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Saturated He^4 near Its Critical Temperature*

M. H. EDWARDS AND W. C. WOODBURY
Royal Military College, Kingston, Ontario

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Measurements of the refractive index n of saturated He^4 liquid and vapor have been made at $\lambda=5462.27$ Å from 4.2°K nearly to the critical temperature ($T_c=5.1994$°K). Careful determinations of n and dn/dT as a function of temperature were made using a metal optical cryostat and a Jamin interferometer modified to produce a chart record of the interference fringes. The measurements extended to within 50 mdeg of T_c for saturated vapor, and to within 36 mdeg of T_c for saturated liquid. These results, combined with the Lorenz-Lorentz equation, then give the density ρ of both saturated liquid and saturated vapor, and the expansion coefficient β_s of the saturated liquid. These n, ρ, and β_s measurements are the first ever made above 4.4°K except for two early measurements of density at 4.6 and 4.7°K. The critical density is found to be $\rho_c=(0.06948\pm0.00030)$ g cm^{-3}, or the critical molar volume, $V_c=(57.628\pm0.25)$ cm^3 mole^{-1}.

We have modified and extended the Landau-Lifshitz theory of the properties of a substance "near" the critical point, and then find excellent agreement with our experimental values of the molar volumes of saturated He^4 within about 110 mdeg of T_c. This agreement is taken as evidence that $(\partial^3P/\partial V^3)_T$ is *negative* at the critical point—in clear contradiction to theories which suggest that this third derivative is zero at T_c. In terms of the "reduced" parameters $V'=V/V_c$ and $P'=P/P_c$, we find $(\partial^3P'/\partial V'^3)_{T_c}=-(10.4\pm1.8)$ for He^4. In addition, we can then calculate saturated vapor and liquid molar volumes, and liquid coefficient of expansion values right up to the critical temperature, assuming the continued validity of the modified Landau-Lifshitz theory.

1. INTRODUCTION

IN 1822, Baron de la Tour discovered[1] the phenomenon of the critical point. He rolled a ball inside a heated closed cannon barrel and noted the difference in the sound when the substance was a liquid and when it was a gas. Later investigations, especially by Andrews,[2-5] led to the concept that each gas has a lowest temperature above which it cannot be liquefied regardless of the applied pressure. This temperature is called the critical temperature T_c. Few experiments have been performed on liquid He^4 near its critical temperature, $T_c=5.1994$°K. Nearly all the experimental work on liquid He^4 has been done at temperatures below its normal boiling point, 4.215°K. Upon the discovery of the superfluidity of liquid helium II, a large proportion of subsequent work was concentrated on the region near and below the lambda temperature of 2.172°K. The nature of the λ transition is now becoming clearer (see review by Buckingham and Fairbank[6]), but the nature of critical points is still somewhat obscure.

This paper reports measurements of n_g, the refractive index of saturated He^4 vapor, and n_l, the refractive index of saturated He^4 liquid above 4.2°K. From the known molar polarizability[7] of He^4 we then deduce the saturated vapor density ρ_g, the saturated liquid density ρ_l, and the coefficient of thermal expansion β_s of the saturated liquid. These measurements extend to 50 mdeg below T_c for the vapor, and to 36 mdeg below T_c for the liquid. We use these measurements to determine the critical density of He^4 by a short extrapolation.

Theoretical statements of the properties of a substance at its critical point differ considerably. Extensive reviews have been given by Rice[8] and by Kobe and Lynn.[9] We compare our results to a recent theory due to

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[1] C. de la Tour, Ann. Chim. Phys. [2] 21, 127 (1822).

[2] T. Andrews, Proc. Roy. Soc. (London) **18**, 42 (1869).

[3] T. Andrews, Trans. Roy. Soc. (London) **A159**, 575 (1869).

[4] T. Andrews, Trans. Roy. Soc. (London) **A166**, 421 (1876).

[5] T. Andrews, Trans. Roy. Soc. (London) **A178**, 45 (1887).

[6] M. J. Buckingham and W. M. Fairbank, *Progress in Low-Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1961), Vol. III, p. 80.

[7] M. H. Edwards, Can. J. Phys. **36**, 884 (1958).

[8] O. K. Rice, in *Thermodynamics and Physics of Matter* (Princeton University Press, Princeton, New Jersey, 1955), p. 419.

[9] K. A. Kobe and R. E. Lynn, Chem. Rev. **52**, 117 (1953).

TABLE I. Density of saturated He^4 vapor from 1.5 to 4.2°K calculated from $(n-1)_g$ by Edwards.[a]

T_{58} (°K)	$10^3\rho_g$ (g cm^{-3})	T_{58} (°K)	$10^3\rho_g$ (g cm^{-3})
1.5	0.159±0.010	2.9	3.955
1.6	0.230	3.0	4.512
1.7	0.328	3.1	5.126±0.031
1.8	0.455	3.2	5.791
1.9	0.609	3.3	6.507
2.0	0.793±0.010	3.4	7.284
2.1	1.003	3.5	8.128
2.2	1.254	3.6	9.059±0.036
2.3	1.530	3.7	10.077
2.4	1.832	3.8	11.207
2.5	2.174	3.9	12.454
2.6	2.558±0.026	4.0	13.753±0.051
2.7	2.978	4.1	15.271
2.8	3.453	4.2	16.876±0.077

[a] See reference 12.

Landau and Lifshitz[10] and show that their theory does not apply to saturated He^4. We shall show, however, how Landau and Lifshitz's theory may be modified and extended to produce excellent agreement with the measured molar volumes of saturated He^4 within about 110 mdeg of T_c. This agreement implies that $(\partial^3P/\partial V^3)_T$ is ***negative*** at the critical point, so that there is ***not*** a finite horizontal portion on the critical isotherm in a PV diagram.

2. MEASUREMENTS

We measured refractive index changes as a function of temperature, using an optical cryostat and a Jamin interferometer.[7,11–13] The copper optical cell is a horizontal cylinder about 9.58 cm long and 1.2 cm in diameter. The end windows of the cell are plane parallel fused silica flats, 5 mm thick. At a wavelength of 5462.27 Å, one fringe displaced corresponds to a change of $(5.699\pm0.003)\times10^{-6}$ in refractive index. The Jamin telescope has been modified by the addition of a beam splitter and a photomultiplier so that fringes may be observed visually and also recorded on a chart recorder.[13]

Slits were placed on the outer windows of the optical cryostat so that a "slice" of about 1-mm depth and 1.2-cm width, along the length of the cell was observed. By adjusting the level of the liquid in the partially filled cell, we then could observe refractive index changes in either saturated liquid, or saturated vapor. To obtain clear interference fringes at all requires rather stringent temperature uniformity in the "slice" of liquid or gas being observed. Temperature changes must, therefore, occur rather slowly also, or the interference pattern becomes obscured. Since dn/dT approaches infinity for both liquid and vapor as the critical temperature is approached, the highest temperatures are the hardest. Furthermore, measurements of n as a function of temperature, above 2.172°K were only possible as the temperature was lowered—never as it was raised, or the interference pattern would vanish (presumably due to irregular temperature gradients in the optical cell). Our measurements now extend up to 5.1635°K for the liquid and to 5.1498°K for the vapor. These were the highest temperatures at which clear fringes occurred, when we cooled slowly from the critical temperature (after a 2–3 h wait at, or slightly above, the critical temperature[14] $T_c=5.1994$°K). At these temperatures, 36 mdeg below and 50 mdeg below T_c, a change of 10^{-4}°K then gave a change of about one-half a fringe in the interference pattern.

The 1958 scale of temperatures[14] was used to convert vapor pressures to temperatures, T_{58}. This scale is appreciably different from previous scales, especially above 4.5°K. In this whole series of measurements[7,11–13] we have assumed that the temperatures in the bath *outside* the copper cell are identical to the temperatures of the sample of helium vapor or liquid *inside* the cell. See reference 13 for a discussion of this point.

Measurements of n and dn/dT at the saturated vapor pressure may be converted to density ρ, and coefficient of expansion β_s measurements using

$$\rho=(7.675\,23\pm0.0077)(n^2-1)(n^2+2)^{-1}, \tag{1.1}$$

which is Eq. (3.2) of reference 13 and

$$\beta_s=-6n(n^2-1)^{-1}(n^2+2)^{-1}(dn/dT), \tag{1.2}$$

which is Eq. (4) of reference 11.

These equations are obtained from the Lorenz-Lorentz law, assuming that the polarizability per mole of He^4 is constant and equal to $(0.124\,54\pm0.000\,21)$ cm^3 mole^{-1}, for $\lambda=5462.27$ Å, as was measured by Edwards.[7] For a full discussion of the evidence in favor of the as-

TABLE II. Present results for saturated He^4 from 4.2 to 5.15°K: Refractive index n_g and n_l of saturated vapor and liquid He^4 at $\lambda=5462.27$ Å, densities ρ_g and ρ_l of saturated vapor and liquid, and liquid coefficient of thermal expansion β_s along the SVP curve at even temperatures. Extrapolated values are given at $T_c=5.1994$°K.

T_{58} (°K)	$10^6(n-1)_g$	$10^3\rho_g$ (g cm^{-3})	$10^6(n-1)_l$	$10^3\rho_l$ (g cm^{-3})	β_s (deg^{-1})
4.2	3300	16.88	24 504	124.85	0.158
4.3	3650	18.67	24 099	122.80	0.174
4.4	4017	20.54	23 659	120.57	0.193
4.5	4438	22.69	23 180	118.14	0.216
4.6	4915	25.13	22 650	115.45	0.247
4.7	5457	27.90	22 046	112.38	0.293
4.8	6089	31.13	21 355	108.87	0.348
4.9	6852	35.02	20 541	104.74	0.432
5.0	7825	39.98	19 519	99.54	0.602
5.05	8450	43.18	18 864	96.21	0.769
5.10	9231	47.16	18 021	91.93	1.085
5.15	10 450	53.38	16 818	85.81	...
5.1994	13 610	69.48	13 610	69.48	∞

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[10] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, New York, 1958), para. 81.

[11] M. H. Edwards, Can. J. Phys. **34**, 898 (1956).

[12] M. H. Edwards, Phys. Rev. **108**, 1243 (1957).

[13] M. H. Edwards and W. C. Woodbury, Can. J. Phys. **39**, 1833 (1961).

[14] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Research Natl. Bur. Standards **64A**, 1 (1960).

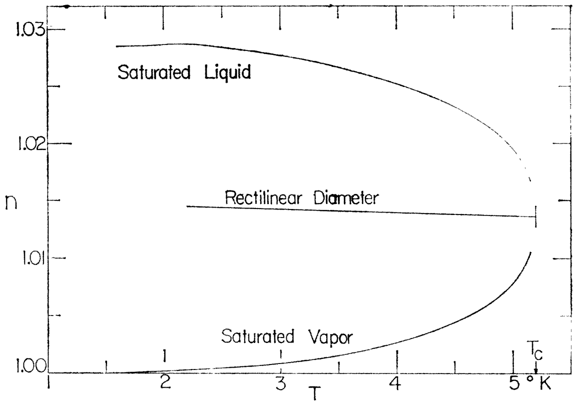

FIG. 1. Refractive index of saturated He^4, showing the rectilinear diameter. The measurements below 4.2°K are taken from references 7 and 12.

sumptions involved, see Edwards[7] and Edwards and Woodbury.[13] The molar volume V may be obtained from the density using

$$V=4.003\,864/\rho,$$

or

$$V=(0.521\,672\pm0.000\,89)(n^2+2)(n^2-1)^{-1}. \quad (1.3)$$

Table I shows the saturated vapor densities ρ_g that result from the application of Eq. (1.1) to Edwards' earlier saturated vapor refractive index measurements.[12]

Table II shows the new measurements of n, ρ, and β_s. The subscript l or s refers to saturated liquid; the subscript g refers to saturated vapor. Too many experimental points were taken for us to record here all the original data. Instead, only these interpolated values are given, at 0.1-deg intervals from 4.2 to 4.9°K, and then at 0.05-deg intervals to 5.15°K. In the course of comparing the present n_l results directly with the single absolute measurement[7] at 3.7°K, we repeated some of the previous liquid measurements. From 3.0 to 4.2°K the two sets of measurements of n_l agreed within $\pm3\times10^{-6}$, except at 4.2°K. Our present value of n_l at 4.2°K is 7×10^{-6} lower than the earlier value, and is to be preferred to it.

The present results and previous measurements[7,12] in this series of experiments now give n_g and n_l, and the corresponding ρ_g and ρ_l values for saturated He^4 from 1.5 and 1.6°K to T_c. Figure 1 shows the refractive index measurements and the rectilinear diameter (see later).

The temperature variation of the coefficient of thermal expansion β_s of saturated liquid He^4 is now also clear from this series of measurements, and from earlier direct measurements by Atkins and Edwards.[15,16]

At absolute zero β_s is zero, according to the third law of thermodynamics. It is positive above 0.85°K, passing through a maximum at about 0.9°K, and falling to zero at about 1.12°K.[15,16] Above 1.12°K, β_s is negative and becomes negatively infinite[7,16,17] at the λ point as $\ln(T_\lambda-T)$. Above the λ point, β_s is also believed to be negatively infinite, as $\ln(T-T_\lambda)$, passing through zero again and becoming positive just above the λ point.[7,17] Kerr and Taylor[6] have shown that β_s is zero at 6–8 mdeg above T_λ. Then β_s increases again, tending to $+\infty$, as the critical point is approached.

3. DISCUSSION

3.1. The "Rectilinear Diameter" and the Critical Density

Cailletet and Mathias long ago noticed[18] that curves of the density of saturated liquid and vapor as a function of temperature have roughly the shape of an inclined parabola with its apex at the critical point. The rectilinear diameter of this parabola, given by plotting $\frac{1}{2}(\rho_l+\rho_g)$ at each temperature, was supposed to be a straight line, whose intersection with the parabola gave the critical density. We find that if

$$(n_R-1)=\tfrac{1}{2}(n_l+n_g-2) \quad (3.1)$$

is plotted, where n_R means the refractive index along the rectilinear diameter, we get very nearly a straight line also. Figures 1 and 2 show such lines. Figure 2 is a graph of the n_l and n_g measurements above 5.00°K. The rectilinear diameter has the form

$$10^6(n_R-1)=15\,125-291.333T, \quad (3.2)$$

which represents the data of Table II with a standard deviation of about 3×10^{-6}. We assume that the saturated liquid and saturated vapor branches continue to

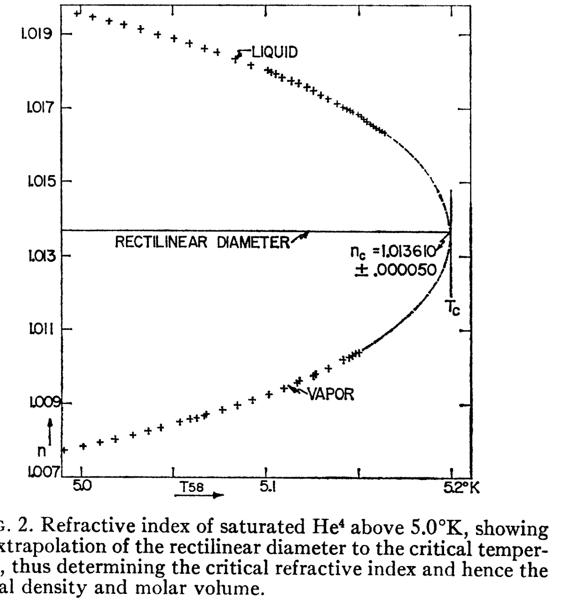

FIG. 2. Refractive index of saturated He^4 above 5.0°K, showing the extrapolation of the rectilinear diameter to the critical temperature, thus determining the critical refractive index and hence the critical density and molar volume.

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[15] K. R. Atkins and M. H. Edwards, Phys. Rev. **93**, 1416 (1954).

[16] K. R. Atkins and M. H. Edwards, Phys. Rev. **97**, 1429 (1955).

[17] C. E. Chase, E. Maxwell, and W. E. Millett, Physica **27**, 1129 (1961).

[18] L. Cailletet and E. Mathias, Compt. Rend. **102**, 1202 (1886).

the "apex" with no unusual features. Then Eq. (3.2) implies the following values at the critical point, taking[14] $T_c=5.1994$°K:

$$\begin{aligned} n_c&=1.013\,610\pm0.000\,050,\\ V_c&=(57.628\pm0.25)\ \mathrm{cm^3\ mole^{-1}},\\ \rho_c&=(0.069\,48\pm0.000\,30)\ \mathrm{g\ cm^{-3}}. \end{aligned} \tag{3.3}$$

Mathias *et al.*[19] measured ρ_l and ρ_g at 4.245, 4.599, and 4.714°K. They used these measurements and adjusted earlier measurements[20] of ρ_l to agree with these. After extrapolating about 485 mdeg they concluded $\rho_c=0.069\,30$ gm cm^{-3}, stating no error. Their data before extrapolation, however, could not have been presumed to be more accurate than 1%. The excellent agreement between our result and theirs must be considered fortuitous. Kerr[21] measured ρ_l to 4.4°K and extrapolated 800 mdeg to T_c in several ways. He concluded

$$\rho_c=(0.0675\pm0.0005)\ \mathrm{g\ cm^{-3}}.$$

Kerr's value differs from ours by about three times the combined errors. It is not clear how much of this difference is due to Kerr's use of the 1955*E* scale[22] of temperatures, and our use of the 1958 scale[14] of temperatures.

TABLE III. Experimental points within 250 mdeg of T_c. Refractive index n_g and n_l of saturated vapor and liquid He^4 at $\lambda=5462.27$ Å, and corresponding molar volume differences from the critical molar volume ($v=V-57.628$), at various temperature differences from the critical temperature ($t=T-5.1994$).

Saturated vapor			Saturated liquid		
$-t$ (mdeg)	$10^6(n_g-1)$	v_g (cm^3 mole^{-1})	$-t$ (mdeg)	$10^6(n_l-1)$	$-v_l$ (cm^3 mole^{-1})
49.6	10 430.9	17.5225	35.9	16 361.7	9.6690
51.3	10 386.4	17.8438	36.7	16 393.1	9.7606
52.9	10 343.4	18.1570	38.3	16 430.1	9.8680
54.5	10 289.5	18.5533	39.9	16 482.0	10.0181
57.8	10 202.6	19.2056	41.5	16 529.9	10.1556
65.9	9983.5	20.8842	43.2	16 582.9	10.3069
73.3	9813.4	22.2429	44.8	16 646.7	10.4878
74.1	9778.9	22.5243	46.4	16 707.7	10.6593
81.6	9612.5	23.9093	48.0	16 777.2	10.8534
82.3	9588.9	24.1099	49.6	16 846.2	11.0444
89.8	9422.7	25.5490	52.9	16 911.7	11.2243
90.6	9414.2	25.6241	54.5	16 953.3	11.3378
98.1	9252.9	27.0730	56.1	16 996.0	11.4538
106.4	9111.6	28.3845	57.8	17 042.8	11.5801
114.8	8973.4	29.7071	61.1	17 130.5	11.8152
123.2	8840.9	31.0137	65.9	17 258.8	12.1548
131.6	8706.4	32.3812	70.0	17 373.3	12.4535
133.1	8693.0	32.5196	74.1	17 474.2	12.7136
137.3	8619.7	33.2852	77.4	17 573.4	12.9664
140.1	8585.0	33.6522	82.3	17 673.6	13.2189
145.8	8502.6	34.5354	85.7	17 743.2	13.3925
156.2	8357.0	36.1391	90.6	17 846.9	13.6487
163.0	8267.8	37.1488	93.9	17 917.6	13.8217
171.2	8157.8	38.4255	96.4	17 972.8	13.9558
180.4	8047.0	39.7460	98.4	18 022.4	14.0756
189.1	7941.3	41.0400	98.9	18 024.1	14.0798
197.9	7841.8	42.2905	107.3	18 162.6	14.4108
207.6	7733.5	43.6880	107.3	18 169.5	14.4271
215.6	7644.6	44.8648	115.7	18 315.1	14.7694
226.3	7534.4	46.3615	125.7	18 482.3	15.1560
233.4	7459.4	47.4062	132.5	18 597.2	15.4175
242.4	7375.6	48.5968	140.5	18 740.5	15.7392
			149.1	18 866.4	16.0178
			157.7	18 983.9	16.2746
			167.2	19 117.2	16.5620
			175.8	19 226.1	16.7937
			183.7	19 328.6	17.0096
			192.5	19 439.8	17.2411
			201.3	19 542.9	17.4534
			210.1	19 638.7	17.6488
			219.1	19 744.1	17.8614
			228.0	19 846.1	18.0652
			237.0	19 935.0	18.2410
			246.0	20 027.3	18.4218

3.2. Landau-Lifshitz Theory

Landau and Lifshitz[10] have recently attempted to give a theory of the properties of a substance *near* the critical point. Their assumptions are that the conditions

$$(\partial P/\partial V)_T=0, \tag{3.4}$$

$$(\partial^2P/\partial V^2)_T=0, \tag{3.5}$$

and

$$(\partial^3P/\partial V^3)_T<0 \tag{3.6}$$

hold at the critical point, where P is the pressure, T is the temperature, and V is the molar volume. Condition (3.6) has never been shown experimentally to hold. Introducing the notation $t=T-T_c$, $v=V-V_c$, where T_c and V_c are the values at the critical point, they expand $(\partial P/\partial V)_T$ as

$$-(\partial P/\partial V)_T=At+Bv^2 \tag{3.7}$$

for small values of t and v. Note that if Eq. (3.6) holds,

$$(\partial^3P/\partial V^3)_T=-2B \tag{3.8}$$

must be negative, therefore B must be positive.

Equation (3.7) may be integrated to give, for the equation of any isotherm

$$P=-Atv-\tfrac{1}{3}Bv^3+f(t), \tag{3.9}$$

where $f(t)$ is unimportant here. To solve for the values of v_g and v_l of saturated vapor and saturated liquid in equilibrium (along the "coexistence curve"), they use the two conditions

$$\mu_l=\mu_g, \tag{3.10}$$

where μ is the chemical potential, and

$$P_l=P_g. \tag{3.11}$$

Equation (3.10) is used in the form

$$\int_l^g d\mu=\int_l^g v(\partial P/\partial v)_t dv=0, \tag{3.12}$$

where $\int_l^g$ means the integral along the transition curve from a state with one phase to a state with the other phase. Evaluating Eq. (3.12) using Eq. (3.7) gives

$$\tfrac{1}{2}At(v_g^2-v_l^2)+\tfrac{1}{4}B(v_g^4-v_l^4)=0. \tag{3.13}$$

Equation (3.11) combined with Eq. (3.9) gives

$$At(v_g-v_l)+\tfrac{1}{3}B(v_g^3-v_l^3)=0. \tag{3.14}$$

Simultaneous solution of Eqs. (3.13) and (3.14) gives

$$v_g+v_l=0, \tag{3.15}$$

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[19] E. Mathias, C. A. Crommelin, H. K. Onnes, and J. C. Swallow, Commun. Phys. Lab. Univ. Leiden 172b (1925).

[20] H. K. Onnes and J. D. A. Boks, Commun. Phys. Lab. Univ. Leiden 170b (1924).

[21] E. C. Kerr, J. Chem. Phys. **26**, 511 (1957).

[22] J. R. Clement, J. K. Logan, and J. Gaffney, Phys. Rev. **100**, 743 (1955). See their "Note added in proof."

$$v_l = -(-3At/B)^{1/2} \quad \text{or} \quad v_l^2 = -3At/B, \tag{3.16}$$

and

$$v_g = +(-3At/B)^{1/2} \quad \text{or} \quad v_g^2 = -3At/B. \tag{3.17}$$

In other words, Landau and Lifshitz predict that along the coexistence curve, at temperatures near T_c, v_g and v_l should be equal and opposite, and that v_l^2 and v_g^2 should be equal and proportional to $-t = T_c - T$. Experimental confirmation of Eqs. (3.15), (3.16), and (3.17) could be taken as confirmation of Eq. (3.6) and the intervening arguments.

3.3. Experimental Test of the Landau-Lifshitz Theory

In order to make a careful check of the Landau-Lifshitz theory, we must examine in detail the measurements made near the critical point. The actual experimental points obtained within 250 mdeg of T_c are therefore listed in Table III, together with the corresponding t and v values, where $t = T - 5.1994$ and $v = V - 57.628$. Thirty-two of the vapor refractive index measurements, and 45 of the liquid refractive index measurements were within 250 mdeg of T_c. Note that all t values are negative, while the v_g values are positive and v_l values are negative.

Figure 3 is a plot of v_l^2 and v_g^2 against $-t$, which should give one straight line, of slope $3A/B$ if Eqs. (3.16) and (3.17) were valid. Note that neither the liquid nor the vapor branch is straight, down to 36 mdeg and 50 mdeg from the critical temperature. Thus, either the Landau-Lifshitz theory does not apply, or measurements within perhaps 5 mdeg of T_c are needed before we are "near" to the critical point in the sense of the Landau-Lifshitz theory.

However, the Landau-Lifshitz theory is in even more profound disagreement with the measurements as may be seen from Fig. 4. Figure 4 is a graph of $v_g + v_l$ against $-t$, which should be a horizontal straight line through the origin if Eq. (3.15) were true. The values of v_g and v_l used in Fig. 4 were read by graphical interpolation from the measurements listed in Table III. The experimental results are a clear contradiction of the Landau-Lifshitz prediction on this point. For this reason, their theory is an unsatisfactory representation of the properties of saturated He⁴ "near" its critical temperature. We shall now undertake a modification and extension of the Landau-Lifshitz theory to show that it *can* give a satisfactory representation of the properties of saturated He⁴ near its critical temperature. We shall do this without altering their basic assumptions as outlined in Eqs. (3.4), (3.5), and (3.6); but only by altering their subsequent arguments.

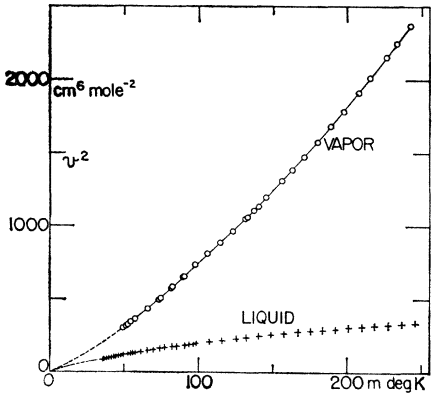

FIG. 3. Graph of v^2 against $-t$, where $v = V - 57.628$, and $t = T - 5.1994$. The Landau-Lifshitz theory predicts [see Eqs. (3.16) and (3.17)] one straight line of slope $3A/B$.

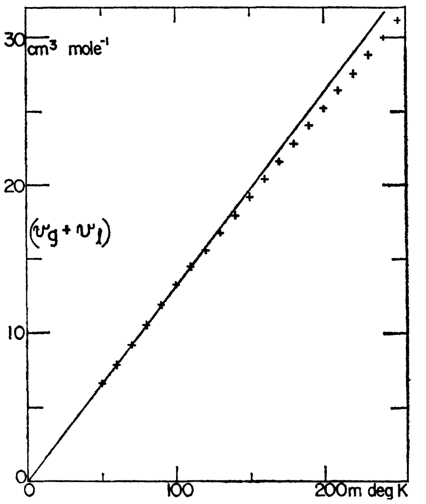

FIG. 4. Graphs of $(v_g + v_l)$ against $-t$. The Landau-Lifshitz theory predicts [see Eq. (3.15)] a horizontal straight line through the origin. The modified Landau-Lifshitz theory predicts [see Eq. (3.15)′] a straight line of slope C/B.

3.4. Modification and Extension of Landau-Lifshitz Theory

We now expand $(\partial P/\partial V)_T$, for small t and v, as

$$-(\partial P/\partial V)_T = At + Bv^2 + Ctv + Dt^2, \tag{3.7′}$$

instead[23] of only including the terms in t and v^2 as in Eq. (3.7). (We now number each modified equation with a prime to permit the same numbers as for equivalent equations in paragraph 3.2.) Integrating Eq. (3.7′) we get for the equation of any isotherm,

$$P = -Atv - \tfrac{1}{3}Bv^3 - \tfrac{1}{2}Ctv^2 - Dt^2v + f(t). \tag{3.9′}$$

For saturated liquid and saturated vapor in equilibrium along the coexistence curve we obtain the two conditions:

$$\tfrac{1}{2}(At + Dt^2)(v_g^2 - v_l^2) + \tfrac{1}{4}B(v_g^4 - v_l^4) + \tfrac{1}{3}Ct(v_g^3 - v_l^3) = 0, \tag{3.13′}$$

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[23] We are grateful to Dr. M. A. Preston for suggesting that additional second-order terms might be needed in this expansion.

and

$$(At+Dt^2)(v_g-v_l)+\tfrac{1}{3}B(v_g^3-v_l^3)+\tfrac{1}{2}Ct(v_g^2-v_l^2)=0. \quad (3.14')$$

Simultaneous solution of Eqs. (3.13′) and (3.14′) yields

$$v_g+v_l=-Ct/B, \quad (3.15')$$

$$v_l=-Ct/2B-[3t^2(C^2/4B^2-D/B)-3At/B]^{1/2}, \quad (3.16')$$

or

$$(v_l+Ct/2B)^2/-3t=-(C^2/4B^2-D/B)t+A/B,$$

and

$$v_g=-Ct/2B+[3t^2(C^24B^2-D/B)-3At/B]^{1/2}, \quad (3.17')$$

or

$$(v_g+Ct/2B)^2/-3t=-(C^2/4B^2-D/B)t+A/B.$$

Experimental confirmation of Eqs. (3.15′), (3.16′), and (3.17′) could be taken as confirmation of Eq. (3.6) and our intervening reasoning.

As a further extension of this modified Landau-Lifshitz theory we may use Eq. (3.16′) to calculate the coefficient of thermal expansion β_s of liquid He^4 along the saturated vapor pressure curve, and near the critical temperature, since

$$\beta_s=V_l^{-1}(\partial V_l/\partial T)_s=(V_c+v_l)^{-1}(\partial v_l/\partial t)_s.$$

The result is

$$\beta_s=\frac{-C/2B-[3C^2t^2/4B^2-3Dt^2/B-3At/B]^{-1/2}[3C^2t/4B^2-3Dt/B-3A/2B]}{V_c-Ct/2B-[3C^2t^2/4B^2-3Dt^2/B-3At/B]^{1/2}}. \quad (3.19)$$

3.5. Experimental Test of Modified Landau-Lifshitz Theory

Figure 4 shows clearly that there is now excellent agreement between Eq. (3.15′) and the interpolated experimental points, out to 110 mdeg from T_c. The straight line shown has been fitted by least squares so as to pass through the origin, and the seven interpolated (v_g+v_l) points out to 110 mdeg from T_c. This results in the value

$$C/B=(131.81\pm0.99)\text{ cm}^3\text{ mole}^{-1}\text{ deg}^{-1}, \quad (3.20)$$

where the usual assumption has been made that the abscissa is free of random error. The value ±0.99 is twice the standard deviation, which was also calculated by least squares.

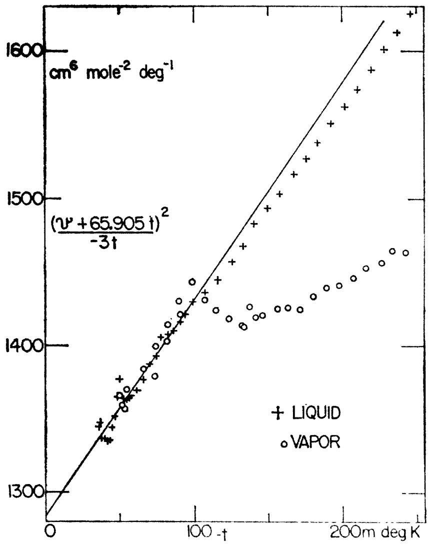

FIG. 5. Graph of $(v+65.905t)^2/(-3t)$ against $-t$. The modified Landau-Lifshitz theory predicts [see Eqs. (3.16′) and (3.17′)] a straight line of slope $(C^2/4B^2-D/B)$ and intercept A/B.

Figure 5 is a plot of the data of Table III using the second form of Eqs. (3.16′) and (3.17′), and incorporating the value of C/B obtained above. Here also there is satisfactory agreement between the modified Landau-Lifshitz theory and these experiments out to 110 mdeg from T_c for both the vapor and liquid branches. Beyond 110 mdeg below T_c, the liquid results then deviate slightly, and the vapor results deviate markedly from the straight-line agreement. The straight line shown in Fig. 5 has been fitted by least squares, using all points within 110 mdeg of T_c, again assuming that the abscissa is free of random error. From the intercept of this line we obtain

$$A/B=(1284.4\pm9.6)\text{ cm}^6\text{ mole}^{-2}\text{ deg}^{-1}, \quad (3.21)$$

and the slope

$$(C^2/4B^2-D/B)=(1474\pm102)\text{ cm}^6\text{ mole}^{-2}\text{ deg}^{-2}, \quad (3.22)$$

giving

$$D/B=(2870\pm170)\text{ cm}^6\text{ mole}^{-2}\text{ deg}^{-2}, \quad (3.23)$$

where standard deviations were calculated by least squares also and then doubled.

Our experiments have, therefore, shown that our modified Landau-Lifshitz theory of the properties of a substance "near" its critical point applies within 110 mdeg of T_c, or above $T/T_c=0.98$, for saturated He^4. We believe that this excellent agreement is clear evidence that $(\partial^3P/\partial V^3)_T$ is indeed negative at the critical point, as Landau and Lifshitz assumed. [See Eq. (3.6).]

3.6. The Value of $(\partial^3P/\partial V^3)_T$ at The Critical Point

The fact that saturated He^4 liquid is correctly represented by Eq. (3.16′), to within 2% of v_l even 200 mdeg below T_c (see Fig. 5), permits us to evaluate B. The present authors have measured the isothermal compressibility $k_T=-V^{-1}(\partial V/\partial P)_T$ of saturated He^4 liquid at 5.00°K, obtaining[13] $k_T=(6.5\pm1.0)\times10^{-7}$ cm^2 dyn^{-1}. Note that Eq. (3.7′) can now be rewritten

$$-(\partial P/\partial V)_T=(k_TV_l)^{-1}=(1284.4\pm9.6)Bt+Bv_l^2 \\ +(131.81\pm0.99)Btv_l+(2870\pm170)Bt^2. \quad (3.24)$$

At 5.00°K this may be solved for B, using the appropriate values for t and v_l from this research and the value of k_T from the earlier work.[13] The result is

$$B=(62\pm11) \text{ dyn mole}^3 \text{ cm}^{-11}, \quad (3.25)$$

which when combined with Eq. (3.8) gives

$$(\partial^3P/\partial V^3)_{T_c}=-(124\pm22) \text{ dyn mole}^3 \text{ cm}^{-11}. \quad (3.26)$$

In terms of the usual "reduced" parameters $P'=P/P_c$ and $V'=V/V_c$, where P_c is the critical pressure (1718 Torr[14]) and V_c is the critical molar volume (57.628±0.25 cm^3 mole^{-1}, this research), this gives finally

$$(\partial^3P'/\partial V'^3)_{T_c}=-(10.4\pm1.8). \quad (3.27)$$

It should be noticed that in this modified Landau-Lifshitz theory, only this third derivative is negative at T_c, whereas the first, second, fourth, and all higher derivatives are zero [see Eq. (3.7′)].

3.7. Comparison with Earlier Theories and Experiments

A substance obeying van der Waals' equation, which in reduced coordinates is given by[24]

$$(P'+3/V'^2)(3V'-1)=8T', \quad (3.28)$$

has

$$(\partial P'/\partial V')_{T_c}=0,\ (\partial^2P'/\partial V'^2)_{T_c}=0,\ (\partial^3P'/\partial V'^3)_{T_c}=-9, \\ (\partial^4P'/\partial V'^4)_{T_c}=+126,\ (\partial^5P'/\partial V'^5)=-1485, \text{etc.} \quad (3.29)$$

Note that the first, second, and third, but not higher derivatives of P' with respect to V' at T_c for a substance obeying the classical van der Waals' equation are in agreement with the present results.

Mayer and Harrison,[25] Rice,[8,26] and Zimm[27] have presented theories which suggest that the critical point is a "stop point" at which all derivatives of P with respect to V vanish. On such a picture, the critical isotherm in a PV diagram has a finite horizontal section, and the coexistence curve has a flat, not a rounded top. The present experimental results for He^4 are definitely in favor of the rounded top.

Previous experimental evidence on this point has always been ambiguous, since gravitational effects have tended to flatten the isotherms due to the high compressibility near T_c. A series of experiments on xenon,[28–33] in which the effect of cell depth was carefully investigated, still was not conclusive, since the smallest cell used was still 12 mm deep. Our present measurements are less subject to gravitational corrections, since the density of He^4 is about one-fifteenth the density of Xe, and our cell had always less than 4 mm of liquid over the horizontal "slice" being observed. We calculate that this would produce a fractional increase of V_l of less than 0.05%, or less than 0.3% in v_l in the least favorable case at 5.16°K. In making this calculation we assumed that the liquid compressibility increases by a factor of 20 between 5.00 and 5.16°K. This correction is so small we have ignored it.

Schmidt and Traube[34] have recently made optical measurements of the influence of gravitation on gradients of density in CO_2 near its critical point. The influence is 30 to 50 times larger than they calculate it should be using the "well-known isothermal pressure-density relation of carbon dioxide." Lorentzen's earlier[35] optical measurements of the density of CO_2 near its critical temperature led him to the conclusion that the observed density distributions in his apparatus were consistent with those expected if the isotherms were of the classical type. This only serves to re-emphasize that experiments very near T_c are often both difficult and ambiguous.

3.8. Calculation of the Properties of Saturated He^4 up to its Critical Temperature

The present experiments are in good agreement with the modified Landau-Lifshitz theory over a temperature range from about $0.98T_c$ to about $0.99T_c$. By the nature of the expansions used in Eq. (3.7′) and the ensuing arguments, we would expect increasingly good agreement as the critical temperature is approached. The numerical values of A, B, C, and D obtained above permit us to rewrite Eqs. (3.16′), (3.17′), and (3.19) as

$$v_g=-65.905t+[4422t^2-3853t]^{1/2}, \quad (3.30)$$

$$v_l=-65.905t-[4422t^2-3853t]^{1/2}, \quad (3.31)$$

and

$$\beta_s=\frac{-65.905-[4422t^2-3853t]^{-1/2}[4422t-1926.5]}{57.628-65.905t-[4422t^2-3853t]^{1/2}}. \quad (3.32)$$

These expressions are expected to be valid within about

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[24] See, e.g., reference 10, p. 269.

[25] J. E. Mayer and S. F. Harrison, J. Chem. Phys. **6**, 87 (1938).

[26] O. K. Rice, J. Chem. Phys. **15**, 314, 615 (1947).

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[35] H. L. Lorentzen, Acta. Chem. Scand. **7**, 1335 (1953).

TABLE IV. Properties near T_c calculated for saturated He^4 using Eqs. (3.30), (3.31), and (3.32).

$-t$ (mdeg)	v_g (cm^3 mole^{-1})	$-v_l$ (cm^3 mole^{-1})	β_s (deg^{-1})	$V_g/V_c=\rho_c/\rho_g$	$V_l/V_c=\rho_c/\rho_l$	T/T_c
0	0	0	∞	1.0	1.0	1.0
0.1	0.6277	0.6145	53.26	1.01089	0.98934	0.999981
1	2.0299	1.8981	16.46	1.03522	0.96706	0.999808
2	2.9110	2.6473	10.41	1.05051	0.95406	0.999615
5	4.8429	4.1838	6.845	1.08404	0.92740	0.999038
10	6.9018	5.5837	4.799	1.11977	0.90311	0.998077
20	10.197	7.5605	3.217	1.17694	0.86881	0.996153
30	12.912	8.9577	2.515	1.22406	0.84456	0.994230
40	15.332	10.060	2.097	1.26606	0.82543	0.992307
50	17.568	10.977	1.812	1.30485	0.80952	0.990384
60	19.674	11.765	1.603	1.34139	0.79584	0.988460
70	21.683	12.456	1.441	1.37626	0.78385	0.986537
80	23.618	13.073	1.311	1.40983	0.77315	0.984614
90	25.491	13.628	1.203	1.44234	0.76351	0.982690
100	27.315	14.134	1.111	1.47400	0.75473	0.980767
110	29.108	14.609	1.034	1.50509	0.74650	0.978844

110 mdeg of the critical temperature. Table IV shows the calculated values of v_g, v_l, β_s and the resulting $V_g/V_c=\rho_c/\rho_g$ and $V_l/V_c=\rho_c/\rho_l$ values from 110 mdeg below T_c up to T_c. If a theory of "corresponding states" applies, then the tabulated values of V_g/V_c and V_l/V_c as a function of T/T_c would be expected to be the same for all substances along their coexistence curves.

The v_g and v_l values of Table IV are, of course, in excellent agreement with the experimental values of Table III in the temperature interval common to both, since they were in effect derived from them. The values of β_s agree with the values of Table II where they overlap also. The correctness of the values of Table IV closer to T_c than measurements extended, depends entirely on the assumed applicability of the modified Landau-Lifshitz theory in this temperature range.