equilibrium state and the electron crystal, since both are electrically neutral on a macroscopic scale.<sup>9</sup>

## INTERNAL AND FREE ENERGIES

The inequality (6) for the internal energy u follows from (5) and the general result<sup>10</sup>:

$$u = \frac{3}{2}k_{B}T + \frac{1}{2\Omega}\sum_{\mathbf{k}\neq 0}\frac{4\pi e^{2}}{k^{2}}(S(\mathbf{k}) - 1) \xrightarrow[N/V \to \infty]{N/V \to \infty} \frac{3}{2}k_{B}T + \frac{1}{2}\int \frac{d\mathbf{k}}{(2\pi)^{3}}\frac{4\pi e^{2}}{k^{2}}(S(\mathbf{k}) - 1). \quad (35)$$

<sup>9</sup> Although it is highly implausible that an equilibrium state violating (34) could have lower free energy than a uniform or crystalline state, we are not aware of a proof of this. <sup>10</sup> See, for example, D. Pines and P. Nozieres, *The Theory of* 

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# Effect of the Gravitational Field on the Superfluid Transition in He<sup>4</sup>

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It is shown experimentally that in a liquid helium sample of finite height, He II and He I coexist in thermodynamic equilibrium over a finite temperature range. This is contrary to a recent theoretical prediction. Observations made by noting the position of the boundary between the phases of high and low thermal conductivity as a function of temperature are quantitatively confirmed by high-resolution heat-capacity measurements near the transition region. The rate of movement with temperature of the interface between the two phases yields a slope for the transition line of  $113.9 \pm 4.6$  atm/°K at saturated vapor pressure, in quantitative agreement with recent direct measurements.

# INTRODUCTION

**I**<sup>T</sup> is the purpose of this paper to present experimental evidence which demonstrates that in the gravitational field He<sup>4</sup> II and He<sup>4</sup> I can exist as two phases in equilibrium with each other, although the transition between them is not of first order.<sup>1,2</sup> In homogeneous samples, the coexistence of two phases is possible only if the transition is of first order. However, for inhomogeneous samples, such as tall liquid samples, where the pressure is not constant, it is possible in principle to establish an equilibrium phase boundary even if the transition between the phases is of higher order.<sup>3</sup> Although the experimental demonstration of the existence of such a phase boundary in a system with a higher order transition is of some interest for its own sake, the case of the superfluid transition in helium is of particular interest at the present because it has been predicted<sup>4</sup> on the basis of the phenomenological theory of superfluidity<sup>5</sup> that coexistence of He<sup>4</sup> II and He<sup>4</sup> I is impossible even in the gravitational field. Before proceeding to the experimental section of this paper, a brief discussion of the classically expected effect and of the theoretical predictions will be given.

Placing the lower bound (5) for  $S(\mathbf{k})$  in (35) and evaluat-

Finally (7) follows routinely from (6) by noting that

 $\partial f/\partial e^2 = (1/e^2)u$ ,

replacing the right side of (36) by its lower bound for each  $e^2$ , and integrating with respect to  $e^2$  from zero

Quantum Liquids I (W. A. Benjamin, Inc., New York, 1966), equation on the top of p. 297 (but note that a factor of  $1/\Omega$  is missing on the right). The argument works equally well for the classical internal energy in thermal equilibrium and does not

assume a spatially homogeneous equilibrium state. The proof is routine for impenetrable-wall boundary conditions, following directly from the explicit form (26) for U. The legitimacy of the

operations leading to (35) is somewhat less clear when periodic boundary conditions are used, but the result is widely accepted.

to the actual value of the electronic charge.

ing the integral leads directly to (6).

In a liquid sample of height H, the pressure at the bottom is larger than at the top by

$$\Delta P = \rho g H \,, \tag{1}$$

where  $\rho$  is the density and g the gravitational acceleration. In liquid helium, the temperature derivative of the transition pressure is negative. Therefore, it is to be expected that the transition temperature at the bottom  $(T_{\lambda}^{H})$  is lower than at the liquid surface  $(T_{\lambda}^{S})$  by

$$\Delta T_{\lambda} = \rho g H (dT/dP)_{\lambda} = a H.$$
<sup>(2)</sup>

(36)

<sup>&</sup>lt;sup>1</sup>G. F. Kellers, thesis, Duke University, 1960 (unpublished); W. M. Fairbank, M. J. Buckingham, and C. F. Kellers, in *Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisc., 1958), p. 50. <sup>2</sup>G. Ahlers, Phys. Rev. 164, 259 (1967). <sup>3</sup>A. B. Pippard, *Elements of Classical Thermodynamics* (Cambridge University Press, New York, 1964), p. 155.

<sup>&</sup>lt;sup>4</sup> L. V. Kiknadze, Tu. G. Mamaladze, and O. D. Cheishvili, Zh. Eksperim. i Teor. Fiz., Pis'ma v Redaktsiyu 3, 305 (1966) [English transl.: Soviet Phys.—JETP Letters 3, 197 (1966)]. <sup>5</sup> V. L. Ginzburg and L. P. Pitaevskii, Zh. Eksperim. i Teor. Fiz. 34, 1240 (1958), [English transl.: Soviet Phys.—JETP 34, 858 (1969)].

<sup>(1958) ].</sup> 

Over the small pressure range involved here,  $\rho$  and  $(dT/dP)_{\lambda}$  are taken as constant, and Eq. (2) defines a. Using the data by Kierstead<sup>6</sup> and Kerr and Taylor,<sup>7</sup> one obtains  $a = (1.273 \pm 0.003) \times 10^{-6}$  K/cm at saturated vapor pressure. A sample of liquid helium at a temperature which satisfies

$$T_{\lambda}^{s} > T > (T_{\lambda}^{s} - aH) \tag{3}$$

therefore should have a phase boundary between He<sup>4</sup> I (below this boundary) and He<sup>4</sup> II (above this boundary<sup>8</sup>) at a depth h given by

$$h = (T_{\lambda}^{s} - T)/a. \tag{4}$$

In contrast to this classical situation, it was predicted by Kiknadze et al.<sup>4,9</sup> on the basis of the Ginzburg-Pitaevskii (GP) equation for the phenomenological theory of superfluidity<sup>5</sup> that even in a gravitational field there exists a unique transition temperature which is independent of the height of the sample. According to this theory, the virtual normal fluid which should form at  $T_{\lambda}^{H}$  at the bottom of the sample will remain superfluid until a temperature is reached at which classically the interface would have moved within  $3 \times 10^{-3}$  cm of the surface. At this unique temperature, the entire sample is predicted to change from superfluid to normal fluid without there ever having been coexistence of the two phases. However, the conclusions drawn by Kiknadze et  $al.^4$  are valid only when a certain specific choice is made for a parameter in the theory.<sup>10</sup> It was pointed out by Hohenberg<sup>11</sup> that the choice made by Kiknadze et al. is not within the spirit of the GP theory.<sup>12</sup> If the parameter is chosen within the spirit of this theory, then essentially the classical situation is predicted. However, since it is known that the GP equation does not predict

<sup>9</sup> These calculations have not been carried out with due con-sideration for the boundary conditions of a real sample, and only general properties of the solution for the one-dimensional equation (infinitely wide sample) have been predicted. However, it appears unlikely that the boundaries of a real macroscopic sample, at which the order parameter must vanish, will seriously affect the theoretical predictions (see Ref. 11). <sup>10</sup> Equation 2 of Ref. 4.

<sup>11</sup> P. C. Hohenberg (private communication). <sup>12</sup> The parameter in question is the coefficient  $\alpha$  of the linear term in the GP equation (Eq. 1 of Ref. 4). It was chosen to be equal to zero by Kiknadze et al. for the virtual normal fluid. Within the general theory of second order transitions due to Landau [L. Landau, Phys. Z. Sowjetunion 11, 26 (1937)] there is no reason for this choice. In fact, it can be shown by general Is no reason for this choice. In fact, it can be shown by generative arguments [L. Landau, Phys. Z. Sowjetunion 11, 26 (1937); L. Landau and E. M. Lifshitz, *Statistical Physics*, translated by E. Peierls and R. F. Peierls (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958), p. 435] that  $\alpha > 0$  if  $T > T_{\lambda}$ ,  $\alpha = 0$  at  $T_{\lambda}$  and  $\alpha < 0$  if  $T < T_{\lambda}$ . Thus the simplest choice is  $\alpha = \alpha'(T - T_{\lambda})$ .  $\alpha' > 0$  above as well as below the transition. The GP equation then predicts the existence of a transition region between He II and He I over a vertical length of order  $10^{-3}$  cm (see Ref. 11).

correctly certain other properties of liquid helium,<sup>13</sup> experimental verification of the coexistence of He<sup>4</sup> II and He<sup>4</sup> I under the influence of gravity is very desirable. The results reported in this paper agree with classical expectations. They do not reveal a unique transition temperature, but rather confirm the existence of a two-phase system over the expected temperature range. A brief report on part of this work was given elsewhere.14

## **EXPERIMENTAL**

## **General Considerations**

The virtually discontinuous change in the thermal conductivity of liquid helium at the superfluid transition temperature can be used to distinguish between the two situations considered in the Introduction. To a first approximation He<sup>4</sup> I does not conduct heat, and He<sup>4</sup> II is a perfect conductor. Consider a long, vertical sample of liquid helium in a thermally nonconducting container, and assume that the temperature can be monitored by thermometers at two different heights. Let this sample be warmed through the transition with a heater at the top. If a two-phase system exists over a finite temperature range, then the lower thermometer will warm up only until the interface has passed it. Thereafter, heat flow to it will be blocked by He<sup>4</sup> I. The top thermometer will continue to warm for a temperature increment given by Eq. (2), and then remain at constant temperature. However, if a two-phase system does not exist, both thermometers will indicate the same constant transition temperature starting at the same time. Although this method is based on the determination of the discontinuity of a transport property and employs heat flow, it is possible with sufficient control over the thermal environment to keep the heat current lower than  $10^{-7}$  W/cm<sup>2</sup> and temperature drifts smaller than 10<sup>-6°</sup>K/min. Under these circumstances, it can be assumed that the superfluid fraction of the system and any normal fluid in the immediate vicinity of an interface are virtually in their thermodynamic equilibrium states. Investigations with negligible heat current are also necessary for comparison with the theoretical work,<sup>4</sup> since the calculations pertain only to a system in which there is no heat flow.<sup>15</sup>

The observations made by the technique described above can be confirmed by very high-resolution heatcapacity measurements for the superfluid phase in the

<sup>&</sup>lt;sup>6</sup> H. A. Kierstead, Phys. Rev. **162**, 153 (1967). <sup>7</sup> E. C. Kerr and R. D. Taylor, Ann. Phys. (N. Y.) **26**, 292 (1964).

<sup>&</sup>lt;sup>8</sup> This situation should not be confused with what apparently has been observed by some experimentalists when liquid helium was transferred into a cryostat which previously contained some superfluid helium. Under these conditions it seems possible to have He<sup>4</sup> II at the bottom. However, this is a nonequilibrium state.

<sup>&</sup>lt;sup>13</sup> The GP equation yields a linear specific heat immediately below  $T_{\lambda}$  with a finite discontinuity at  $T_{\lambda}$ , whereas the specific heat in liquid helium is known to exhibit a logarithmic singularity at  $T_{\lambda}$ In Iquid Helium is known to exhibit a logarithmic singularity at  $T_{\lambda}$ (see Ref. 1). The GP equation predicts a superfluid density  $\rho_{\bullet}$ which varies linearly with  $T_{\lambda} - T$  immediately below  $T_{\lambda}$ , whereas  $\rho_{\bullet}$  is known to vary as  $(T_{\lambda} - T)^{2/8}$  [J. R. Clow and John D. Reppy, Phys. Rev. Letters 16, 887 (1966); J. A.Tyson and D. H. Douglass, Jr., *ibid.* 17, 472 (1966)]. <sup>14</sup> G. Ahlers, Bull. Am. Phys. Soc. 12, 1063 (1967). <sup>15</sup> The GP accuration was investigated (see Bef. 4) or before the

<sup>&</sup>lt;sup>15</sup> The GP equation was investigated (see Ref. 4) only for real order parameters, i.e., constant phase and thus zero superfluid velocity.

transition region. If a two-phase temperature range exists, then the heat capacity of the superfluid alone should decrease to zero continuously, over the temperature interval predicted by Eq. (2), because the quantity of superfluid decreases to zero. A unique transition temperature would imply that the heat capacity of the superfluid phase should discontinuously drop to zero because the superfluid phase would disappear discontinuously.

Since both of the proposed experimental techniques require extreme temperature stability, it was attempted to design the experiment so that it could be carried out under rigidly controlled thermal conditions. This aim was accomplished by using a permanently sealed sample to prevent heat transfer by superfluid flow through a capillary, by exercising careful control over conduction heat leaks, and by virtually eliminating radiation heat leaks. The temperature of the resulting system could be stabilized within  $10^{-6^{\circ}}$ K for hours, and the lower limit for heat flow in the sample was determined almost entirely by the thermometer power of  $10^{-8}$  to  $10^{-7}$  W.

The use of a sealed sample container requires that the thermometers have to be mounted on the outside rather than in the liquid, and that the sample diameter is not too large. Both of these limitations are caused by the pressure of about 1 kbar which exists in the sample when it is at room temperature.

The problem associated with mounting the thermometers on the outside was readily overcome by using walls of low thermal conductivity (stainless steel). The time constant for radial heat transfer to the thermometers is then still very small (of order  $10^{-2}$  sec) because of the short path through the walls and the relatively low heat capacity of the walls. For longitudinal heat transfer, the time constant is also very small when He II is adjacent to the thermometers. Thus, rapid thermometer response can be expected in the superfluid region. This was confirmed experimentally. However, when He I is adjacent to the thermometers, the longitudinal time constant becomes quite long even for short distances because it is now determined by the conductivity of the stainless steel and the He I, both of which are small, and the very large heat capacity of He I. This was also confirmed experimentally.

The small diameter of the container may cast very slight suspicion upon comparison of the experimental results with the theory.<sup>4,9</sup> Although it is not immediately obvious what, if any, effect the diameter of the container has on the theoretical predictions, it does not seem likely that the qualitative conclusions from the theory will be different for a sample of 1 cm diam than for an infinitely wide sample.<sup>11</sup>

#### Sample

The sample container is shown in Fig. 1. It consists of a stainless steel tube, 0.97 cm o.d. and 0.71 cm i.d.,



FIG. 1. Sample chamber. The insert shows the method of attachment of the top thermometer.

silver soldered into two copper end pieces. A stainless steel capillary (0.08 cm o.d. and 0.03 cm i.d.) was silver soldered into the top end piece. The container was filled at 2.5°K with He<sup>4</sup> which had been passed through a charcoal trap at 78°K. The room-temperature end of the capillary was then pinched off with a modified bolt cutter between two surfaces of semicircular cross section with a diameter of 0.6 cm,<sup>16</sup> and a small copper cup was silver soldered over the seal. After warming to room temperature, the pressure is calculated to be about 1 kbar. The capillary was wound around the top end piece. The amount of sample was determined by weighing and was found to be 0.41 mole. One thermometer was mounted on the bottom end piece, and a second thermometer was thermally attached to a copper wire which had been silver soldered to the stainless steel tube. The width of the wire and silver solder on the tube

<sup>&</sup>lt;sup>16</sup> Such a seal by itself bursts at a pressure of about 0.5 kbar (this same limit also applies to copper capillaries). Failure does not occur at the cold weld, but rather just beyond the cold weld where the wall thickness has become very small. Therefore, the copper cup was silver soldered over the seal. It was observed on other occasions that silver soldering was possible only with internal pressures of less than 0.13 kbar. This is consistent with the lower ultimate strength of stainless steel at soldering temperatures.



FIG. 2. Schematic drawing of the lower portion of the apparatus.

was about 0.12 cm (see Fig. 1). The separation between the thermometers was  $15.6 \pm 0.2$  cm. The thermometers consisted each of 22 carbon resistors (nominally  $56\Omega$ each) connected in series. The resistance at 2.17°K was about 60 k $\Omega$ . Self-heating of the thermometers due to the measuring current was about  $1.5 \times 10^{-5}$ °K at  $10^{-8}$  W. A 6-k $\Omega$  manganin heater was wound around the steel tube 7.3 cm above the top thermometer. The liquid level of the sample was well above this point. All electrical leads were thermally attached to a thermal post on the top end piece. Also wound onto this post was a 60-k $\Omega$  manganin reference resistor to be used with the top thermometer and a 4-k $\Omega$  auxiliary heater. The leads between this heater and the liquid helium bath were intentionally made of heavy manganin wire, and with the bath at 1.4°K and the sample at 2.17°K provided a heat leak out of the sample of  $6 \times 10^{-7}$  W. This heat leak could be balanced by means of the auxiliary heater against the power dissipated in the thermometers and the reference resistor.

The sample was suspended in a vacuum can from a stainless steel wire by means of two cotton strings and could be raised and lowered from the outside. This is shown in Fig. 2. Additional spring loaded cotton strings applied a downward force to the sample which assured good thermal contact at the bottom when the sample was lowered. The contact surfaces were indium coated. All electrical leads (not shown in Fig. 2) were thermally attached to thermal posts at the top of the vacuum can. A radiation shield completely closed off the pump line when the sample was raised. The above arrangement assures that there is essentially no radiation heat leak to the sample, and that all conduction heat leaks go to the top end piece, and thus, when balanced by the auxiliary heater, cause no heat flow in the sample. The only heat flow generated in the sample is that due to the measuring current in the thermometers. This was varied during the experiments, but usually the power was about  $6 \times 10^{-8}$ W per thermometer.

# Thermometry

The thermometer resistances were measured by an ac-bridge method. Because of the very high thermometer resistance, it was felt that a two-lead method was adequate. Actually, it was found later that the longterm stability of the bridge may have been limited by changes in lead resistance. However, this was no serious handicap. Two separate bridges were used. The currents were provided by the reference signals of Princeton Applied Research Corporation model HR-8 precision lock-in amplifiers. The bridges were isolated from the reference signals by General Radio Company type 578-B shielded transformers. Gertsch model RT-9 Ratiotrans were used for two arms of the bridges. The reference resistor for thermometer II was mounted on the thermal post on the sample. The balance of this bridge, therefore, should be essentially independent of room temperature fluctuations, and Johnson noise should be at a minimum. The reference resistor for thermometer I was at room temperature, but shielded against temperature fluctuations. Variable capacitors parallel to the thermometers were used to balance the stray capacitances in the system. The bridges were operated at two different frequencies to avoid mutual interference, and generally at 27 and 38 cps. The bridge unbalances were determined by measuring the signal between the Ratiotran output and the lead common to the thermometer and reference resistor. These signals were measured with Type C preamplifiers for the HR-8's, and the dc outputs from the HR-8's were attenuated and recorded by a Leeds and Northrup Speedomax G two-pen recorder. An indication of the noise levels of the systems when operated with a time constant of 3 sec is given in Fig. 3. With thermometer II, a temperature resolution of about 10<sup>-7°</sup>K appears possible. However, it was not always possible to operate under these nearly ideal conditions. Frequently the noise level was a factor of 2 greater because of outside interference.

The thermometers were calibrated between 1.8 and 2.17°K against the 1958 He<sup>4</sup> vapor-pressure scale of temperatures<sup>17</sup> with a precision of  $10^{-4}$ °K after completion of the experiment. Exchange gas was used during the calibration and the bath vapor pressure was measured. It is believed that the temperature deriva-

<sup>&</sup>lt;sup>17</sup> F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. 64A, 1 (1960).

tives of the thermometer resistances near  $2.172^{\circ}$ K are known with a precision of 0.1%.

The long-term stabilities of the bridge systems were checked by repeatedly measuring transition temperatures over a 5-h period. The bridge ratios at the transition temperatures were found to be slightly timedependent. They varied at a rate equivalent to a change in  $T_{\lambda}$  of  $6 \times 10^{-8^{\circ}}$ K per min. The mean deviations of the measurements of  $T_{\lambda}$  as a function of time from a straight line were  $3 \times 10^{-7^{\circ}}$ K. The time dependence may be caused, at least partially by changes in lead resistances, because of changes in thermal gradients along the leads due to the dropping of the bath liquid level with time. However, the possibility of actual changes with time in the thermometers cannot be ruled out. The time dependence observed here is only 2.5% of that observed by Kellers.<sup>1</sup>

The response times of the thermometer systems were checked with the sample in the superfluid state by turning the main heater on and off at different power levels. When a heater power of  $6.5 \times 10^{-5}$  W, corresponding to a heating rate of  $10^{-4^{\circ}}$ K/min, was turned off, the thermometers continued to warm by  $3 \times 10^{-6}$ °K. This overheating was proportional to the heating rate, and corresponded to time lags of 1.8 sec. It is believed to be caused primarily by the time constants of the measuring circuits. During the experiment, heating rates were two orders of magnitude smaller, and thermometer responses were virtually instantaneous. With the sample in the normal state, no response of the thermometers to the heater could be detected until extreme overheating in the vicinity of the heater caused convection.

#### RESULTS

## **Transition Temperatures**

The sample was cooled by means of the thermal contact at the bottom until it was superfluid along its entire length, and then heated to a temperature slightly below the transition. Without any heat input, it then cooled at the rate of  $10^{-6°}$ K/min because of the net heat loss due to the thermal link to the bath of  $6 \times 10^{-7}$  W and the heat input to the thermometers and reference resistor of  $1.8 \times 10^{-7}$  W. This is shown in Fig. 4 in the section to the left of point A. At point A,  $4 \times 10^{-7}$  W was supplied to the auxiliary heater. This resulted in a constant sample temperature between A and B. At B,  $1.9 \times 10^{-6}$  W was supplied to the main heater (Fig. 1). Between Band C, the sample warmed uniformly at the rate of  $5 \times 10^{-6}$  K/min. At C, the heating rate measured by the bottom thermometer discontinuously dropped, whereas the heating rate measured by the top thermometer continuously increased until D was reached. This can be understood on the basis of there being He I adjacent to the bottom thermometer from point C on. This normal fluid partially blocks the heat flow from the main heater to the bottom thermometer. The heating rate indicated



FIG. 3. Noise level of the two thermometers. The time constant is 3 sec.

by the bottom thermometer beyond point C is caused primarily by the power dissipated in the thermometer  $(6 \times 10^{-8} \text{ W})$ . This heat can be distributed only over a limited effective volume of He I because of the low thermal conductivity of this fluid, and thus causes appreciable warming in spite of its small magnitude. The fact that the top thermometer did not also show a discontinuous decrease of the heating rate shows that it was still in good thermal contact with the main heater. and that there was superfluid adjacent to and above it. An interface between He I and He II therefore exists. As the temperature of the superfluid was raised further (C to D), this interface moved up the liquid column and the total amount of superfluid over which the heat from the heater could be distributed decreased. This caused the continuous increase of the heating rate between Cand D shown by the top thermometer. At point D the interface passed the top thermometer, and the heating rate indicated beyond D is similar to that indicated by the bottom thermometer beyond C and is caused by the dissipation of the top thermometer power over the adjacent normal fluid.

About 30 sec after D, the main heater was turned off. The thermometers, of course, did not respond to this because they were now thermally shielded from the heater by He I. At point E, the auxiliary heater was also



FIG. 4. Indicated temperature for the top and bottom thermometer for a thermal cycle from the He II region (left of point C) completely through the two-phase region (to point D) and back to the He II region (point G). The dashed lines are lines of constant temperature. Their slope is based on the measured long term bridge drift, and their positions are determined by points F and G.



FIG. 5. Indicated temperature for the top and bottom thermometer for a thermal cycle from the He II region partially through the two-phase region and back to the He II region. The dashed lines are lines of constant temperature as in Fig. 4.

turned off, causing a net heat loss from the sample of  $4 \times 10^{-7}$  W. This caused the interface to drop again, and to pass the top thermometer at point F. Just prior to F, there was, of course, a sharp drop in the temperature indicated by the top thermometer because the normal fluid which had been overheated by the thermometer power had to cool to its transition temperature as the interface approached. Just beyond F, there was a slight hesitation because the normal fluid just below the top thermometer, and therefore just below the interface, still had to be cooled to the transition temperature as the interface dropped. At G, the interface passed the bottom thermometer. Immediately after G, a somewhat longer hesitation was again observable, this time for both thermometers. The greater length of the time period of almost constant temperature at G as compared with F is consistent with the greater length of time over which the normal fluid at the bottom thermometer was being heated by the thermometer power (C to G as compared to D to F). Then, up to H, the cooling rate was 10<sup>-6°</sup>K/min as expected for a net heat loss of  $4 \times 10^{-7}$  W. At H,  $4 \times 10^{-7}$  W was again supplied to the auxiliary heater, resulting in a constant temperature thereafter.

A number of variations of this experiment were carried out. One of them is shown in Fig. 5. The indicated points are equivalent to those in Fig. 4, except for D'. In this case, the main heater power was  $6 \times 10^{-7}$  W, and the heating rate between B and C was therefore only about  $1.5 \times 10^{-6}$  K/min. The heating rate indicated by the bottom thermometer beyond C was the same as in Fig. 4, since the same thermometer power was used. The discontinuity in the heating rate at C for the bottom thermometer was therefore not as obvious. At D', the main heater was turned off. The interface now was about 8 cm  $(10 \times 10^{-6} \text{°K})$  above the bottom thermometer. It was kept between the two thermometers for 22.5 min. Over this period the temperature increase of the top thermometer  $(2.1 \times 10^{-6^{\circ}} \text{K})$  indicated that the interface moved up by 1.6 cm (0.071 cm/min). When

the auxiliary heater was turned off at E, the top thermometer responded immediately because it was still adjacent to He II, and the cooling rate was the same as in Fig. 4 before point G. The existence of the interface between the two thermometers for an extended time period is strong indication that coexistence of the two phases is a thermodynamic equilibrium property of liquid helium.

During these measurements the transition temperatures were determined many times. Points C, D, F, and G are shown for the top thermometer in Fig. 6. The small drifts in the measured transition temperatures due to the long-term drift of the bridge are evident. It is clear that the transition temperatures were quite reproducible and the same upon heating and cooling to  $\pm 0.3 \times 10^{-6}$  K when sufficiently small heater powers were used. The separation between the two lines is  $(19.3\pm0.5)\times10^{-6^{\circ}}$ K, in quantitative agreement with the classical expected value. It corresponds to a slope of the  $\lambda$  line at saturated vapor pressure of  $113.9 \pm 4.6$ atm/°K, and is in agreement with the values obtained by Kierstead<sup>6</sup> (111.0 atm/°K) and Elwell and Meyer<sup>18</sup> (114 atm/°K) by extrapolation of direct pressure and temperature measurements on the  $\lambda$  line to saturated vapor pressure.



FIG. 6. Transition temperatures measured with the top thermometer as a function of time. The slope represents the drift in the bridge, and is equivalent to 1.2 ppm/h.

<sup>18</sup> D. Elwell and H. Meyer, Phys. Rev. 164, 245 (1967).

# Heat Capacity

The results presented in the previous section show that He<sup>4</sup> II and He<sup>4</sup> I can coexist in equilibrium in a gravitational field. Furthermore, the temperature change required to move the interface from the bottom to the top thermometer corresponds to that predicted from the classical phase diagram. However, these results are based only on measurements at two heights. A continuous record of the interface movement with temperature can be obtained by measuring the heat capacity of the superfluid fraction of the sample. This is possible because, to a first approximation at least, the heat supplied by the main heater does not get distributed over the normal phase. A qualitative indication of the changing heat capacity, and thus of the changing fraction of superfluid, with changing temperature was already given in Fig. 4, by the changes in heating and cooling rates for the top thermometer between C and D, and between F and G. However, quantitative measurements were also made. Before presenting them in detail, the heat capacity expected on the basis of the phase diagram will be derived.

It is known that at saturated vapor pressure and below the transition temperature the molar heat capacity should be of the form<sup>1</sup>

$$C_s = A + B \ln(T_\lambda^s - T). \tag{5}$$

At a depth h, a similar relation should hold. Of course  $T_{\lambda}{}^{s}$  must be replaced by  $T_{\lambda}{}^{s}-ah$ . Although, in general, A and B should be pressure-dependent, the absolute pressure change with depth is so small that this can be neglected. Thus, at depth h,

$$C(h) = A + B \ln(T_{\lambda}^{s} - T - ah).$$
(6)

The average heat capacity of a sample of finite height is thus

$$\bar{C} = \frac{1}{H} \int_0^H C(h) dh , \qquad (7)$$

where density changes have been neglected. In detail, this gives

$$\bar{C} = A + B \left[ \ln(T_{\lambda}^{s} - T) - 1 - \frac{T_{\lambda}^{s} - T - aH}{aH} \ln\left(1 - \frac{aH}{T_{\lambda}^{s} - T}\right) \right]$$
(8)  
or

$$\bar{C} = C_s - B \left[ 1 + \frac{T_\lambda^s - T - aH}{aH} \ln \left( 1 - \frac{aH}{T_\lambda^s - T} \right) \right]. \tag{9}$$

The second term in Eq. (9) represents an excess heat capacity (B < 0) attributable to the fact that the bottom of the sample is closer to the transition temperature than the top. As T approaches the transition temperature at the bottom, one has in the limit the very simple relation

$$\bar{C}(T_{\lambda}^{s}-aH)=C_{s}(T_{\lambda}^{s}-aH)-B.$$
 (10)



FIG. 7. A typical high-resolution heat-capacity measurement.

It depends on H only through the mild temperature dependence of  $C_s$ . This expression is valid also for the superfluid fraction in the two-phase region, provided His treated as a variable and set equal to the depth h at which the interface exists. Therefore, the total heat capacity of the superfluid in the two-phase region is given by

$$\bar{C}_t(T_\lambda^s - ah) = \left[C_s(T_\lambda^s - ah) - B\right](T_\lambda^s - T)/aH, \quad (11)$$

where  $(T_{\lambda}^{s}-T)/aH=h/H$  is the superfluid fraction.

The heat capacity was measured with the top thermometer over the range  $6 \times 10^{-2} > T_{\lambda}^{s} - T > 1 \times 10^{-5}$ . In the two-phase region accessible to the top thermometer  $(3.1 \times 10^{-5} > T_{\lambda}^{s} - T > 1 \times 10^{-5})$ , temperature increments of about  $5 \times 10^{-60}$ K were used. It is estimated that these increments could be determined with a probable error of  $2 \times 10^{-7}$ °K or 4%. A typical high resolution heat capacity point is shown in Fig. 7. The lower dashed line indicates the drift in the bridge and corresponds to constant temperature. In the one-phase region, larger temperature increments were used and the random probable error far away from the transition is 0.1%. The data for  $5 \times 10^{-3} > T_{\lambda}^{s} - T > 5 \times 10^{-5}$  were used to determine A and B by means of a least-squares fit to Eq. (8) with appropriate weighting factors.<sup>19</sup> Details of the results in the single-phase region are not the subject matter of this paper. However, they are consistent with the work of Kellers.<sup>1</sup>

The results for  $10^{-4} < T_{\lambda}^{S} - T < 10^{-5}$  are given in Fig. 8. The solid line corresponds to Eq. (8) in the single-phase region, and to Eq. (11) in the two-phase region, with A and B obtained as described above. The dashed

<sup>&</sup>lt;sup>19</sup> The data were analyzed also in terms of the relation  $C=A + B[(T_{\lambda}^{s}-T-aH)^{1-\alpha'}-(T_{\lambda}^{s}-T)^{1-\alpha'}]$ , which is equivalent to Eq. (8) for a singularity of the type  $(T_{\lambda}-T)^{-\alpha'}$ . The value obtained for  $\alpha'$  is  $-0.002\pm0.008$ . Significant deviations (0.2% of C) from the equation occurred for  $(T_{\lambda}^{s}-T)\geq 5.8\times10^{-3}$ °K. A similar analysis of Keller's data (see Ref. 1) yields  $\alpha'=0.015\pm0.032$  when appropriate weights (see Ref. 1) are used. Tyson and Douglass [Phys. Rev. Letters 17, 472 (1966)] also analyzed Keller's data, but employed unit weights and used too large a temperature range. It happens that systematic errors introduced into  $\alpha'$  by these two factors cancel and that the value quoted for  $\alpha'$  is correct; but the quoted probable error is too small.

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FIG. 8. The heat capacity of the superfluid from  $7 \times 10^{-5}$  K below to  $2 \times 10^{-5}$  K above the lower transition. The data are normalized to one mole of total helium. The dashed line is the heat capacity calculated from the coefficients and Eq. (5) for a short sample.

line shows the corresponding heat capacity of a flat sample [Eq. (5)]. The error bars on the points correspond to the estimated probable errors. Where no error bars are shown, the estimated errors are smaller than the size of the points.

In the two-phase region the measurements agree well with Eq. (11). The scatter is somewhat larger than expected from the estimated probable errors. This may be due to slight irregularities in the foredrifts and afterdrifts due to heat transfer into the normal phase. The data fully confirm the classical behavior of the system.

# Superheating of He<sup>4</sup> II

Although it was the purpose of this work to determine equilibrium properties of He<sup>4</sup>, it was observed occasionally with certain heater powers that He<sup>4</sup> II can be superheated above its equilibrium transition temperature. This is already evident in Fig. 4 at point *D* for the top thermometer. The equilibrium-transition temperature should have been observed at the dashed line. In reality, with a heater power of  $1.9 \times 10^{-6}$  W, corresponding to an interface velocity of 9 cm/min, the transition occurred at  $1.0 \times 10^{6-\circ}$ K above the equilibrium-transition temperature. This corresponds to a height lag of 0.8 cm and a time lag of 5.5 sec. Point *D*,



FIG. 9. Superheating of He II at the top thermometer.

Fig. 4, is also shown in Fig. 6, and is seen to be high. A similar effect was seen on some other occasions. Figure 9 shows the observed transition temperature at the top thermometer upon several heating and cooling cycles. Cooling was always at  $4 \times 10^{-7}$  W, and, therefore, gave the equilibrium-transition temperature. Heating was at 2.6×10<sup>-6</sup> and 6×10<sup>-7</sup> W. At 2.6×10<sup>-6</sup> W, the transition temperature was raised by  $2.7 \times 10^{-6^{\circ}}$ K. It does not appear possible to explain these findings on the basis of thermal time constants of the walls and the thermometer, or on the basis of other experimental factors, and the observed effect is believed to be a property of liquid He<sup>4</sup>. However, the effect could not be consistently reproduced and appeared to depend on the thermal history of the sample. At very large heating rates  $(10^{-4} \text{ W})$ , generally no overheating was observed.

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# Erratum

Study of  $H_2^++H_2 \rightarrow H_3^++H$  Using Merging Beams, R. H. NEYNABER AND S. M. TRUJILLO [Phys. Rev. 167, 63 (1968)]. In Fig. 2 the line designated as Gioumousis and Stevenson (GS) should be ignored. The other line has the energy dependence predicted by GS, since it is a  $W^{-1/2}$  fit to the low-energy experimental points. The last column in Table I should be disregarded. These changes result in obvious, minor corrections to the text but do not alter any of the general conclusions reached in the paper.