

are in this approximation less than the experimental values.⁶

The stability of the solution obtained was investigated. It was shown that the longitudinal ion acoustical waves in the after-body region are unstable. The wave frequency $\omega \sim (0.1-1)\Omega_i$, where $\Omega_i = (4\pi e^2 N_0/M)^{1/2}$ is the Langmuir ion frequency. It is possible that the plasma oscillations in the ionosphere observed by Bowen, Boyd, Henderson, and Willmore⁷ in the wake of a body are the result of this instability mechanism.

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¹Y. L. Alpert, A. V. Gurevich, and L. P. Pitayevsky, "Artificial Satellites in Rarefied Plasma" (to be published).

²L. D. Landau and E. M. Lifshitz, Fluid Mechanics (Pergamon Press, New York, 1959), p. 353.

³A. V. Gurevich and L. P. Pitayevsky, Geomagnetizm i Aeronomiya 4, 817 (1964); Zh. Eksperim. i Teor. Fiz. 49, 2 (1965).

⁴A. V. Gurevich, Planetary Space Sci. 9, 321 (1962).

⁵K. Norman and A. P. Willmore, Planetary Space Sci. 13, 1 (1965).

⁶U. Samir and A. P. Willmore, Planetary Space Sci. 13, 285 (1965).

⁷P. I. Bowen, R. L. F. Boyd, C. L. Henderson, and A. P. Willmore, Proc. Roy. Soc. (London) A281, 541 (1964).

NONANALYTIC FORM OF THE COEXISTENCE CURVE OF HELIUM AT THE CRITICAL POINT*

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During the years between 1956 and 1963 I measured the density of saturated He⁴ liquid and vapor along the coexistence curve from 0.30 to 0.994T_c, by refractive index measurements with a modified Jamin interferometer.¹⁻³ We analyzed our data on the coexistence curve between 0.98 and 0.994T_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, singularities occur at the critical 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.⁴ A reanalysis of these same data will now be presented, without the use of a Taylor-series expansion. The result of this analysis confirms that the critical point is indeed a nonanalytic point.

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 He⁴ would extrapolate linearly to $1.1\rho_c$ 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

$$(\rho_l - \rho_g)/2\rho_c = A(T_c - T)^\beta, \quad (1)$$

where A and β are constant, then classically (van der Waals), $\beta = \frac{1}{2}$, whereas a variety of experiments suggests that $\beta = \frac{1}{3}$ 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. Buckingham⁵ has suggested that the shape of the coexistence curve should be analyzed using the natural variable

$$X \equiv \frac{\rho_l - \rho_g}{\rho_l + \rho_g} \equiv \frac{V_g - V_l}{V_g + V_l} \neq \frac{\rho_l - \rho_g}{2\rho_c}. \quad (2)$$

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 (where $n = 1/\beta$) against T , we need not know T_c or ρ_c or V_c and, in fact, may determine T_c by such plots.

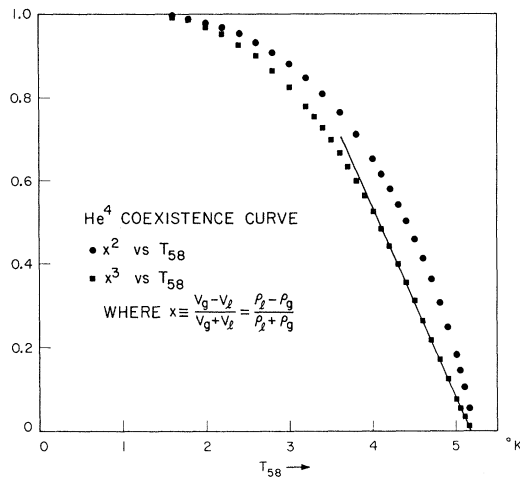


FIG. 1. Temperature dependence of X^2 and X^3 for He^4 . X^3 is linear above $0.8T_c$.

Figure 1 shows how plots of X^2 (or $\beta = \frac{1}{2}$), and X^3 (or $\beta = \frac{1}{3}$), appear for helium-four over the whole range of measurements¹⁻³ from 0.3 to $0.99T_c$. Clearly, X^3 is nearly linear (or $\beta = \frac{1}{3}$), above about $0.8T_c$ (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.

The coexistence curve near T_c .—Buckingham has shown⁵ 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 $T \rightarrow T_c$ is given by

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

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 temperatures⁶). The temperature of each data point was obtained directly from the measured saturated vapor pressure.

These optical-density measurements near the critical point should be particularly reliable for the following reasons:

- (1) High resolution of density to $\sim 0.01\%$ is

possible.

(2) There are no dead-space corrections to the observed densities.

(3) The local density of a horizontal “slice” only 1 mm deep is measured and hydrostatic head effects were always less than 0.5% in density.

(4) If temperature inhomogeneities of $\sim 10^{-4}^\circ\text{K}$ appear in the optical cell, the fringes disappear and no results are obtained.

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

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

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

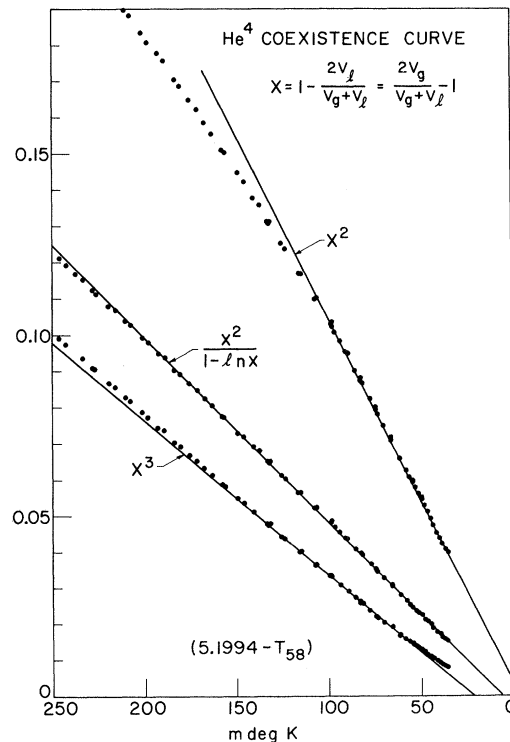


FIG. 2. Tests of the asymptotic form of the coexistence curve for He^4 above $0.95T_c$.

Table I. Linear fits of coexistence-curve data to three functional forms.

$f(X)$	Range of data in fit			
	$t < 100$ mdeg (39 points)		$t < 200$ mdeg (65 points)	
	$10^3 a$ [(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	$+14.2 \pm 0.9$
$X^2/(1-\ln X)$	0.527 ± 0.002	-7.5 ± 0.3	0.513 ± 0.001	-5.9 ± 0.3
X^3	0.404 ± 0.003	-18.0 ± 0.5	0.429 ± 0.002	-20.8 ± 0.4

from 0.6% at $t = 35.9$ mdeg to below 0.3% 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-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 nonanalytic function $X^2/(1-\ln X)$. Note particularly the marked curvature of X^3 as $T \rightarrow T_c$. The liquid points and vapor points, treated

separately, lead to the same conclusions.⁷

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

$$f(X_i) = at_i + a\Delta T_c, \quad (5)$$

where $f(X)$ is X^2 , $X^2/(1-\ln X)$, or X^3 , and where $t = 5.1994 - T_{58}$, in millidegrees, and ΔT_c is the shift in critical point implied by a linear extrapolation of $f(X)$ to zero. None of these asymptotic fits extrapolates to the value $T_c = 5.1994^\circ\text{K}$ assumed⁶ in the T_{58} scale of temperatures. Yang and Yang⁸ 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

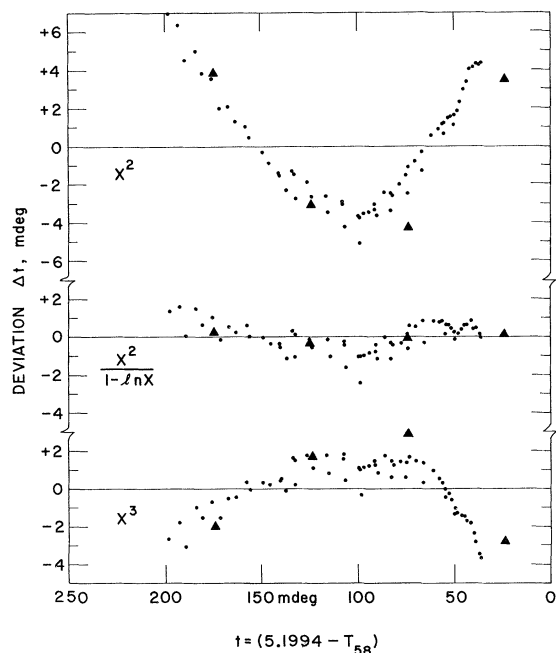


FIG. 3. Deviations from linearity, expressed in millidegrees, for linear fits of the He^4 data for $t < 200$ mdeg for the three functions $f(X) = X^2$, $X^2/(1-\ln X)$, and X^3 . The triangles are taken from Sherman's⁹ recent He^3 isochores. For the He^3 data $t = (3.324 - T_{58})$.

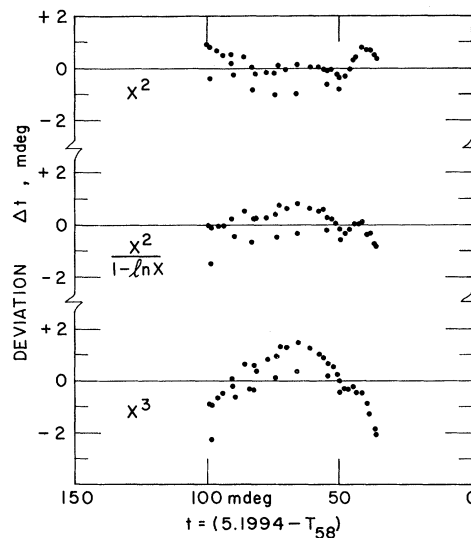


FIG. 4. Deviations from linearity, expressed in millidegrees, for linear fits of the He^4 data for $t < 100$ mdeg for the three functions $f(X) = X^2$, $X^2/(1-\ln X)$, and X^3 .

residuals

$$\Delta t_i = t_i - (1/a)f(X_i) - \Delta T_c \quad (6)$$

for each of the six fits with $f(X)$ equal to X^2 , $X^2/(1-\ln X)$, and X^3 , over the ranges $t < 200$ 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_c . 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. Figure 3 also shows the same test for He^3 , using Sherman's⁹ recent He^3 data. Linear fits for the same three functions were attempted for his four smoothed values of ρ_l and ρ_g at temperatures above $0.95T_c$. The nonanalytic form $X^2/(1-\ln X)$ gives the best fit for He^3 also, over the widest temperature range, and the deviations from linearity are strikingly similar for the He^3 and He^4 data.

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

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

(2) X^2 can be shown to be asymptotically linear only above $0.98T_c$, with the critical temperature 4 mdeg above the T_{58} value. (These conclusions are also reached by Tisza and Chase.⁴) Such a shift in T_c is in the opposite sense to that expected,⁸ and this functional form is inconsistent with the observed¹⁰ logarithmic singularity in C_v below T_c .

(3) $X^2/(1-\ln X)$ is the best asymptotic form, fitting well above $0.96T_c$, with the critical point lowered 6 to 8 mdeg below the T_{58} value. This shift is in the sense expected,⁸ and this non-analytic functional form is consistent⁵ with the observed¹⁰ logarithmic singularity in C_v below T_c .

On the basis of Sherman's four smoothed points on the coexistence curve of He^3 above $0.95T_c$, we conclude that $X^2/(1-\ln X)$ is the best asymptotic form for He^3 also,¹¹ with the critical point lowered 2 mdeg to 3.322°K .

It is quite possible that Eq. (3) is rather gen-

erally applicable to a wider class of critical points since, for example, the data¹² on magnetization of EuS also may be well represented above about $0.97T_c$ in this form, with X now defined as $\nu(T)/\nu(0)$, where $\nu(T)$ and $\nu(0)$ are the zero-field nuclear-magnetic-resonance frequencies at temperature T and at zero temperature, respectively.

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¹M. H. Edwards, *Can. J. Phys.* **34**, 898 (1956); **36**, 884 (1958).

²M. H. Edwards, *Phys. Rev. Letters* **108**, 1243 (1957).

³M. H. Edwards and W. C. Woodbury, *Phys. Rev.* **129**, 1911 (1963).

⁴L. Tisza and C. E. Chase, *Phys. Rev. Letters* **15**, 4 (1965), have recently published another power-series analysis of the data expanding in density and temperature.

⁵M. J. Buckingham, *Proceedings of the Conference on Phenomena in the Neighborhood of Critical Points*, National Bureau of Standards, Washington, D. C., 5-9 April 1965 (to be published).

⁶F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, *J. Res. Natl. Bur. Std.* **64A**, 1 (1960).

⁷As evidence of the superiority of the natural variable X to the density ρ for displaying the true symmetry of the coexistence curve, compare the upper curve of Fig. 2 with Fig. 1 of reference 4, where the same data are displayed, but the liquid and vapor "branches" appear separated.

⁸C. N. Yang and C. P. Yang, *Phys. Rev. Letters* **13**, 303 (1964).

⁹R. H. Sherman, *Phys. Rev. Letters* **15**, 141 (1965).

¹⁰M. R. Moldover and W. A. Little, in *Proceedings of the Ninth International Conference on Low Temperature Physics*, Columbus, Ohio, 1964 (to be published); and *Proceedings of the Conference on Phenomena in the Neighborhood of Critical Points*, National Bureau of Standards, Washington, D. C., 5-9 April 1965 (to be published).

¹¹The quantity aT_c for He^3 is approximately 0.8 times its value for He^4 . This difference may be associated with quantum corrections to the law of corresponding states.

¹²P. Heller and G. Benedek, *Phys. Rev. Letters* **14**, 71 (1965).