

The Logarithmic Anomaly in the Pressure Coefficient of Helium Close to the Lambda Line*

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Introduction

Several investigators have reported logarithmic anomalies in the heat capacity [1], thermal expansion [2-6], and pressure coefficient [7-8] of liquid helium in the neighborhood of the lambda transition. Unfortunately, all of these experiments except those of Lounasmaa [7] and of Lounasmaa and Kaunisto [8] were done on the vapor pressure curve, where the anomalous behavior is confined to a very narrow temperature interval. The experiments of Lounasmaa and Kaunisto [8] at various pressures along the lambda curve show that the anomalous behavior is spread out over a larger temperature interval at higher pressures. Consequently, we have measured the pressure coefficient, $\beta_r = (\partial P / \partial T)_r$, of liquid helium along the isochore which crosses the lambda line at the melting curve. This intersection is called the upper lambda point (T_λ , P_λ).

Experimental Procedure

The apparatus used in these experiments is essentially the same as that used by Lounasmaa [7]. Therefore, it will be described only briefly here. It is shown schematically in figure 1.

Helium gas was purified in a trap (not shown) immersed in liquid helium, and was condensed into the piezometer G through the low-temperature valve A, which was kept closed during measurements. G was isolated from the liquid helium bath by the vacuum case B. Its temperature was controlled by the heater F and by pumping on liquid helium in E.

Changes in the pressure on the sample were measured by the oil manometer K and read with a cathetometer to 0.01 mm, which corresponded to about a millionth of an atmosphere. The absolute pressure was read to 0.01 atm on the Bourdon gage P, which was calibrated against a dead weight tester.

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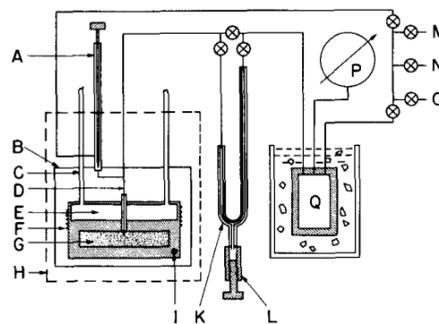


FIGURE 1. Schematic drawing of the apparatus. (A) needle valve; (B) vacuum case; (C) pumping and vapor pressure tubes (2) for (E); (D) 30 percent Cu-Ni capillary tubing, 0.1 mm ID; (E) temperature and vapor pressure compartment; (F) heater; (G) piezometer packed with fine copper wire for rapid equilibrium (volume 39.83 cm³ at 1.76 °K, height 10 mm to keep hydrostatic pressure differences small); (H) dashed lines enclose space immersed in liquid helium bath; (I) germanium thermometer; (K) differential oil manometer, 0.060 in. ID constant bore glass capillary (left arm 40 cm long, right arm 90 cm long); (L) oil reservoir and leveling device filled with Apiezon B oil; (M) to He⁴ supply tank and purifier; (N) to pump; (O) to atmosphere; (P) 25-cm dial test gauge calibrated against a dead weight tester; (Q) ballast volume (1461 cm³) for balancing the right-hand side of K, held at constant temperature by an ice bath; & needle valves.

Small changes in the sample density could be made by raising the oil in the left limb of the manometer, forcing gas to condense into G. A change of 0.01 mm in the oil level caused a change of 2×10^{-9} g/cm³ in the density.

Temperatures were measured with a germanium resistance thermometer in a potentiometer circuit using a double potentiometer. At the upper lambda point the thermometer resistance was 1483 Ω , and its sensitivity was 636 microdegrees per ohm. With 50 μ A of measuring current, the resistance could be measured with a precision of 0.002 Ω . The measuring current heated the thermometer above the cell temperature; but this effect was reproducible, and the same measuring current was used in calibrating the thermometer. It was calibrated against the vapor pressure of helium in E on the T_{58} scale [9], using a tube separate from the pumping tube. The change in the thermometer resistance at the upper lambda point after warming to room temperature and recooling corresponded to a temperature change of less than 10^{-4} °K. All

temperatures were referred to the upper lambda point in order to correct for small changes in the thermometer or the measuring circuit.

Points on the lambda curve were found by warming the sample slowly at constant volume. Because of the large change in thermal conductivity at the lambda transition, the heating curve showed a sharp break, which could be located to within a micro-degree. The sample was held at this temperature until equilibrium was established before reading the manometer. Then the density was changed slightly by raising the oil in the left limb of the manometer, and the new lambda point was found. The break in the heating curve was especially sharp with solid present in the cell, because the heat of melting increased the apparent heat capacity. Thus the upper lambda point could be determined directly, rather than as the intersection of two independently measured curves.

The pressure coefficient $\beta_r = (\partial P / \partial T)_r$ was determined by keeping the oil level in the left limb of the manometer constant and measuring the height of oil in the right limb at successively lower temperatures. After the lambda point was passed, as judged by the thermal response, the temperature was raised slowly in order to determine the lambda point exactly.

Results

The pressure coefficient $\beta_r = (\partial P / \partial T)_r$ was measured along an isochore which crossed the lambda line very close to T_λ . Results are shown in figure 2, plotted against $\log_{10}(T - T_\lambda)$. The equation of the line is

$$\beta_r = 9.39 + 7.69 \log_{10}(T - T_\lambda) \text{ atm/}^\circ\text{K}, \quad (1)$$

where T_λ is the lambda transition temperature for the isochore. This graph contains points taken on two different cooling runs. The lambda point for one run was 15 μ deg below T_λ , and for the other it was 5 μ deg above. These small differences are not regarded as significant, but the observed lambda point was used in each run in plotting $T - T_\lambda$. Since this isochore meets the melting curve at the lambda point, the measurements in figure 2 refer to He I. One point was measured in supercooled He II, where β_r was found to be -27.6 at $T - T_\lambda = -1.08 \times 10^{-5}$. This point is not plotted in figure 2, but it is approximately the value to be expected for $T - T_\lambda = 1.08 \times 10^{-5}$.

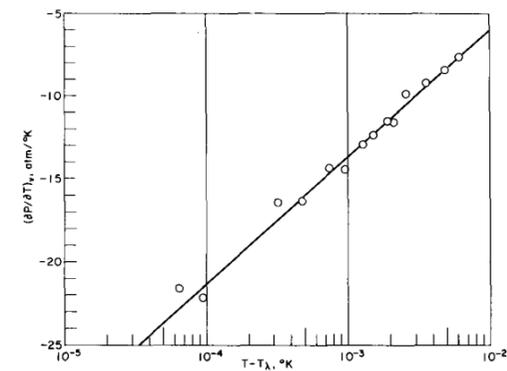


FIGURE 2. Pressure coefficient $\beta_r = (\partial P / \partial T)_r$ of He I along the isochore $V = V(T_\lambda)$. Equation of line: $\beta_r = 9.39 + 7.69 \log_{10}(T - T_\lambda) \text{ atm/}^\circ\text{K}$.

In connection with these experiments we have measured the change of pressure and density with temperature along the lambda line. These experiments, which are reported in detail elsewhere [10], can be summarized by the equations

$$\left(\frac{dP}{dT}\right)_\lambda = -55.54 - 96(T_\lambda - T_\lambda) \text{ atm/}^\circ\text{K} \quad (2)$$

$$\left(\frac{d\rho}{dT}\right)_\lambda = -43.7 - 230(T_\lambda - T_\lambda) \text{ mg/cm}^3 \text{ }^\circ\text{K} \quad (3)$$

$$\left(\frac{d\rho}{dP}\right)_\lambda = 0.7868 + 2.8(T_\lambda - T_\lambda) \text{ mg/cm}^3 \text{ atm}, \quad (4)$$

where T_λ is the lambda temperature for the pressure P and density ρ , and T_λ is the temperature of the upper lambda point, 1.7633 °K.

Discussion

The logarithmic dependence of β_r on $T - T_\lambda$ is similar to that found by Lounasmaa [7] and by Lounasmaa and Kaunisto [8] at lower densities, and is consistent with their observation that the two constants in eq (1) both increase with increasing density. The measurements of Lounasmaa at 13 atm pressure ($T_\lambda = 2.023$ °K) are of particular interest since he found that β_r fitted an equation of the same form as (1) to within 2×10^{-5} °K of the lambda point for both He I and He II, the constants being different for the two cases. In the same paper Lounasmaa presents measurements of the compressibility $\kappa_T = \rho^{-1}(\partial \rho / \partial P)_T$ along an isotherm

passing through the same lambda point. He finds no evidence for anything but a slow linear variation of κ_T with $P - P_\lambda$ to within 10^{-3} atm from the lambda line (corresponding to 2×10^{-5} °K for $T - T_\lambda$) and a small discontinuity at the lambda point.

Since an isochore cannot cross the lambda line with a slope greater in magnitude than that of the lambda line, $(dP/dT)_\lambda$ is a lower bound for β_r (both are negative); so eq (1) must break down for some small value of $T - T_\lambda$. On the other hand, there is no such restriction on κ_T . In fact, Buckingham and Fairbank [11] have shown that if C_p becomes infinite at the lambda line, κ_T must also. The experiments seem to suggest that β_r becomes infinite and κ_T does not. This situation can be examined more closely with the help of the equation

$$\beta_r = (dP/dT)_\lambda - (\rho\kappa_T)^{-1}(d\rho/dT)_\lambda, \quad (5)$$

which should apply to any point close enough to the lambda line that β_r and κ_T depend only on the distance from the lambda line. Solving for κ_T we have

$$\kappa_T = \frac{(d\rho/dT)_\lambda}{(dP/dT)_\lambda - \beta_r}. \quad (6)$$

This equation shows that κ_T will not vary much until β_r becomes nearly equal to $(dP/dT)_\lambda$. If β_r becomes equal to $(dP/dT)_\lambda$, as must happen if C_p becomes infinite, then κ_T becomes infinite. If β_r were to exceed $(dP/dT)_\lambda$ in magnitude, κ_T would become negative and a first-order phase transformation would ensue. Equation (6) has been used to calculate κ_T along the isotherm studied by Lounasmaa, [7] using his equation for β_r and Lounasmaa and Kaunisto's [8] data for $(dP/dT)_\lambda$ and $(d\rho/dT)_\lambda$. These calculated values are plotted as the solid line in the lower part of figure 3. The circles are Lounasmaa's measured points and the dashed lines are the ones he drew through his data. Although the agreement is not very good, it is apparent that he could not have expected to see an anomaly at the pressure resolution he attained. A similar calculation using the data reported in this paper is shown in the upper part of figure 3. The much larger change in κ_T results from the larger magnitude of β_r and the smaller magnitude of $(dP/dT)_\lambda$ at the higher pressure.

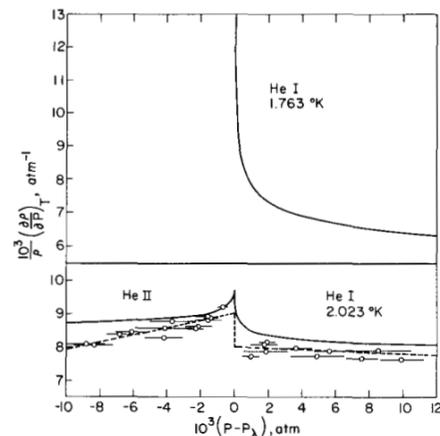


FIGURE 3. Compressibility $\kappa_T = \rho^{-1}(\partial\rho/\partial P)_T$ of liquid helium. Open circles: Points measured by Lounasmaa [7]. Dashed lines: lines drawn by Lounasmaa through his points. Solid lines: calculated from logarithmic relations for β_r .

We plan to measure κ_T near the upper lambda point in the near future.

To investigate the nature of the lambda transformation, it is very important to study how κ_T goes to infinity and how β_r approaches $(dP/dT)_\lambda$ (if indeed they do) at temperatures so close to T_λ that eq (1) breaks down. This is probably only possible near the upper lambda point. In Lounasmaa's experiment at 13 atm the logarithmic relation predicts that, for $T - T_\lambda = 10^{-6}$, β_r will be less than a fourth of $(dP/dT)_\lambda$. In the present experiment, β_r was a fourth of $(dP/dT)_\lambda$ at $T - T_\lambda = 10^{-3}$; and if eq (1) remains valid, β_r will be two-thirds of $(dP/dT)_\lambda$ at $T - T_\lambda = 10^{-6}$. We are at present engaged in extending the measurements to smaller temperature intervals.

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The Nature of the Cooperative Transition

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1. Introduction

A thermodynamic singularity arises in statistical mechanics only in the limit $N \rightarrow \infty$, where N is the number of atoms in the system. By regarding an infinite system as made up of an infinite number of large but finite parts, called cells, with M atoms each, the singularity is seen to arise from the interactions between the cells—which for M large correspond to surface interactions, since the interatomic forces are short-ranged. For the same reason interactions between other than nearest neighbor cells are zero. Thus any thermodynamic singularity may be regarded as an example of a generalized near-neighbor lattice problem.

For very large M , one might expect the approximation of neglecting the surface interactions between cells to be a very good one since it corresponds to the neglect of only a fraction $1/M^{1/3}$ of all interactions. Indeed for a homogeneous stable thermodynamic system the approximation is extremely good. However it is not good near a singularity or in a two phase region, since the correct partition function for the system is then singular, whereas the exact solution of the zero-interaction-between-cells problem results in some power of the partition function for a finite system of M atoms, which is nonsingular.

It is easy to see the nature of the solutions in the two phase region. The correct solution describes a system with two phases separated in space by some minimum-area boundary. In the zero-inter-

action solution, each cell is properly described as a piece of one or other of the phases, but in the absence of the interaction these are mixed at random. The qualitative effect of the interactions between cells is thus the segregation or phase separation of the cells. The entropy associated with this separation is constant (depending on composition) in the two phase region and is, of course, zero in the one phase region—except for a very small temperature interval in the immediate neighborhood of the transition temperature.

At first sight the very small magnitude of the mixing entropy—associated with but one degree of freedom out of M , would suggest that it is entirely negligible. However the extreme smallness of the temperature interval ($\sim 1/M$)^{1/3} over which it can change means that, in some circumstances, it may be far from negligible—indeed accounting for the asymptotic form of the thermodynamic singularity. An example is the ordinary first order transition from gas to liquid phase, as mentioned below. The case of the critical transition is much more subtle, but by incorporating the assumption that the pair correlation function is just a function of r/r_0 where r_0 is the correlation length, we show below that a system, with finite range forces only, ostensibly possessing a "classical" van der Waals critical point would in fact have to have a logarithmic singularity in its specific heat. The discussion that follows is not intended as a "theory of the critical point" but as a preliminary account of the viewpoint that is being developed.