections to standard temperature and gravity were applied to the measured vapor pressure. The $T_{58}$ scale[23] was used to convert pressure to temperature.

The measured ratio values were converted to resistance values and a least-squares-fit technique was applied to the resistance-temperature relation

$$T^{-1} = \sum_{j=-1}^{2} A_j[\log_{10}(R) - K]^j , \qquad (1)$$

where $K$ is determined by iteration. The deviations between the resulting curve and the measurements were random and gave a mean-square temperature deviation of 0.2 mK. We estimate the accuracy of our temperature scale to be within 0.5 mK of $T_{58}$.

The heat capacity of the empty calorimeter (addenda) was then measured in the same temperature interval. A least-squares fit of the addenda heat capacity versus temperature gave the relation

$$C_A = 1.294T + 0.129T^3 \ (\text{mJ/K}) , \qquad (2)$$

where $C_A$ is the addenda heat capacity. The mean square deviation of the data from this curve was approximately 1% of $C_A$. The relative contribution $C_A/(C_A + C_S)$, where $C_S$ is the sample heat capacity, ranged from a minimum of 3% near $T_c$ to a maximum of 12% at 3.6 K.

### C. Procedure

During filling of the sample cavity the chamber was maintained at a constant temperature (3.435 K) in the one-phase region. Fluid was then pushed into the cavity by means of a Toepler pump until the desired pressure in the cavity was attained, under equilibrium conditions. This pressure was measured with a mercury manometer at room temperature. Corrections to standard temperature and gravity and for the density gradient in the vertical length of fill tube in the cryostat were applied to the manometer measurement. The $P$-$V$-$T$ data[6(c)] of WM was used to determine the correct pressure for a desired density. Then the low-temperature valve and another valve in the sample line at the top of the cryostat were simultaneously tightly closed. This procedure trapped some fluid between the two valves at a pressure that was unknown, but presumably was near the sample-chamber pressure. Thus there was never a large pressure difference across the low-temperature valve.

It was found that this procedure produced small systematic deviations in the final density from that expected. These were apparently due to local frictional heating developed while closing the low-temperature valve and which could slightly alter the density of the fluid. The final densities assigned to the isochores were then determined from the transition temperatures of the $C_v$ data through the coexistence curve relation given by WM. We estimate that our reported values for $\rho/\rho_c$ have a precision of ± 0.25%.

A successful shutting-off of the low-temperature valve was assumed when the same transition temperature and heat capacity was found for the particular isochore on three different passes through the transition, taken on different (usually consecutive) days. Isochores that did not meet this criterion were discarded.

At the end of the experiment the sample-chamber fluid was transferred to a storage can of known volume at room temperature and the number of moles of gas determined. This measurement, combined with the known density of the last sample on which data was taken, allowed the determination of the sample-cavity volume to an accuracy of ± 1.5%. Any error in this volume would affect only the absolute value of the specific heat reported and not the temperature dependence.

During measurement of the specific heat, the temperature drift was monitored for periods extending from a few minutes up to about thirty minutes before and after the administration of a heat pulse to the sample. The pulses had a duration of between one and two and a half minutes, and the temperature intervals involved varied from

20 mK far from $T_{tr}$ to 50 $\mu$K very near $T_{tr}$. The observed specific heat was found to be independent of the size of the temperature interval in this experiment.

A tabulation of our data is too extensive to be given here, but will be contained in a forthcoming technical report.

## III. DIFFUSION

The decreasing rate of thermal diffusivity in our sample as the critical point was approached had a large bearing on the practical aspects of taking data near the critical point, particularly in the two-phase region. In view of this, and also because of the intrinsic interest of transport properties near the critical point, we have attempted to make a semiquantitative analysis of the diffusivity from our heat-capacity chart recordings. The manner in which the experimental data is produced allows a rough determination of the behavior of the time decay to equilibrium.

The experimental technique used was of course designed to yield the specific heat with maximal sensitivity, rather than the diffusion. Thus the data points near $T_c$ were taken with relatively long heating periods and low values of input power in the heater, while sensitivity for diffusion would be maximized with short heating intervals and larger power.

Theoretically speaking, diffusion data in the one-phase region is the more interesting, since this is a simpler situation than is the two-phase region. The diffusion time constant is however much smaller in the one-phase region. In fact, a drastic drop in the thermal relaxation time proved to be a reliable indication of passage upwards through the transition on the critical isochore. As a result of the decreased time constant we were unable to draw even qualitative information about the relaxation's temperature dependence in the one-phase region. Such information was accessible in the two-phase region which, although less appealing theoretically at first sight, has a definite practical utility. Thus what follows may prove useful to experimentalists attempting to measure static properties of fluids near their critical points. We restrict our attention here to data on the critical isochore in the two-phase region, $(-t) < 5 \times 10^{-3}$, but data on other isochores are also available. We denote the time variable by $\zeta$, to avoid possible confusion with the reduced temperature difference $t$. The approach to thermal equilibrium within a homogeneous sample, following a heating interval, is expected to obey the diffusion relation

$$\frac{\partial v}{\partial \zeta} = D_T \nabla^2 v , \tag{3}$$

where $v(\zeta) = T(\zeta) - T(\zeta = \infty)$ is the displacement of the mean temperature of the sample at time $\zeta$ from its equilibrium value at $\zeta = \infty$, and $D_T$ is the thermal diffusivity. A solution to Eq. (3) would be given by an expression of the type[24]

$$v(\zeta) = A\, e^{-\zeta/\tau_D} , \tag{4}$$

where we indicate explicitly only the time dependence. Here $\tau_D = l^2/D_T$ where $l$ is a characteristic length. Such a behavior was indeed found in our experiment for $\zeta \approx \tau_D$. The time constant thus obtained, plotted as a function of $t$, agreed with that found for $CO_2$ by Lipa *et al.*[4] within about 30%. However it was found in our experiment that for $\zeta > \tau_D$ the system tended to equilibrium in a much slower fashion than given by Eq. (4). We have used the following empirical expression which fitted our data for $\zeta \gtrsim \tau_D$:

$$v(\zeta) = v(0)\,(1 - e^{-\tau_D'/\zeta}) , \tag{5}$$

where $\tau_D'$ is approximately $\frac{1}{2}\tau_D$. Note that the trend to equilibrium given by Eq. (5) is much slower than the more common exponential $e^{-\zeta/\tau_D}$, so that one must wait for many time constants $\tau_D'$ before equilibrium is established is established rather than the four to five time constants sufficient in the case of an exponential decay [Eq. (4)]. This was a source of possible systematically low recorded values of $C_v$ in the two-phase region for $-t < 3 \times 10^{-4}$. We emphasize that no theoretical meaning should be attached to Eq. (5). This is a closed expression with only one parameter and therefore it is convenient. In reality, the approach to equilibrium should be described by a sum of terms such as in Eq. (4) with various relaxation times $\tau_{D,i}$.[24]

Equation (5) was used to determine $\tau_D'$ as a function of $(-t)$. This temperature dependence of $\tau_D'$ is shown in Fig. 2. This figure indicates that $\tau_D' \propto (-t)^{-2/3}$, approximately, in an asymptotic

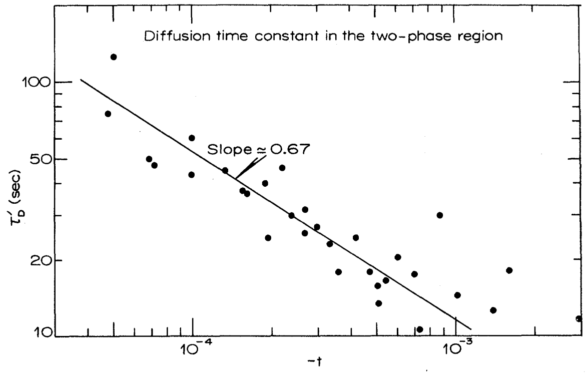

FIG. 2. Divergence of the diffusion time constant given in Eq. (5) in the two-phase region. The solid straight line indicates $\tau_D' \propto |t|^{-2/3}$ in an asymptotic region extending over approximately one and one-half decades in $(-t)$.

region extending from $5\times10^{-6}\lesssim(-t)\lesssim10^{-3}$. It is probable that the heat diffusion process in the two-phase region is limited by the liquid-gas boundary and that because of this Eq. (4) with only one relaxation time is not really justified. The disappearance of this boundary at $T_{tr}$ then leads to a drastic decrease in $\tau_D$.

## IV. CRITICAL ISOCHORE

### A. Asymptotic Scaling

In the course of taking data on the critical isochore it was noted that the specific heat always dropped precipitously by at least a factor of two within a temperature range of 0.2 mK.[25] In this same range, the maximum of the diffusion time constant $\tau_D'$ was also sharply defined. If we identify the *center* of this range with $T_c$ we can say that the transition temperature is sharply determined by the direct $C_v$ data and is found at $T_c=3.3092\pm0.0001$ K, relative to our temperature calibration. We find below that this choice of $T_c$ is corroborated by the results of a least-squares fit to the data. Our value for $T_c$ is compared with previous determinations[6, 8] in Table II, and in the discussion at the beginning of Sec. V.

Scaling laws allow two slightly different forms for the asymptotic temperature variation of the specific heat as the critical point is approached.[26] By convention these are characterized by the critical exponent $\alpha$ that takes on values (a) $\alpha=0$ or (b) $\alpha>0$. Case (a) represents a logarithmic singularity in $C_v$, which is then expressed by

$$C_v/R=\mathcal{A}^{\pm}\ln|t|+\mathcal{B}^{\pm}\ , \tag{6}$$

where $R$ is the gas constant. Here and below the ± symbol refers to quantities defined below (−) or above (+) the critical temperature $T_c$. The scaling laws require that this be a symmetric logarithmic infinity, with in general a superposed finite discontinuity. This implies then that $\mathcal{A}^{+}=\mathcal{A}^{-}$, and that a plot of $C_v(\rho_c, t)$ vs $\log|t|$ should be asymptotically linear, with equal slopes for the branches above and below $T_c$.

Such a plot of our data is shown in Fig. 3, utilizing the value of $T_c$ given above. Here we see that the scaling prediction of equal slopes in the two branches is untenable unless rather stringent and arbitrary restrictions are placed on the size of the asymptotic regions. Different reasonable choices of $T_c$ do not alter this conclusion. We find below that case (b) ($\alpha>0$) is not subject to such *ad hoc* restrictions, and consequently we exclude the possibility of a logarithmic divergence in the rest of our analysis.

In case (b) the asymptotic behavior of the specific heat is given by

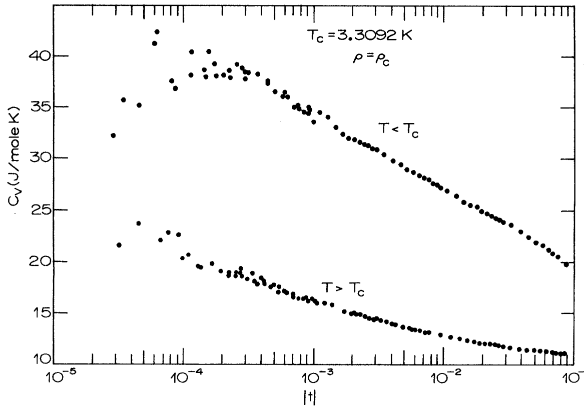

FIG. 3. Semilog plot of $C_v$ data on the critical isochore. Linear behavior asymptotically with equal slopes on the two branches would indicate a logarithmic singularity ($\alpha=0$). This possibility is evidently not the case, and is excluded in our analysis.

$$C_v/R=A^{\pm}|t|^{-\alpha^{\pm}}+B^{\pm}\ . \tag{7}$$

Here the scaling laws predict that $\alpha^{+}=\alpha^{-}$ and $B^{+}=B^{-}$, but in general $A^{+}\neq A^{-}$. This implies that a plot of $\log C_v$ vs $\log|t|$ should be asymptotically linear with equal slopes for the branches above and below $T_c$. Our data is presented in this form in Fig. 4, where qualitative agreement with Eq. (7) is evident. In this figure we have again used the value of $T_c$ given above.

In Fig. 4 we present as well a comparison between our data and that of Moldover and Little[9, 10] on a sample of He$^3$ with a nominal density $\rho=0.985\rho_c$. These data were analyzed in terms of a logarithmic singularity (see, however, Ref. 2) but are evidently not inconsistent with the interpretation[6] of a positive $\alpha\approx0.1$.

For any sample of finite vertical dimension in a gravitational field the measured specific heat will be significantly distorted from its asymptotic behavior for $t$ less than some cutoff temperature $t_h$. The effect of the gravitational potential on the specific heat of Xe has recently been discussed in terms of the linear model of the parametric equation of state by Barmatz and Hohenberg.[27] A very extensive discussion, again on the Xe system, has been given by Schmidt,[28] who utilizes the proposed form of the equation of state given by MSG.[1] Both of these theories give a result that is qualitatively consistent with the expression of the cutoff temperature given by Lipa, Edwards, and Buckingham[4]:

$$t_h=(mgh/2k_B T_c)^{1/\beta\delta}\ , \tag{8}$$

where $m$ is the atomic mass of the fluid sample, $h$ is the height, and $g$ is the local gravitational

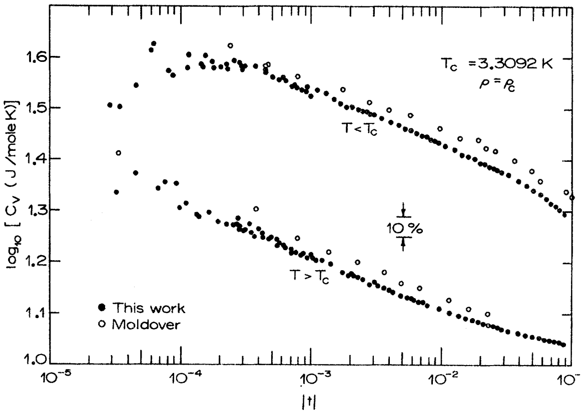

FIG. 4. Log-log plot of $C_v$ data on the critical isochore. Asymptotic linear behavior here indicates that $\alpha^- \simeq \alpha^+ \simeq 0.1$. For comparison we display the data of Moldover and Little on a He$^3$ sample of nominal density $\rho = 0.985\rho_c$, which appears to be consistent with our values for $\alpha^\pm$.

constant.

For a He$^3$ sample of height 0.5 mm, Eq. (8) with various reasonable choices of the exponents $\beta$ and $\delta$ would lead us to expect a cutoff temperature $t_h$ of between $5\times 10^{-5}$ and $10^{-4}$. Figure 4 indicates that the high-temperature branch of our measured specific heat starts deviating from the straight line at this value of $t_h$, but the low-temperature branch starts curving at approximately $t = 3\times 10^{-4}$. This latter value is larger by a factor of three than the theoretical upper limit for gravity effects. This corresponds to a factor of approximately five in the height $h$. An effective height of 2.5 mm in our sample would require a tilt of no less than three degrees from the horizontal, a possibility we consider extremely unlikely. An alternative explanation is that thermal equilibrium within the sample was not achieved for $|t| < 3\times 10^{-4}$ in the two-phase region in spite of the long waiting times we used in this region. We have taken a conservative attitude toward this point, and have discarded data points in the two-phase region with $|t| < 3\times 10^{-4}$. However in the one-phase region we were able to include all data points having $|t| > 5\times 10^{-5}$. Thus the temperature range of our analysis is given by $t^\pm_{\min} \leqslant |t| \leqslant 0.1$, where $t^-_{\min} = 3\times 10^{-4}$ and $t^+_{\min} = 5\times 10^{-5}$.

A least-squares-fit method was applied to our data to compare it with Eq. (7), using as free parameters $T_c^\pm$, $\alpha^\pm$, $A^\pm$, and $B^\pm$. In this procedure the data points were weighted by an estimate of their respective errors, and the fit was applied within a temperature range given by $t^\pm_{\min} \leqslant |t| \leqslant t_{\max}$. The best-fit values of the parameters were found to be independent of $t_{\max}$ for $t_{\max} \lesssim 0.01$. Within this temperature range we find $T_c^+ = T_c^-$ and $B^+ = B^- = 0.0 \pm 0.5$. The data are fitted equally well by Eq. (7) or Eq. (9):

$$C_v/R = A^\pm |t|^{-\alpha^\pm}\,, \tag{9}$$

i.e., the fit to Eq. (9) produces a mean-square deviation less than one standard deviation larger than the fit to Eq. (7). The difference between these two equations is insignificant within the confidence level of our fits, and we shall tentatively state that $B^- = B^+ = 0$.

Scaling implies that $B^+ = B^-$, which is consistent with our results. This is in contradiction with the analysis of Lipa, Edwards, and Buckingham on their CO$_2$ data.[4] We have listed the best-fit values of the parameters of Eq. (9) in Table I(a). The data are consistent with the scaling theory prediction that $\alpha^- = \alpha^+$. The *a priori* imposition of this last constraint leads to the result $\alpha = 0.105$ with no change in $T_c$ or $A^\pm$ from the values of Table I(a). The mean-square deviation of the fit increases by only one standard deviation under this additional constraint.

The assignment of meaningful error limits to critical exponents is a very uncertain procedure, in the sense that the statistical errors found from multiparameter least-squares fits are often misleadingly small. We note in our case however that the "one-standard-deviation" error on our value for $T_c$ agrees very well with the precision for this quantity that we have estimated above from the "drop width" and the maximum in $\tau_D'$ in the experimental data. We have indicated that our data are

TABLE I. Best-fit parameters to asymptotic and extended scaling, $\rho = \rho_c$. Quoted uncertainties reflect only statistical errors derived from the least-squares-fit procedure, and should be used only to compare the two different functional forms.

| | |
|---|---|
| (a) Asymptotic scaling | |
| $\frac{C_v}{R} = A^\pm \lvert t\rvert^{-\alpha^\pm}$, $\begin{cases} 3\times 10^{-4} \le (-t) \le 0.01 \\ 5\times 10^{-5} \le t \le 0.01 \end{cases}$ | |
| $T_c = 3.3092 \pm 0.0001$ K | |
| $t<0$ | $t>0$ |
| $\alpha^- = 0.10 \pm 0.01$ | $\alpha^+ = 0.11 \pm 0.01$ |
| $A^- = 2.07 \pm 0.06$ | $A^+ = 0.92 \pm 0.03$ |
| (b) Extended scaling | |
| $\frac{T_c{}^2 C_v}{T} = \lvert t\rvert^{-\alpha^\pm} \{A_1^\pm + A_2^\pm \lvert t\rvert^{1/\epsilon^\pm}\}$, $\begin{cases} 3\times 10^{-4} \le (-t) \le 0.1 \\ 5\times 10^{-5} \le t \le 0.1 \end{cases}$ | |
| $T_c = 3.3092 \pm 0.0001$ K | |
| $t<0$ | $t>0$ |
| $\alpha^- = 0.10 \pm 0.01$ | $\alpha^+ = 0.11 \pm 0.01$ |
| $A_1^- = 57.14 \pm 3.0$ J/mole | $A_1^+ = 25.11 \pm 1.0$ J/mole |
| $A_2^- = -1.47 \pm 6.0$ J/mole | $A_2^+ = 2.60 \pm 1.5$ J/mole |

consistent with the constraints $T_c^+ = T_c^-$, $B^+ = B^- = 0.0$, and $\alpha^+ = \alpha^-$ applied to Eq. (7). Under these conditions we find $\alpha = 0.105 \pm 0.015$, where the error limits indicate a variation of one standard deviation from the best-fit value. One may check on the reasonableness of this error by graphical estimates for $\alpha^\pm$ from log-log plots of $C_v$ vs $|t|$ plotted for the extreme values of $T_c$ given above. The variation in $T_c$ tends to make $\alpha^+$ and $\alpha^-$ move in opposite directions, but the various graphical estimates for the $\alpha^\pm$ always lie within the error quoted above, giving us some added confidence in these error limits.

### B. Extended Scaling

GCS[16] have developed an extended scaling theory based on a generalization of the parametric equation of state given by Schofield.[18] In this theory the specific heat along the critical isochore is given by[29]

$$(T_c^2/T)\, C_v(\rho_t, t) = |t|^{-\alpha}\{A_1^\pm + A_2^\pm |t|^{1/\epsilon} + A_3^\pm |t|^{2/\epsilon} + \cdots\}, \qquad (10)$$

where $\epsilon$ is a new critical exponent found by GCS to be $1/\epsilon = \beta\delta - 1 = 1 - \beta - \alpha^-$. Thus $1/\epsilon \approx 0.54$. The distinction between the subscripted coefficients (with dimensions J/mole) of Eq. (10) and the unsubscripted coefficients (dimensionless) of Eq. (7) should be noted. For $|t| \lesssim 10^{-2}$ and within the accuracy of our determinations the coefficients $A_1^\pm$ are equivalent to the $A^\pm$ of Eq. (7), differing only by the dimensional factor $RT_c = 27.52$ J/mole.

A straightforward least-squares fit was applied to all our data ($\rho = \rho_c$, $t_{\min}^\pm \leq |t| \leq 0.1$) using the form of Eq. (10). We took as free parameters $T_c$, $\alpha^\pm$, and $A_\nu^\pm$ ($\nu = 1, 2, \ldots$), with the definition $1/\epsilon^\pm = 1 - \beta - \alpha^\pm$. If we retain only the first higher-order term, $A_2^\pm |t|^{1/\epsilon^\pm}$, the best-fit result for the parameters is that given in Table I(b). The values found here for $T_c$, $\alpha^\pm$, and $A_1^\pm$ are in complete agreement with those found in the asymptotic fit to Eq. (7), indicating good consistency of this form with the conventional "simple" scaling. The inclusion of the next higher-order term, $A_3^\pm |t|^{2/\epsilon^\pm}$, produced only marginal improvement in the fit to the data, and is not considered further.

The relative deviation of the data from the nominal best fit to Eq. (10) is shown in Fig. 5. Systematic deviations are present, but their magnitude is only 0.5%. We conclude that Eq. (10) is an adequate and consistent representation of our data over a range of $|t|$ approximately a factor of ten larger than the asymptotic range appropriate to Eq. (7). Because of the limited precision in the $C_v$ data, the coefficients of the nondivergent terms are not determined very precisely. Hence it is not excluded that another extended scaling expression could be made to represent the data equally well.

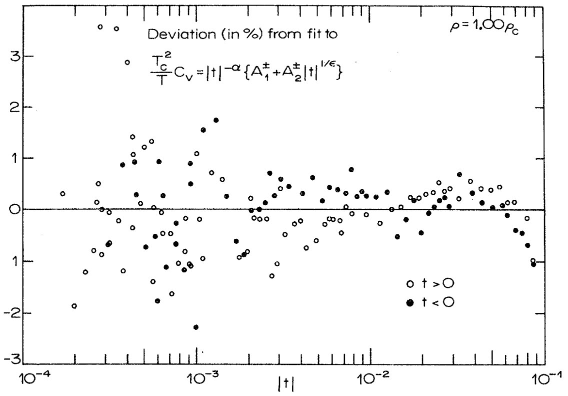

FIG. 5. Percent deviation of the critical isochore $C_v$ data from the extended scaling form of Eq. (10), using the nominal values of the coefficients given in Table I(b). In this presentation $T_c^- \equiv T_c^+$ is a constraint, so that the center of gravity of each branch ($t \lessgtr 0$) is not necessarily zero, but only their weighted sum.

## V. GENERAL RESULTS AND DISCUSSION

The critical temperature $T_c = 3.3092$ K used in this analysis is identified with the transition temperature found for the isochore considered in Sec. IV. This value is somewhat lower than that found by WM, who used the same sample of He$^3$ as in the present work. The difference between our value for $T_c$ and that of WM is slightly outside the combined error limits for each of the *absolute* determinations of this temperature (see Table II). We have no explanation of this discrepancy except to note (as has been pointed out before[4]) that specific heat determinations of $T_c$ are very often found to be lower than *P-V-T* determinations. Within the published error limits our $T_c$ value is the same as that found by CZ for a sample with an average impurity of 350-ppm He$^4$.

We have used the parameters given by WM and CZ in the scaling-law relation for the coexistence curve,

$$|\Delta\rho| = \tilde{B}(-t)^\beta, \qquad (11)$$

and normalized the extremum of this curve to coincide with our determination of $T_c$. This procedure can be self-consistent only if the isochore we have labeled as the "critical" one is actually within 0.5% of the critical density $\rho_c$. Figure 6 below indicates that this condition is satisfied.

### A. Comparison with *P-V-T* Data

As a check on the internal thermodynamic consistency and in order to compare the $C_v$ data with *P-V-T* data on He$^3$ we consider first the identity

TABLE II. Critical parameters and properties of $He^3$. The symbols used are for the most part standard, and are listed, e.g., in Ref. 6(a) or Ref. 17.

| Ref. | $\beta$ | $\delta$ | $\gamma^+$ | $\gamma^-$ | $\alpha^+$ | $\alpha^-$ |
|---|---|---|---|---|---|---|
| This work | | | | 1.18 | 0.105 ± 0.015 | 0.105 ± 0.015 |
| Ref. 6 | 0.361 ± 0.005 | 4.21 ± 0.10 | 1.17 ± 0.05 | 1.17 ± 0.05 | | > 0.05 |
| Ref. 8 | 0.365 ± 0.005 | 4.12 ± 0.15 | 1.19 ± 0.03 | 1.08 ± 0.07 | | 0.13 ± 0.08 |
| | $\tilde{B}$ | $\Gamma^+$(Torr$^{-1}$) | $\Gamma^-$(Torr$^1$) | | $A_1^+$(J/mole) | $A_1^-$(J/mole) |
| This work | | | ~ 6.7 × $10^{-5}$ | | 25.1 ± 1.0 | 57.1 ± 3.0 |
| Ref. 6 | 1.31 | 2.48 × $10^{-4}$ | 6.9 × $10^{-5}$ | | | |
| Ref. 8 | 1.33 | ~ 2.38 × $10^{-4}$ | ~ 8.4 × $10^{-5}$ | | | |
| | $T_c$(K) | $P_c$(Torr) | $\rho_c\left(\frac{g}{cm^3}\right)$ | | $\frac{dP}{dT}(\rho_c, T_c)\left(\frac{Torr}{K}\right)$ | $-T\frac{d^2\mu}{dT^2}\left(\frac{J}{mole\ K}\right)$ |
| This work | 3.3092 ± 0.0006 | | | | | 5.5 ± 0.5 |
| Ref. 6 | 3.3105 ± 0.0007 | 860.5 | 0.04145 ± 0.0002 | | 882 | ~ 6.1 |
| Ref. 8 | 3.3093 ± 0.0005 | 859.5 ± 0.3 | 0.04119 ± 0.0001 | | | |
| Scaling-law equalities ($\gamma^- = \gamma^+$, $\alpha^- = \alpha^+$) | | | $\gamma + 2\beta + \alpha = 2$ | | $\beta(\delta + 1) + \alpha = 2$ | $\gamma\left(\frac{\delta+1}{\delta-1}\right) + \alpha = 2$ |
| Experimental[a] | | | 2.00 ± 0.07 | | 1.99 ± 0.07 | 2.01 ± 0.11 |

[a] Using values from this work and Ref. 6.

$$\rho C_v = -\rho T\left(\frac{\partial^2\mu}{\partial T^2}\right)_\rho + T\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho . \tag{12}$$

If the sample is large enough that surface energy contributions to the free energy can be ignored, then both $\mu$ and $P$ in the two-phase region are independent of density. We can then write

$$\rho C_v = -\rho T\left(\frac{d^2\mu(\rho_c, T)}{dT^2}\right) + T\left(\frac{d^2 P(\rho_c, T)}{dT^2}\right) \tag{13}$$

in the two-phase region.

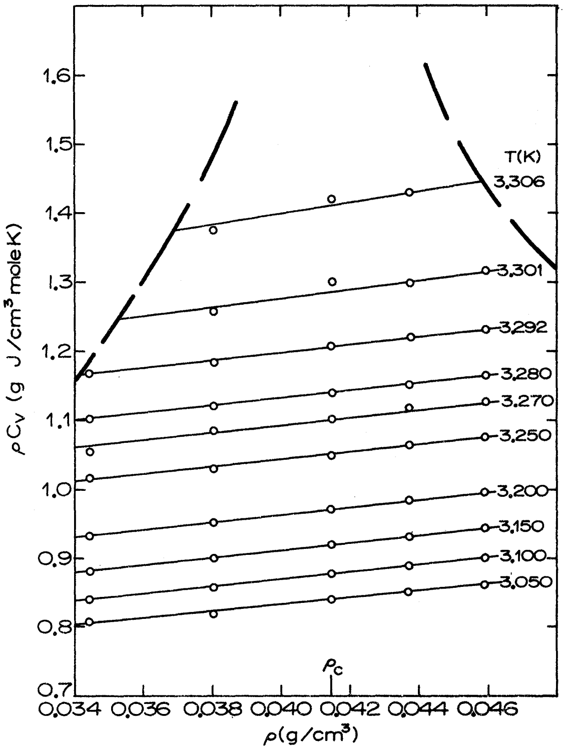

FIG. 6. Linear dependence of $(\rho C_v)_T$ with $\rho$ in the two-phase region. The slope of the isotherms gives $-Td^2\mu(\rho_c, T)/dT^2 = 5.5 \pm 0.5$ J/mole K. The dashed curve is the projection of the coexistence curve.

Thus $(\rho C_v)_T$ is proportional to $\rho$ in this region. Several such isotherms are exhibited in Fig. 6. Their slopes relatively far from $T_c$ yield an approximately constant value of $T d^2\mu(\rho_c, T)/dT^2 = -5.5 \pm 0.5$ J/mole K. This result is not sensitive to any *weak* temperature dependence of $d^2\mu/dT^2$. In particular the leading factor of $T$ can be replaced by $T_c$ with no change in the accuracy of the figure quoted, so long as $T$ is within 5% or so of $T_c$. We assume in the rest of the analysis that this quantity is a constant throughout the temperature range considered.

Integration of Eq. (13) gives for $\rho = \rho_c$

$$\frac{1}{\rho_c}\left.\frac{\partial P^*}{\partial T}\right|_{\rho_c} = \left.\frac{\partial \mu^*}{\partial T}\right|_{\rho_c} + \int_{T_c}^{T}\frac{C_v}{T}\,dT , \tag{14}$$

where the quantities with asterisks are taken relative to their values at the critical point. Numerical evaluation of the right-hand side of this equation may then be compared with the $(\partial P/\partial T)_{\rho_c}$ data given by WM. Such a comparison is consistent with the assumption that $d^2\mu/dT^2$ is nondivergent at the critical point, although the scatter in the available $\partial P/\partial T$ data precludes any conclusive statement in this regard. We have not shown this comparison in a figure, since such a plot [using our data in Eq. (14)] is not perceptibly different from Fig. 8 in Ref. 6(a). Kierstead[30] has made precision measurements of $(\partial P/\partial T)_{\rho_c}$ in $He^4$ which, with the $C_v$ measurements of Moldover,[2] indicate that $d^2\mu/dT^2$ is nondivergent at $T_c$ in the $He^4$ system as well.

The jump in the specific heat at the coexistence curve is related to the isothermal compressibility $k_T$ via

$$\rho C_{v\,\text{II}} - \rho C_{v\,\text{I}} \equiv \Delta(\rho C_v) = \frac{T}{M}\left(\frac{\partial\mu}{\partial\rho}\right)_T \left(\frac{d\rho}{dT}\right)^2 , \qquad (15)$$

where $M(\partial\rho/\partial\mu)_T = \rho^2 k_T$ and $M$ is the molecular weight. Extrapolation of our data to the coexistence curve then allows an estimation of $\gamma_T^-$, the critical exponent associated with $\rho^2 k_T$. From the four available isochores we estimate $\gamma_T^- \approx 1.18$. A comparison of our derived values of $k_T$ and those of WM is shown in Fig. 7. It is also easily shown[17] that $\Delta(\rho C_v) \propto (-t)^{-\alpha^-}$, which might be expected to give another determination of $\alpha^-$. Unfortunately, the scatter in the data near the coexistence curve and the uncertainties involved in extrapolating to the coexistence curve preclude this method as a practical means to determine $\alpha^-$. The four available points allow any choice within the range $0.0 \lesssim \alpha^- \lesssim 0.13$.

An extensive comparison of various critical parameters determined from $C_v$ and $P$-$V$-$T$ measurements on $He^3$ is given in Table II.

### B. Comparison with MSG Scaling

We have chosen to test our $C_v(\Delta\rho, t)$ data against the scaling formulation suggested by Griffiths[1(a)] and presented explicitly by MSG.[17] Here the Helmholtz free energy per unit volume is given by

$$a(\rho, t) = A_0(t) + \rho\mu(\rho_c, t) + |\Delta\rho|^{\delta+1} a_\alpha(X) . \qquad (16)$$

$a_\alpha(X)$ is a scaled function depending only on the reduced variable $X = t\,|\Delta\rho|^{-1/\beta}$, defined in the range $-X_0 < X < \infty$, where $X_0 = (\tilde{B})^{-1/\beta}$; viz., Eq. (11). The factor $a_\alpha(X)$ is related to the scaled function $h(X)$ defined in the equation of state

$$\mu(\rho, t) - \mu(\rho_c, t) = \Delta\rho\,|\Delta\rho|^{\delta-1} h(X) \qquad (17)$$

via

$$-X a_\alpha'(X) + (2-\alpha)\, a_\alpha(X) = \beta h(X) . \qquad (18)$$

Primed quantities refer to derivatives with respect to $X$. $A_0(t)$ and $\mu(\rho_c, t)$ are assumed regular everywhere in the neighborhood of $T_c$, including the point at $T_c$.

We use a system of units in which $\mu(\rho, t)$, $A_0(t)$, and $a_\alpha(X)$ are energy densities with dimensions J/m. The scaled function $a_\alpha(X)$ is then related to the specific heat by

$$-a_\alpha''(X) = |\Delta\rho|^{\alpha/\beta}\left(\frac{T_c^2}{T}\frac{\rho}{\rho_c} C_v(\Delta\rho, t) + \frac{d^2A_0(t)}{dt^2} + \frac{d^2\mu(\rho_c, t)}{dt^2} + \Delta\rho\frac{d^2\mu(\rho_c, t)}{dt^2}\right) \qquad (19a)$$

in the one-phase region, and

$$-a_\alpha(-X_0)\,(X_0)^{\alpha-2}(2-\alpha)(1-\alpha) = (-t)^\alpha\left(\frac{T_c^2}{T}\frac{\rho}{\rho_c} C_v(\Delta\rho, t) + \frac{d^2A_0(t)}{dt^2} + \frac{d^2\mu(\rho_c, t)}{dt^2} + \Delta\rho\,\frac{d^2\mu(\rho_c, t)}{dt^2}\right) \qquad (19b)$$

in the two-phase region. Along the critical isochore Eq. (19) reduces to

$$\frac{T_c^2}{T} C_v(\rho_c, t) = A_1^\pm |t|^{-\alpha} + \left(-\frac{d^2A_0(t)}{dt^2} - \frac{d^2\mu(\rho_c, t)}{dt^2}\right), \qquad (20)$$

where the coefficients $A_1^\pm$ may be taken to be identical with those of Eq. (10). Hence in the two-phase region

$$A_1^- = -a_\alpha(-X_0)\,(X_0)^{\alpha-2}(2-\alpha)(1-\alpha) . \qquad (21)$$

The terms in brackets in Eq. (20) are thus identical with the nondivergent terms of Eq. (10), to the same extent that Eq. (10) is a valid representation of the specific heat along the critical isochore. We have found that these terms are quite small, in the sense that their effect on the calculated curve for $-a_\alpha''(X)$ is smaller than the effect of the uncertainty of $\pm 0.25\%$ in the densities, even when $t > 0.01$. Thus in this presentation we have arbitrarily set

$$A_2^\pm |t|^{(1/\epsilon)-\alpha} \simeq \left(-\frac{d^2A_0(t)}{dt^2} - \frac{d^2\mu(\rho_c, t)}{dt^2}\right)$$

equal to zero throughout the temperature range of

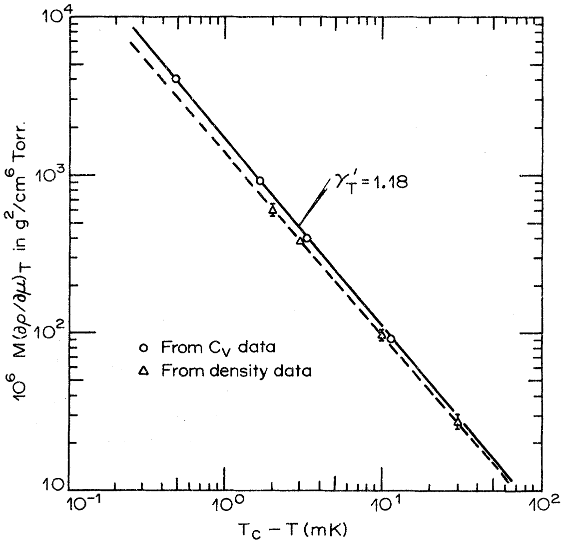

FIG. 7. Isothermal compressibility along the vapor-pressure curve: O, this work; Δ, $P$-$V$-$T$ data of Ref. 6.

our data.

All of the other parameters having been previously determined, we need only substitute our experimental data into the right-hand side of Eq. (19) to calculate $a''_\alpha(X)$ and $a_\alpha(-X_0)$. To this purpose we have used the values $\beta = 0.361$ as given by WM and CZ. All of the data points are treated in the same way, with no attempt to define *a priori* an "asymptotic region."

The result in the two-phase region is presented in Fig. 8. We have plotted our calculated function $\mathcal{R} = \log_{10}[-a(X_0)X_0^{\alpha-2}(2-\alpha)(1-\alpha)]$ vs $(-t)$ in order that any systematic deviations as a function of temperature or density might be apparent. The scaling prediction is well borne out, with all of the data falling essentially on a constant value, thus defining the constant left-hand side of Eq. (19b). By Eq. (21) this constant value should be identical with the coefficient $A_1^-$, which is known to within ± 5% from Sec. IV, and is represented in Fig. 8 by a horizontal bar. The identity given by Eq. (21) is apparent in the figure.

Note that in Fig. 8 no significant deviation from the scaling prediction is apparent for $(-t) \lesssim 0.1$, even though we have ignored the nondivergent terms in the specific heat on the critical isochore. This insensitivity of the density scaling to the nondivergent terms is apparently due to a near cancellation of the terms $d^2A_0(t)/dt^2$ and $d^2\mu(\rho_c, t)/dt^2$. This effect may be peculiar to the $\mathrm{He}^3$ system.

The points in Fig. 8 that drop sharply away from the scaled constant value appear to lie on the transition itself, which in our measurements is seen to broaden[25] with increasing $|\Delta\rho|$.

In the one-phase region we expect that the data from the various isochores should fall on a common curve as a function of $X$ if the scaling theory is correct. In Fig. 9(a) and 9(b) this is seen to be the case, to within a few percent in $a''_\alpha(X)$. For $X \gg 1$, $-a''_\alpha(X)$ should approach the asymptotic form $A_1^+ X^{-\alpha^+}$ with the same values of $A_1^+$ and $\alpha^+$ found on the critical isochore. This asymptotic form is represented in Fig. 9(b) by the solid line.

There are two possible sources of systematic error in the calculation of $a''_\alpha(X)$: (a) the uncertainty of ± 10% in the value of $d^2\mu/dt^2$, which should be included independently for each isochore, since we have not strictly shown that this term is temperature independent, and (b) the uncertainty of ±0.25% in the assignment of $\rho/\rho_c$ for the various isochores. The total possible systematic error introduced into $a''_\alpha(X)$ by these two terms ranges from $\sim \pm 1.3\%$ to $\sim \pm 2.0\%$ for the various isochores in the range $-X_0 \leqslant X \lesssim 4.0$. The uncertainty in the density is the dominant source of error here and comprises (60–90)% of the total possible systematic error. We emphasize that because we determined the reduced densities $\rho/\rho_c$ as described in Section II C, we have not optimized the assignment of our nominal densities so as to achieve perfect scaling. Such a manipulation brings the points from the various densities to lie practically on the same curve, within this restricted range of $X$. The systematic deviations from perfect scaling behavior seen in Fig. 9(a) are thus marginal in terms of our density resolution, and indicate that the unambiguous exhibition of scaling to better than one percent requires density resolution better than 0.1%.

The systematic deviations from perfect scaling for larger values of $X$, seen in Fig. 9(b), are more difficult to asses. These deviations increase with increasing $\Delta\rho$, and are only slightly affected by the choice of a new set of $\Delta\rho$'s which yields perfect scaling in the range $-X_0 \leqslant X \lesssim 4.0$. The inclusion

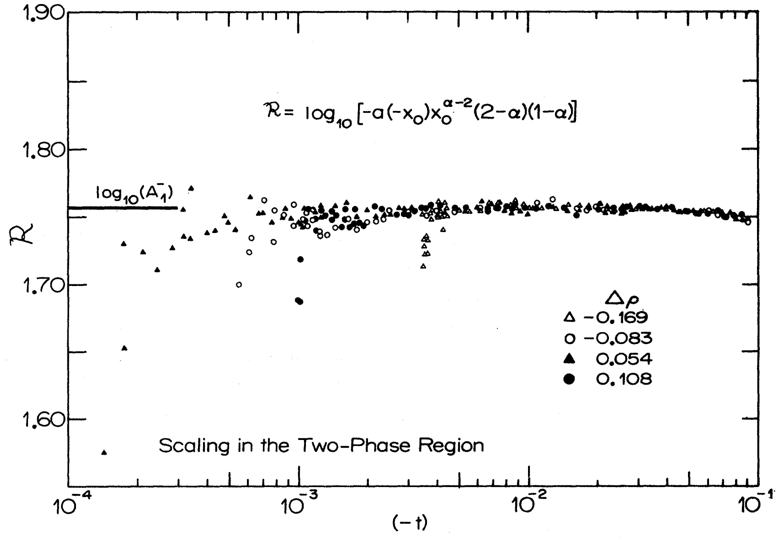

FIG. 8. Density and temperature scaling of the specific heat in the two-phase region. The value of the leading coefficient of $C_v(\rho_c, t<0)$, as given in Table I(b), is indicated by the horizontal bar. The points dropping sharply away from the constant value lie on the transition itself, and indicate a broadening of the observed transition with $|\Delta\rho|$ (see Ref. 25).

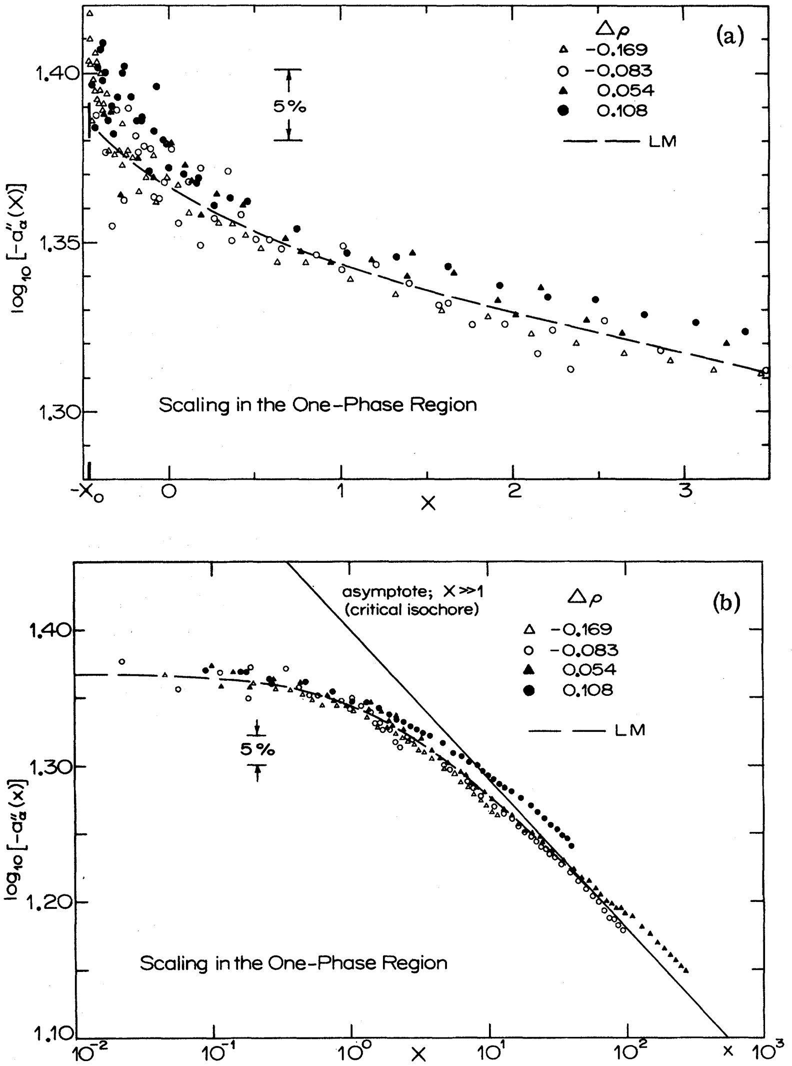

FIG. 9. Density and temperature scaling of the specific heat in the one-phase region. The dashed curve is calculated from the linear model of Refs. 19 and 20. The apparent systematic deviations are discussed in the text. (a) $-X_0<X\leq 3.5$ (semilog plot); (b) $X>0$ (log-log plot). The solid line represents the asymptotic behavior of the critical isochore.

of the term

$$\left(-\frac{d^2A_0(t)}{dt^2}-\frac{d^2\mu(\rho_c,t)}{dt^2}\right)\simeq A_2^+|t|^{(1/\epsilon)-\alpha}$$

from our extended scaling fit to the critical isochore also has a negligible effect. In our opinion these deviations are most easily explained by a weak temperature dependence of $d^2\mu(\rho_c,t)/dt^2$ [which multiplies $\Delta\rho$ in Eq. (19a)] in the one-phase region. We have not attempted to determine explicitly the form of this factor that would yield perfect scaling throughout our temperature range, since this would involve the introduction of new free parameters with no firm theoretical basis.

### C. Comparison with Linear Model

It is interesting to compare our data with the particularly simple approximation of scaling behavior given by the linear model (LM)[18–20] of the parametric formulation. In this theory a definite form is found for the scaling function $a''_\alpha(X)$,[31] given by

$$-a''_\alpha(X)=A_1^+(k|\theta|)^{\alpha/\beta}, \tag{22}$$

where $X=(1-b^2\theta^2)(k|\theta|)^{-1/\beta}$; $-1<\theta<1$ and $b^2=(\gamma-2\beta)/[\gamma(1-2\beta)]$. The static scaling equalities listed in Table II are automatically incorporated in the LM. As seen below the scaling function is completely determined by a knowledge of the critical exponents $\gamma$ and $\beta$ together with two dimensionless free parameters $a$ and $k$.

The linear model has the distinction of predicting critical coefficients in terms of the critical exponents. The leading coefficients for the specific heat, $A_1^+$ and $A_1^-$, are given by[19,20]

$$\left(\frac{\rho_c}{P_cM}\right)A_1^+=\frac{ak\gamma^2(\gamma-1)(1-2\beta)}{2(\gamma-2\beta)(2-\gamma-2\beta)}, \tag{23}$$

$$\frac{A_1^+}{A_1^-}=\frac{1}{4}\left(\frac{\gamma}{\beta}\right)^2\left(\frac{2\beta}{1-2\beta}\;\frac{\gamma-1}{\gamma}\right)^{\gamma+2\beta} . \qquad (24)$$

For $He^3$ we use the values $a=4.20$ and $k=0.915$. These results are taken from an analysis by Ho and Litster[32] of the $P$-$V$-$T$ data of WM,[6(a)] and are quoted in Ref. 20. For various choices of $\gamma$ and $\beta$ consistent both with experimental determinations (WM and CZ) and with the scaling equality $\gamma+2\beta+\alpha=2$ (using $\alpha$ as determined from this work), Eqs. (23) and (24) yield $A_1^+=23\pm3$ J/m and $A_1^+/A_1^-=0.42\pm0.07$. These are in substantial agreement with our experimental values of, respectively, $25\pm1$ J/m and $0.44\pm0.04$.

In calculating the scaling function $a_\alpha''(X)$ we have used in Eq. (22) the values for $A_1^+$ and $\alpha$ from our own analysis of the critical isochore. This procedure reduces the uncertainty in the calculated function and avoids the systematic deviation seen in the presentation of Ref. 20. The calculated right-hand side of Eq. (22) is shown in Fig. 9(a) and 9(b) as a dashed curve, where the agreement with the data in the range $X \gtrsim 0.0$ appears to be quite good.

We note that for $X \lesssim -0.2$ our extreme isochores at $\Delta\rho=-0.169$ and $\Delta\rho=0.108$ are systematically higher than the LM prediction by amounts that cannot be explained by our limited density resolution. These data may then be evidence of a breakdown in the LM as the transition is very closely approached in the one-phase region. (No such conclusion is implied in the case of the thermodynamic scaling of Sec. V B.)

### D. Remarks on the Critical Coefficients

For the convenience of the reader and to facilitate this discussion we have listed in Table III selected critical exponents and critical coefficients for various fluid systems. It is generally accepted by now that quantum effects have a very small bearing on the critical exponents, except perhaps $\alpha$, which is borne out in the table. This may not be true for the coefficients. For example a strictly classical law of corresponding states would imply that the coeffcient in the coexistence curve relation $X_0$ is independent of material, while we see that this coefficient is apparently different for $He^3$ and $He^4$, and both of these are clearly different from the heavier fluids.

Having noted the case of $X_0$, we might expect that other critical coefficients have magnitudes that are

TABLE III. Selected critical exponents and critical coefficients for several fluid systems. For the purpose here ot comparison between different systems we have used reduced units, such that $\Gamma^\pm$ is written in units of $(1/P_c)$ and $A_1^\pm$ is written in units of $(MP_c/\rho_cT_c)$, where $M$ is the molecular weight. $\Lambda^*$ is the DeBoer parameter. [*Note added in proof.* We forgot to quote the value $\alpha=0.125$ for $CO_2$ from Ref. 4. Also we mention the new value of $\mathfrak{a}=0.73$ reported by A. B. Cornfeld and H. Y. Carr, Bull Am. Phys. Soc. <u>17</u>, 277 (1972)].

| | $H_2O$ | $CO_2$ | Xe[a] | Ar | $H_2$ | $He^4$ | $He^3$ |
|---|---|---|---|---|---|---|---|
| $\alpha$ | | 0.04[b] | 0.04[b] | | | 0.05[b] | 0.11[c] |
| $\beta$ | 0.336[d] | 0.35[b] | 0.35[b] | 0.362[d] | | 0.359[b] | 0.361[e] |
| $\gamma$ | | 1.26[b] | 1.26[b] | 1.20[m] | | 1.24[b] | 1.17[e] |
| $10^2\times\Gamma^+$ | | 5.26[b] | 5.9[b] | 8.6[m] | | 13.0[b] | 20.4[e] |
| $10^2\times\Gamma^-$ | | 1.19[b] | 1.43[b] | | | 3.59[b] | 5.45[e] |
| $\Gamma^+/\Gamma^-$ (obs) | | 4.4[b] | 4.1[b] | | | 3.6[b] | 3.7[e] |
| $\Gamma^+/\Gamma^-$ (LM)[f] | | 4.4 | 4.4 | | | 4.1 | 3.8 |
| $A_1^+$ (obs) | | 106[b] | 92.5[b] | | | 21.2[b] | 3.00[c] |
| $A_1^+$ (LM)[f] | | | | | | 22.4 | 2.8 |
| $A_1^-$ (obs) | | 145[b] | 120[b] | | | 28.4[b] | 6.83[c] |
| $A_1^+/A_1^-$ (obs) | | 0.73[b] | 0.77[b] | | | 0.75[b] | 0.44[c] |
| $A_1^+/A_1^-$ (LM)[f] | | 0.77 | 0.77 | | | 0.75 | 0.42 |
| $X_0$ | 0.102[d] | 0.135[b] | 0.186[b] | 0.183[d] | 0.224[h] | 0.36[b] | 0.474[e] |
| $\Lambda^*$ | | | 0.064[g] | 0.187[g] | 1.73[g] | 2.64[g] | 3.05[g] |
| $T_c$(K) | 647.5[d] | 304.12[b] | 289.75[b] | 150.7[d] | 32.98[h] | 5.19[b] | 3.31[e] |
| $P_c$ (atm) | 218.5[d] | 72.85[b] | 57.64[b] | 48.1[d] | 12.76[h] | 2.25[b] | 1.13[e] |
| $\rho_c$ (g/cm$^3$) | 0.325[d] | 0.468[b] | 1.105[b] | 0.530[d] | 0.0313[h] | 0.0696[b] | 0.0415[e] |
| $MP_c/\rho_cT_c$ (J/mole K) | 1.91 | 2.28 | 2.40 | 2.43 | 2.45 | 2.52 | 2.52 |
| $\mathfrak{a}$ | 1.60[d] | 0.825[k] | 1.30[i] | 0.65[d] | 0.37[i] | $\begin{cases}0.18^{i}\\0.05^{l}\end{cases}$ | $\begin{cases}-0.03^{j}\\-0.01^{l}\end{cases}$ |

[a] Ref. 39.

[b] Ref. 17.

[c] This work.

[d] Ref. 34.

[e] Ref. 6.

[f] Calculated from Eqs. (34) and (25) using values of $\gamma$ and $\beta$ of this table and the constants of Ref. 20.

[g] Ref. 33.

[h] Ref. 35.

[i] Ref. 36.

[j] Ref. 8.

[k] Ref. 38.

[l] Ref. 37.

[m] C. Pings (private communication).

substance-dependent, or at least show some quantum effects. We show specifically in Table III the ratio of critical coefficients for the isothermal compressibility ($\Gamma^+/\Gamma^-$) and the specific heat ($A_1^+/A_1^-$) along the critical isochore. These critical coefficient ratios are quite sensitive to small variations in the critical exponents. This is particularly bothersome in the case of $A_1^+/A_1^-$, where most experimental determinations of $\alpha$ have uncertainties of ±25% or more, leading to a similar uncertainty[28] (±30%) in $A_1^+/A_1^-$. Still there is evidence of a possible trend in these coefficients for the quantum fluids, particularly in $\Gamma^+/\Gamma^-$, which in general is more precisely known than $A_1^+/A_1^-$. We believe that our determination of $A_1^+/A_1^-$ in $\mathrm{He}^3$ is evidence of a similar trend in this ratio. Our value differs significantly from the value for all the other fluids in Table III, including that of $\mathrm{He}^4$.

For comparison we have also listed in Table III the values predicted for $\Gamma^+/\Gamma^-$ and $A_1^+/A_1^-$ from the LM, using the listed values of the critical exponents in the LM equations. The equation for $A_1^+/A_1^-$ is Eq. (24), and the corresponding relation for $\Gamma^+/\Gamma^-$ is

$$\frac{\Gamma^+}{\Gamma^-}=\frac{\gamma}{\beta}\left(\frac{1-2\beta}{2\beta}\,\frac{\gamma}{\gamma-1}\right)^{\gamma-1} . \tag{25}$$

The agreement between Eqs. (24), (25), and experimental determinations of these coefficients is remarkable, particularly in its qualitative reflection of changes in the coefficients in the quantum fluids.

The critical coefficient that is most strikingly substance-dependent is the parameter $\mathfrak{a}$ defined in the equation[40] for the rectilinear diameter $\rho_d$

$$\rho_d=\tfrac{1}{2}(\rho_L+\rho_v)=\rho_c[1+\mathfrak{a}\,(-t)] , \tag{26}$$

where $\rho_L$ and $\rho_v$ are the densities at equal temperature of the liquid and gas phases, respectively, along the coexistence curve. The value for $\mathfrak{a}$ varies by an order of magnitude between the $\mathrm{H_2O}$ and $\mathrm{He}^4$ systems, and appears moreover to change sign as one goes from the $\mathrm{He}^4$ to the $\mathrm{He}^3$ system.

## VI. CONCLUSIONS

We find in general that a scaling-law formulation in which the chemical potential is assumed analytic at the critical point adequately describes our specific-heat data for $\mathrm{He}^3$. There is no discernible evidence of any anomalous behavior of $d^2\mu(\rho_c, t)/dt^2$. A sensitive experimental test of this assumption would now be given by precision measurements of $(\partial P/\partial T)_V$ along the critical isochore in $\mathrm{He}^3$. Such measurements would not be subject to any possible ambiguity in the temperature scale, such as was encountered by Kierstead[30] with $\mathrm{He}^4$.

The Green, Cooper, and Sengers extended scaling form for the nondivergent correction terms to the specific heat is consistent with our data and extends the range in $t$ over which theory describes the data by a factor of about 10. However, the data are not precise enough to exclude some other form of extended scaling.

General consistency is also seen between these measurements and the Wallace and Meyer[6] $P$-$V$-$T$ measurements on this system. The two sets of data are thus found to be both independently and mutually consistent with the scaling hypothesis. One possible exception to the general consistency between the two data sets is the measurement of the critical temperature $T_c$.

There appears to be sufficient experimental evidence that the critical coefficients show significant substance dependence, particularly in the quantum fluids. A theoretical treatment of this variation would be welcome, and may be particularly fruitful in the case of the rectilinear diameter which has been the object of much recent interest.[40]

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$$(MP_c/\rho_c)f(X) = -a_\alpha''(X) - A_1^+ X^{-\alpha}$$

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