In the one phase region the two curves on figure 4 differ drastically. This suggests particular attention to density measurements will be required to determine behavior at the critical density. We also note the transition to the one phase region is particularly well marked in the case of $\rho = 1.07\ \rho_c$. This suggests specific heat measurements may be a sensitive method of determining the coexistence curve.

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The Coexistence Curve of He^4

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During the years between 1956 and 1963 I measured the density of saturated He^4 liquid and vapor along the coexistence curve from 0.30 to 0.99 T_c, by refractive index measurements with a modified Jamin interferometer [1–3]. Between 0.95 and 0.993 T_c, 76 experimental points were taken. Advantages of this method of density measurement near the critical point are

1. High resolution of density to ~0.01 percent is possible.

2. There are *no* dead space corrections to the observed densities.

3. The density of a horizontal "slice" only 1 mm deep is measured and hydrostatic head effects were always less than 0.05 percent in density.

4. If temperature inhomogeneities of $\sim 10^{-4}$ °K appear in the optical cell the fringes disappear and *no* results are obtained.

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We analyzed our data on the coexistence curve between 0.98 and 0.993 T_c by extending Landau and Lifshitz's theory using a fit to a power series expansion in volume and temperature [3]. If, as is now believed, the critical point is a singular point, this whole expansion procedure is questionable, since the coexistence curve cannot in principle be represented asymptotically by a Taylor series in the density about such a nonanalytic point. A reanalysis of this same data will now be presented, without the use of a Taylor series expansion.

The coexistence curve of saturated liquid and vapor densities ρ_l and ρ_g as a function of temperature, is symmetrical, not about the critical density, but about a "rectilinear diameter." This line of mean densities of vapor and liquid passes through ρ_c, the critical density, and for He^4 would extrapolate linearly to 1.1 ρ_c at $T=0$. The symmetry of the coexistence curve is obscured on a plot of saturated molar volume V_l and V_g of liquid and vapor since the mean volume curves sharply away from the temperature axis at lower temperatures. In examinations of the shape of coexistence curves, it is customary to consider the quantity $(\rho_l - \rho_g)$ or $(\rho_l - \rho_g)/2\rho_c$ as a function of $(T_c - T)$. If one attempts to write

$$\frac{\rho_l - \rho_g}{2\rho_c} = A(T_c - T)^{\beta}, \tag{1}$$

where A and β are constants, then classically (van der Waals), $\beta = 1/2$, whereas a variety of experiments suggest that $\beta = 1/3$ for a certain range of temperatures. Accurate values of T_c are needed for meaningful tests of such a relationship. Furthermore, the slope of the "rectilinear diameter," or line of mean densities, differs from substance to substance, so that the similarity of coexistence curves may be obscured by comparing experimental data in that manner. M. J. Buckingham has suggested that the shape of the coexistence curve should be analyzed using the natural variable

$$X = \frac{\rho_l - \rho_g}{\rho_l + \rho_g} = \frac{V_g - V_l}{V_g + V_l} \neq \frac{\rho_l - \rho_g}{2\rho_c}. \tag{2}$$

Advantages of this variable are

(1) X ranges from 1 to 0 as T ranges from 0 to T_c for any substance,

(2) there is equal symmetry using either density or molar volume, and the effect of the slope of the "rectilinear diameter" is entirely removed, and

(3) if we plot X^n, $\left(\text{where } n = \frac{1}{\beta}\right)$, against T, we need not know T_c or ρ_c or V_c and in fact may determine T_c by such plots.

Figure 1 shows how plots of X^2 (or $\beta = 1/2$), and X^3 (or $\beta = 1/3$), appear for He^4 over the whole range of measurements [1, 2, 3] from 0.3 to 0.99 T_c. Clearly, X^3 is nearly linear, (or $\beta = 1/3$), above about 0.8 T_c (but not too near T_c, see later), in agreement with many other measurements for many fluids. Note that the classical X^2 is not linear over any extended range of temperature.

M. J. Buckingham has shown [4] that the simplest singular entropy surface which is consistent with a logarithmic infinity in C_v at the critical point, would imply a coexistence curve whose asymptotic form as $T \to T_c$ is given by

$$\frac{X^2}{1 - \ln X} = at \tag{3}$$

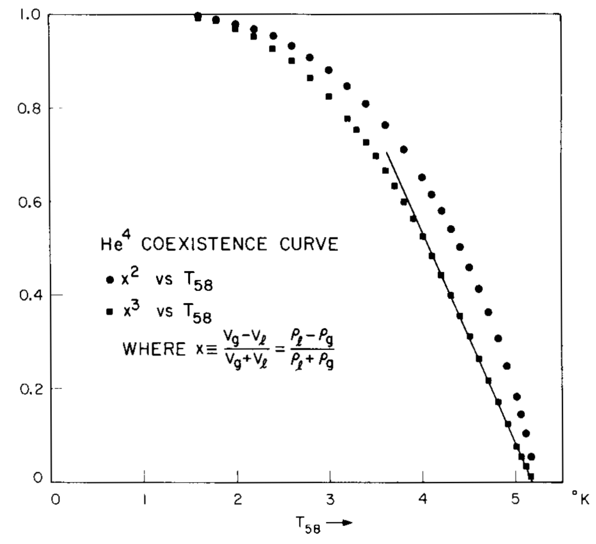

FIGURE 1. *Temperature dependence of* X^2 *and* X^3 *for* He^4. X^3 is linear above 0.8 T_c.

where a is a constant, and $t = T_c - T$. The quantity $X^2/(1 - \ln X)$ lies between X^2 and X^3 for the whole temperature range.

The question of the asymptotic form of the coexistence curve of He^4 will now be examined using the 76 experimental points listed in table III of reference 3. All these points were taken within 250 mdeg of 5.1994 °K (the critical temperature of He^4 on the 1958 He^4 scale of temperatures [5]). The temperature of each data point was obtained directly from the measured saturated vapor pressure. Although both V_g and V_l were not often measured at precisely the same temperature, we may evaluate an X for each experimental point by writing

$$X = \frac{2V_g}{V_g + V_l} - 1, \qquad \text{or } X = 1 - \frac{2V_l}{V_g + V_l}. \tag{4}$$

For each temperature at which either V_g or V_l was measured, the quantity $(V_g + V_l)$, which varies rather slowly and smoothly with temperature, was read by interpolation, or, within 50 mdeg of T_c, by linear extrapolation. Thus 76 values of X are obtained within 250 mdeg of T_c. The added uncertainty in X produced by the uncertainty in the value of $V_g + V_l$ falls from 0.6 percent at $t = 35.9$ mdeg to below 0.3 percent above $t = 50$ mdeg.

Figure 2 shows a graphical test of the three functional forms for the coexistence curve of He^4 for all points within 250 mdeg of 5.1994 °K. The straight line drawn on the plot of X^2 is a least-

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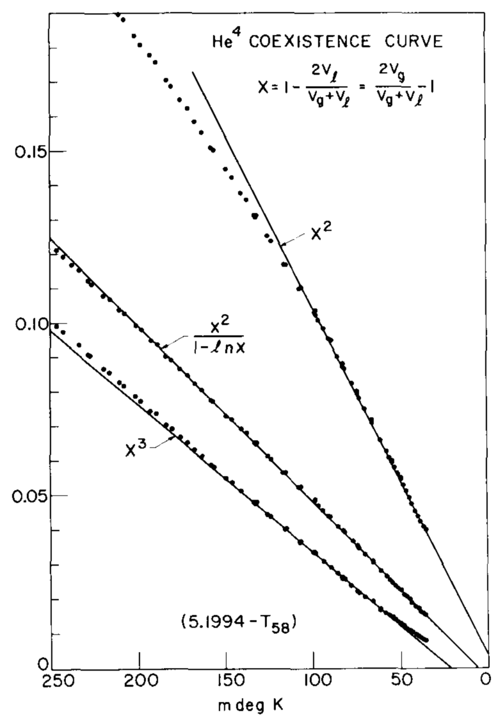

FIGURE 2. *Tests of the asymptotic form of the coexistence curve for* He^4 *above 0.95* T_c.

squares-fitted straight line for the 39 points within 100 mdeg of T_c. The lines shown on the plots of $X^2/(1-\ln X)$ and of X^3 are least-squares-fitted lines for the 65 points within 200 mdeg of T_c. Clearly, over this temperature range the data are represented best by the function $X^2/(1-\ln X)$. Note particularly the marked curvature of X^3 as $T \to T_c$.

Table 1 shows the slopes and intercepts, with standard errors, computed by least squares fits of the data in the form

$$f(X_i) = at_i + a\Delta T_c \tag{5}$$

where $f(X)$ is X^2, $X^2/(1-\ln X)$, or X^3, and where $t = 5.1994 - T_{58}$, in millidegrees, and $\Delta T =$ the shift in critical point implied by a linear extrapolation of $f(X)$ to zero. None of these asymptotic fits extrapolates to the value $T_c = 5.1994$ °K assumed in the T_{58} scale of temperatures. Yang and Yang [6] have suggested that the T_{58} scale may be in error near T_c, and that the actual critical temperature should be lower.

As a more sensitive test of the experimental evidence in favor of any of these functional forms for the coexistence curve, we plot the residuals

$$\Delta t_i = t_i - \frac{1}{a} f(X_i) - \Delta T_c \tag{6}$$

for each of six fits with $f(X)$ equal to X^2, $X^2/(1-\ln X)$ and X^3, over the ranges $t < 100$ mdeg and

TABLE 1. *Linear fits of coexistence curve data to three functional forms*

	Range of data in fit			
	$t < 100$ mdeg (39 points)		$t < 200$ mdeg (65 points)	
$f(X)$	$10^3 a$ (mdeg K)$^{-1}$	ΔT_c mdeg K	$10^3 a$ (mdeg K)$^{-1}$	ΔT_c mdeg K
X^2	1.005 ± 0.004	$+4.2 \pm 0.3$	0.882 ± 0.007	$+14.2 \pm 0.9$
$\frac{X^2}{1-\ln X}$	0.527 ± 0.002	-7.5 ± 0.3	0.513 ± 0.001	-5.9 ± 0.3
X^3	0.404 ± 0.003	-18.1 ± 0.4	0.429 ± 0.002	-20.8 ± 0.4

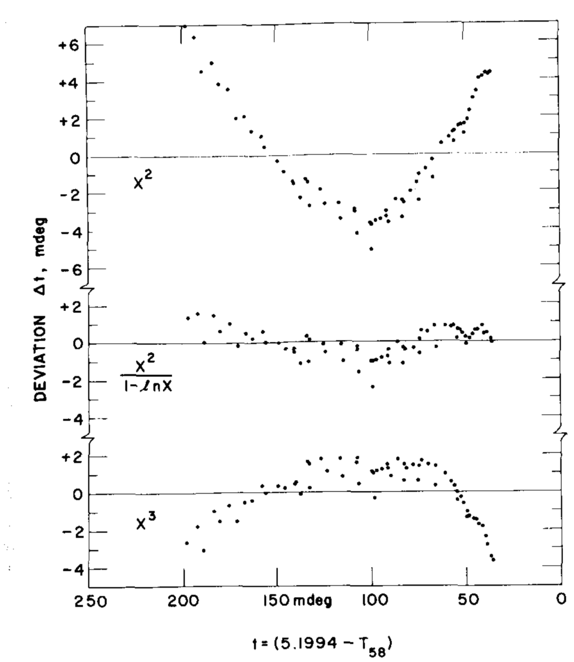

FIGURE 3. *Deviations from linearity, expressed in millidegrees, for linear fits of the data for* $t < 200$ *mdeg for the three functions* $f(X) = X^2$, $X^2/(1 - \ln X)$ *and* X^3.

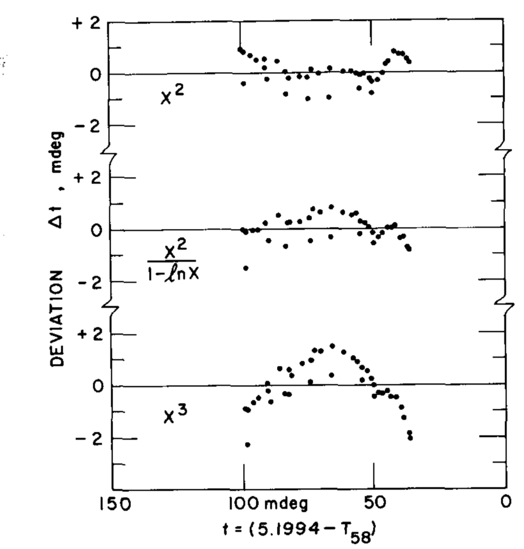

FIGURE 4. *Deviations from linearity, expressed in millidegrees, for linear fits of the data for* $t < 100$ *mdeg for the three functions* $f(x) = x^2$, $x^2/(1 - \ln x)$, *and* x^3.

$t < 200$ mdeg. Figures 3 and 4 are plots of these deviations from linearity, expressed in millidegrees. Figure 3 shows clearly that both X^2 and X^3 show systematic deviations fitted within 200 mdeg of T. Figure 4 shows that, using only the data points within 100 mdeg, both X^2 and $X^2/(1-\ln X)$ appear to give almost equally good fits. However, $X^2/(1-\ln X)$ gives much the best fit when all points within 200 mdeg of T_c are included.

Conclusions

The main conclusions of this analysis of the form of the He^4 coexistence curve are

1. X^3 is not asymptotically linear in T above about 0.98 T_c, despite its linearity from 0.8 to 0.98 T_c.

2. X^2 can be shown to be asymptotically linear only above 0.98 T_c, with the critical temperature 4 mdeg above the T_{58} value. Such a shift is in the opposite sense to that expected [6], and this functional form is inconsistent with the observed [7] logarithmic singularity in C_V below T_c.

3. $X^2/(1-\ln X)$ is the best asymptotic form, with the critical point lowered 6 to 8 mdeg below the T_{58} value. This shift is in the sense expected [6], and the functional form is consistent [4] with the observed [7] logarithmic singularity in C_V below T_c.

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