

helium similar to lambda transition in other substances, and does liquid helium present an idealized experimental model for all lambda transitions? At first glance one might think that liquid helium doesn't. I would, however, like to point out a sense in which liquid helium does present such a model; a sense that has been emphasized by Buckingham in private discussions.

When one goes from the normal liquid to the superfluid in liquid helium, one gets a change from a normal system to something which is suddenly ordered throughout the whole container. In this particular case, it is an ordering in the superfluid. The superfluid atom in one part of the container knows what is happening to the superfluid atom in a different part of the container, and how long that order depends only on the size of the container. One can disturb the system without destroying this order throughout the entire system provided the disturbances, for example rotational speeds, become smaller and smaller as the size of the system becomes larger and larger.

In the case of superconductors one has a quantized magnetic flux over supposedly the distance of the length of the wire in superconducting magnets that may be thousands of feet long. The length of the ordering depends only on the size of the superconducting loop and especially in the case of superconductors, exists in the presence of large quantities of impurities. Now there is different kind of order parameter in superconductors and that is the length of the correlation between electrons in a pair. This is only 10^{-4} cm, but the two electrons in a pair have equal and opposite momentum. The momentum of each pair is zero and therefore every pair throughout the whole superconductor has the same zero momentum. Thus there is a long-range order in momentum throughout the entire superconductor even though each pair is paired over 10^{-4} cm.

One doesn't have this momentum ordering in any other kinds of transition besides superconductors and liquid helium. But on the other hand, as Buckingham is going to point out at the end of the morning, one has a transition from a state where ordering exists within a small cluster in a particular part of a container, to a system where one has suddenly, for example in a liquid gas transition, order through-

out the entire container. Part of the atoms have one special density and they are all together in the container, and all the rest of the atoms have a different density. This sudden transition is to a state of order which depends only on the size of the container.

I want to close with this question. Is the lambda transition in liquid helium, except for the fact that one has a lambda line, an exact model for other transitions when long-range correlations are not cutoff in other experiment systems or theoretical models?

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The Specific Heat of He³ and He⁴ in the Neighborhood of Their Critical Points*

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Introduction

Recently Bagatskiĭ, Voronel', and Gusak [1] showed that the specific heat at constant volume of argon exhibited what appears to be a logarithmic singularity at the critical temperature (T_c) for measurements taken at a density near the critical density. This singular behavior is in sharp contrast to the predictions of the traditional view of this phase transition by Landau and Lifshitz [2]. However, the behavior is precisely that to be expected for the so-called "lattice gas" model for the liquid-gas transition. Lee and Yang [3] have shown that the partition function of a classical gas of particles moving on a discrete lattice with a repulsive force preventing double occupancy of any site, and a nearest neighbor attraction can be mapped precisely onto the partition function of an Ising model of a spin system in an external magnetic field. The specific heat for this Ising model in zero field exhibits a logarithmic singularity at the Curie point. The specific heat for the corresponding lattice gas on the critical isochore exhibits a logarithmic singularity at the critical point. The measurements on argon then indicate that for a *real* gas the specific heat behaves in a similar manner to that of a lattice gas. We have investigated this point further by studying the specific heat at constant volume (C_V) of both He³ and He⁴ at densities close to the critical density. We have done this for two main reasons. Firstly, to see whether the behavior observed for argon is also observed for helium, for which quantum effects should be important, and secondly, to investigate the detailed nature of the singularity in the pressure-density plane, not only *on* the critical density, but also in its immediate neighborhood. Yang and Yang [4] have conjectured that the quantum effects would reduce the magnitude of the singular contribution to the specific heat in helium. Our results confirm this view.

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Experimental Procedure

There are several practical advantages to using helium rather than another noble gas for C_V measurements near the critical point. The low heat capacity of metals at liquid helium temperature permits one to use a massive calorimeter of large surface to volume ratio. Thus the path for heat transfer through the helium may be kept short. In addition, more nearly adiabatic conditions and high resolution thermometry are most easily attained at liquid helium temperatures.

Our calorimeter was built of two OFHC copper parts. The helium was contained in the lower part in 50 slots. Each slot was 0.01 cm wide to facilitate good thermal contact between the calorimeter and the helium. The slots were made only 0.3 cm deep in an effort to minimize possible gravitational effects. [In contrast a thin stainless steel shell 10 cm high and 4 cm in diameter containing a magnetic stirrer was used for the work on argon [1, 5]. This construction was necessary to obtain a low ratio of heat capacity of the calorimeter to its contents while maintaining constant volume at the high critical pressure of argon.] The lower part of our calorimeter was wound with a constantan heater and had a carbon resistor clamped and cemented to it. The calorimeter was supported on nylon threads in an evacuated chamber. Thermal contact to the bath was made with a mechanical heat switch. A stainless steel filling capillary 5 in. in length and 0.006 in. I.D. led from the calorimeter to a needle valve. The dead volume was about 1/2 percent of the total volume of the calorimeter. The helium was admitted to the calorimeter via a Toeppler pump which was used to measure the volume of gas to an accuracy of about 0.2 percent.

One of the precautions taken was the measurement of the stray heat input to the calorimeter before and after each data point. The approach to temperature equilibrium of the calorimeter was observed after each heating interval. As T_c was

approached, the equilibrium time increased from a few seconds to several minutes and became one of the limiting factors in this measurement.

A $\frac{1}{10}$ W Ohmite carbon resistor of nominal resistance 560 Ω was used as a secondary thermometer. Its resistance was measured with a 100 c/s bridge using a lock-in amplifier. Temperature changes of about 2×10^{-6} °K at 5.2 °K and 1×10^{-6} °K at 3.3 °K could be observed. At the end of a run exchange gas was admitted to the vacuum space and the resistor was calibrated against the vapor pressure of the He⁴ bath using the T_{58} scale either from 4.2 to 2.9 °K or from 5.15 to 4.2 °K depending on whether He³ ($T_c = 3.3$ °K) or He⁴ ($T_c = 5.2$ °K) was being studied. A smooth resistance-temperature relation was fitted. Hence relative specific heat measurements near the critical points are not sensitive to errors either in the calibration or in the vapor pressure-temperature scale near T_c . Calibration was always done as the bath temperature was reduced. A hydrostatic head correction was made. All residuals were less than 8×10^{-4} °K from a fit to the Clement-Quinnell [6] formula and less than 3×10^{-4} °K from a four constant formula. Each run, T_c was tentatively defined as the temperature at which C_r for a density near ρ_c fell most abruptly. The final value of T_c was then chosen to give the best fit to

$$\frac{C_r}{R} = -a \log_e \left(\frac{T_c - T}{T_c} \right) + b \quad (1)$$

over the range 10^{-3} °K $< (T_c - T) < 10^{-1}$ °K. The adjustment was less than 3×10^{-4} °K. This value of T_c was also used for analyzing data taken during the same run at densities far from ρ_c . On four separate runs with He⁴, T_c was found to be 5.189 ± 0.001 °K. This is considerably below the value $T_c = 5.1994$ °K defined on the T_{58} temperature scale. A single run with He³ also yielded a value for T_c well below the accepted value.

Results

Figure 1 is a general view of the specific heats at the critical density of He³ and He⁴ at low temperatures [7]. We have indicated the temperature range covered by these measurements. In figure 2 we have plotted on both a linear and logarithmic scale measurements of C_r of He⁴ at a density within 0.5 percent of the critical density. In the two

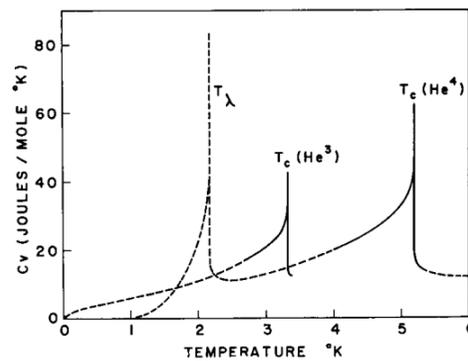


FIGURE 1. C_v of He³ and He⁴ at their respective critical densities is plotted as a function of temperature. The solid curves are the present work.

phase region below T_c , C_r exhibits logarithmic behavior.

In the one phase region above T_c two alternatives have been suggested: First, $C_r \propto \log(T - T_c)$ has been suggested by an exact calculation on a two dimensional Ising model [9], by C_r measurements on argon [1] and oxygen [8], and by velocity of sound measurements on helium four [10]. Second, $C_r \propto (T - T_c)^{-\alpha}$ for some small positive α (such as $\frac{1}{5}$) has been suggested by Fisher [11] on the basis of approximate calculations on a three dimensional Ising model and his analysis of the argon and oxygen data. We do not believe the present data permit one to distinguish between these two alternatives.

In figure 3 similar plots are given for He³ for a density of $0.985\rho_c$. Logarithmic behavior is again observed for $T < T_c$. The data for argon, oxygen [8], and both isotopes of helium expressed in the dimensionless form (1) are summarized in table 1. We see that the coefficient a decreases from Ar to He⁴ to He³ in agreement with the conjecture of Yang and Yang [4]. We note that the coefficient 0.62 for He⁴ is very close to that observed for the specific heat along the saturated vapor pressure curve near the λ -point of He⁴ (0.64) by Buckingham and Fairbank [12] and may have particular significance in explaining the quantum transition.

Yang and Yang [4] have pointed out that one may write in the two phase region,

$$C_r = -NT \left(\frac{d^2\mu}{dT^2} \right)_r + VT \left(\frac{d^2P}{dT^2} \right)_r \quad (2)$$

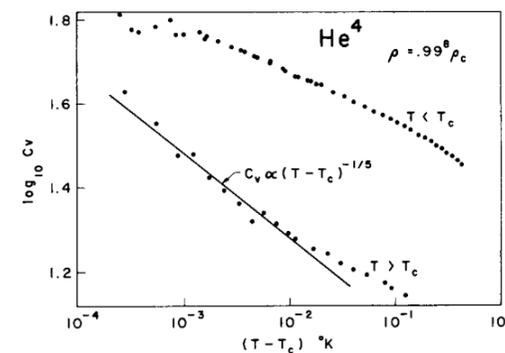
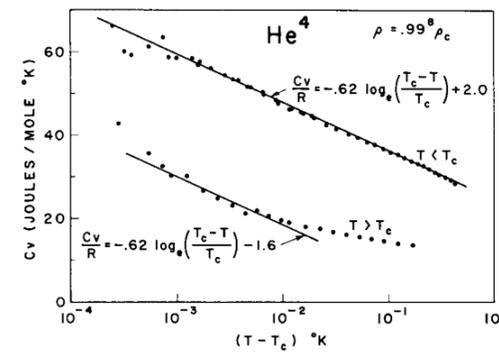


FIGURE 2. C_v of He⁴ is plotted against $|T - T_c|$ at a density of $0.99\rho_c$.

TABLE 1. Coefficients a and b of eq (1) for O₂, Ar, He⁴, and He³

Element	a	$b: T < T_c$
O ₂	2.4	10
Ar	1.8	8
He ⁴	0.62	2.0
He ³	.37	1.7

where μ is the chemical potential. They suggest that both $(d^2\mu/dT^2)_r$ and $(d^2P/dT^2)_r$ become infinite at T_c for a real gas, whereas $(d^2\mu/dT^2)_r = 0$ for the two dimensional Ising model. Figure 4 shows data on He⁴ taken at the densities $0.96\rho_c$ and $1.07\rho_c$. T_c for these plots was chosen from data (not shown) taken during the same run at $0.99\rho_c$. The two phase region (lower temperatures) is the upper branch of each curve. The difference between the upper branches in this region is proportional to $(d^2P/dT^2)_r$. It is clear that $(d^2P/dT^2)_r$

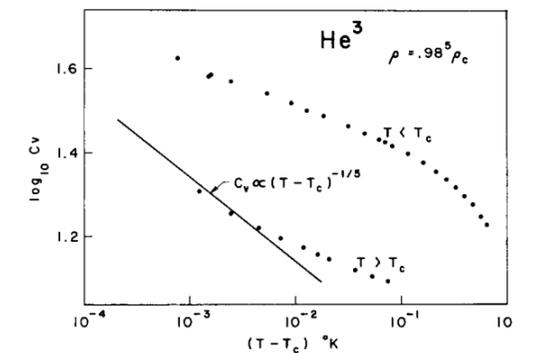
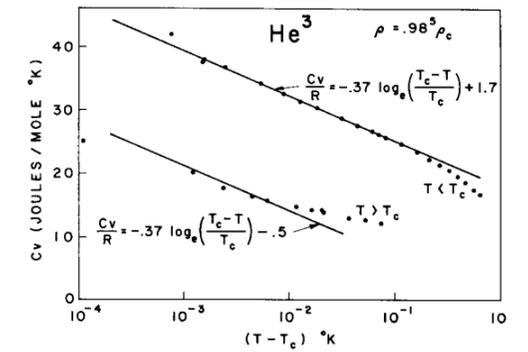


FIGURE 3. C_v of He³ is plotted against $|T - T_c|$ at a density of $0.98\rho_c$.

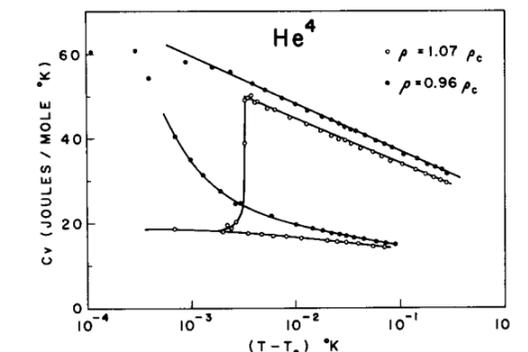


FIGURE 4. C_v of He⁴ is plotted against $|T - T_c|$ at densities of $1.07\rho_c$ and $0.96\rho_c$.

does not approach zero as T approaches T_c . A similar plot with the ordinate heat capacity/volume rather than heat capacity/mole indicates that $(d^2\mu/dT^2)_r$ also does not approach zero as T approaches T_c . This is consistent with the suggestion of Yang and Yang.

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 He⁴

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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 0.99 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 He⁴ would extrapolate linearly to $1.1 \rho_c$ at $T=0$. The symmetry of the coexistence curve is obscured on a plot of sat-

urated 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

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

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

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

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 $n = \frac{1}{\beta}$), against T , we need not know T_c or ρ_c or V_c and in fact may determine T_c by such plots.
- Figure 1 shows how plots of X^2 (or $\beta = 1/2$), and X^3 (or $\beta = 1/3$), appear for He⁴ 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_p at the critical point, would imply a coexistence curve whose asymptotic form as $T \rightarrow T_c$ is given by

$$\frac{X^2}{1 - \ln X} = at \quad (3)$$

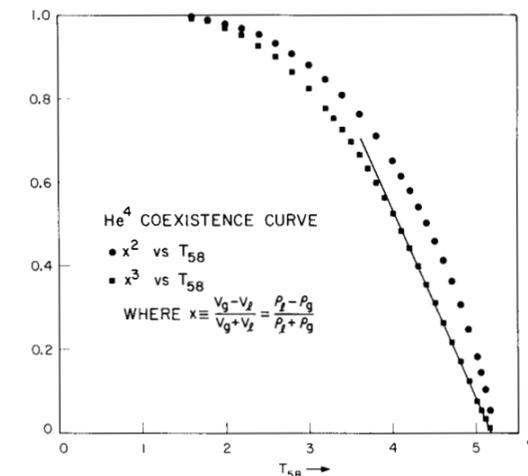


FIGURE 1. Temperature dependence of X^2 and X^3 for He⁴. X^3 is linear above 0.8 T_c .

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 He⁴ 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 He⁴ on the 1958 He⁴ 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

$$X = \frac{2V_g}{V_g + V_l} - 1, \quad \text{or} \quad X = 1 - \frac{2V_l}{V_g + V_l} \quad (4)$$

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 He⁴ for all points within 250 mdeg of 5.1994 °K. The straight line drawn on the plot of X^2 is a least-