# A THEORY OF HELIUM II 

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In this paper, a new possible explanation of the properties of helium II is developed. The basis of the argument is that, due to the internal cohesion of a fluid, potential energy resides within the repulsive field of the atoms. This potential energy will tend to appear as kinetic energy if the fluid expands, but, under its own vapour pressure, the sum of the potential and kinetic energies will be a constant in the system and be intrinsic to it. Arguments based on this conception lead to an understanding of many of the peculiarities of helium II and also to a simple expression for the velocity of the "second sound wave".

## I. Introduction

The theory of helium II, presented in this paper, is based on the assumption that the volume considered to be occupied by the atoms is a function of the specific volume of a fluid. This assumption is not unreasonable, nor is it novel. Bridgman (1949, pp. 110-16) discusses this question. He shows, for example, that the specific volume of helium at $15000 \mathrm{~kg} / \mathrm{cm}^{2}$ and at $65^{\circ} \mathrm{C}$ is only 0.4 times the specific volume of the substance close to the absolute zero under its own vapour pressure. In the latter case, where the actual heat energy is very small, the repulsive field of the atoms balances the forces of attraction and the limiting volume occupied by the atoms is determined by the magnitude of the repulsive field. "It is evident, therefore," he remarks, "that the whole atom is so compressed by a pressure of $15000 \mathrm{~kg} / \mathrm{cm}^{2}$ that its effective boundary-that is, the region in which the repulsive forces rapidly assume the ascendancy-is compressed into less than half of its volume at $0^{\circ} \mathrm{K}$." Later, in his discussion on liquids under pressure, he states that "an explanation of the failure of $(\partial P / \partial T)_{v}$ to be a function of volume only, lies at hand in the compressibility that we have had to ascribe to the molecules." He also draws attention to the fact that, whereas under ordinary pressure liquids are overall attractive systems, under greater pressures they become overall repulsive systems.

Whether the adjustment in the volume actually occupied by the repulsive field of the atoms was due to an actual compressibility or deformation of the atoms, or the result of some kind of repacking, work would be done against the natural resistance of the atoms, and within this volume, potential energy would be stored.

Both the external pressure and the internal cohesion function together to reduce the specific volume of a fluid to a minimum, compatible with the mean kinetic energy of the atoms and their limiting volume. It is not unreasonable therefore to regard the limiting volume of the atoms as a function of both the external pressure and the internal cohesion. In liquids, the internal cohesion is, in general, very large compared with the external pressure. A decrease in the limiting volume of the atoms

[^0]in a monatomic substance such as helium is considered to be accompanied by an increase of potential energy within this volume, equal to $\int P \mathrm{~d} b$, where $P=p+a / v^{2}$, $p$ being the external pressure and $a / v^{2}$ is taken as a measure of the internal cohesion and $b$ is the volume occupied by the atoms. If $b$ is regarded as a rigid constant, this quantity will be zero.

The physical conception at the basis of this paper, is as follows. As the $\lambda$ point is approached from the higher temperature, there is a balance between the repulsive forces, due to the repulsive field of the atoms, together with their kinetic energy due to their temperature acting against the attractive forces between the atoms. At these very low temperatures, the contribution from the heat energy is becoming very small. With increasing density, the repulsive forces increase more rapidly than the attractive forces. It is very probable that the fluid passes through a period of instability when transient regions of excess density appear, together with regions of deficient density. Such a condition probably arises in a saturated vapour immediately preceding condensation. In an ordinary saturated vapour, however, the liquid phase, when once formed, separates itself from the system on account of the marked difference of its density and heat content from that of the vapour. A two-phase system has been formed with widely different constituents.

It is generally accepted that helium becomes a two-phase system below the $\lambda$ point. From the point of view of this paper, regions of excess density are regions of excess potential energy, due to the compression of the repulsive field by the internal cohesion. These regions are transient and pass over to expanded regions where the excess potential energy is transformed into excess kinetic energy. These regions are pictured as being in dynamic equilibrium and the interchange between the potential and kinetic energies an entirely reversible process. In other words, for this process in the system $\int s=0$.

It follows, therefore, that the sum of the potential and kinetic energies associated with this interchange remains a constant for the fluid under its own vapour pressure and throughout its subsequent history. This residual energy, therefore, would not appear in the thermodynamic equation and will be of zero entropy. The quantity of energy involved in this process would, at ordinary temperatures, be an almost negligible part of the total energy of the system, but at temperatures below the $\lambda$ point of helium it could become the controlling factor. Though this energy is of zero entropy it will behave, in the kinetic form, in the same manner as energy of heat origin. It will tend to maintain the fluid in an expanded state and retain its fluidity. As the temperature is reduced below the $\lambda$ point, the density of the normal constituent will increase and more potential energy will be released to maintain the equilibrium. The kinetic energy, thus liberated, will displace an equal quantity of heat energy, but will remain itself a permanent part of the system.

On the basis of these conceptions an analysis of helium II has been attempted by an equation of state. This differs from the analysis based on the statistics of quantum mechanics. By the latter approach, as the temperature falls below the $\lambda$ point, an increasing number of atoms moves down to a lower energy level. The number of atoms interchanging between this level and the next possible one is governed by the particular quantum statistics applicable to the process. The atoms
in the lowest energy level are of zero entropy and the phenomena connected with helium II are a consequence of the properties of such atoms.

In the present paper, the conception of zero entropy is arrived at from a different basis. Further, the atoms of zero entropy are considered to be associated with a certain quantity of energy, which is an intrinsic part of the system. This energy can exist in a potential or kinetic form and the peculiarities of helium II are connected with the interchange of this energy.

The analysis developed in the present paper offers a simple explanation of many of the phenomena connected with helium II and leads to a new equation for the "second sound wave" without the introduction of arbitrary constants.

## II. Van der Waals' Equation

It is assumed, in this paper, that the behaviour of helium is governed by an equation of state. Van der Waals' equation is used because all the quantities in it are capable of a simple physical interpretation. The equation is modified so that while $a$ is regarded as a constant, $b$ is considered to be variable. If now, we express the external pressure $p$ as a ratio of the internal cohesion $a / v^{2}$, so that $p=\left(a / v^{2}\right) x$, where $x$ is a purely numerical quantity, we can rewrite Van der Waals' equation as

$$
v^{2} \frac{R T}{a(1+x)}-v+b=0
$$

or

$$
v=\frac{1 \pm \sqrt{ }\{1-4 R T b / a(1+x)\}}{2 R T / a(1+x)}
$$

It can easily be shown that $V_{1}$, the specific volume of the normal liquid, will be represented by

$$
V_{1}=\frac{1-\sqrt{ }\left\{1-4 R T b_{1} / a\left(1+x_{1}\right)\right\}}{2 R T / a\left(1+x_{1}\right)}
$$

and that this reduces to $V_{t}=V_{0}(1+\alpha t)$ over a short range of temperature.
At the same time $V_{3}$, the specific volume of the vapour or a gas is given by

$$
V_{3}=\frac{1+\sqrt{ }\left\{1-4 R T b_{3} / a\left(1+x_{3}\right)\right\}}{2 R T / a\left(1+x_{3}\right)}
$$

which reduces to $p v=R T$.
The quantity $4 R T b / a(1+x)$ must not be greater than unity for an actual fluid. The quantity $b$ is written as $b_{1}$ and $b_{3}$, allowing for the possibility that $b$ is a function of $v$. At the critical temperature $v_{1}$ and $v_{3}$ become equal. By this approach, this is true when $1-4 R T b / a(1+x)=0$, or $b=a(1+x) / 4 R T$. At the same time, $v=a(1+x) / 2 R T$ or $b_{\mathrm{c}}=\frac{1}{2} V_{\mathrm{c}}$.

This method of interpreting Van der Waals' equation offers a direct explanation of why there can be only one fluid above the critical temperature. The number $x$, in the quantity $4 R T b / a(1+x)$ stands for the ratio of the external pressure to the internal cohesion or $p v^{2} / a$. An examination of the data on the compression of fluids above their critical temperatures, shows that, at constant temperature, $p$ increases more
rapidly than $v^{2}$ decreases, so that $x$ tends to increase with increasing pressure, and the single fluid remains stable. If a denser form of matter, under increased pressure, attempted to separate out, its internal cohesion would be greater than that of the single fluid. At the same time the pressure would be reduced. This would make $x$ for the denser form less and the quantity $4 R T b / a(1+x)$ greater than unity. It remains greater than unity, until, with the reduction of temperature to critical temperature, it becomes equal to unity. Below this temperature two forms of different density are physically possible.

At constant volume, above the critical temperature, $p$ increases more rapidly than $T$, so that $4 R T b / a(1+x)$ remains less than unity.

Table 1
EQUATION OF STATE DATA

| Temp. ( ${ }^{\circ} \mathrm{K}$ ) | Atomic Vol. Liq. Vap. |  | $p$ | $p+a / V^{2}$ |  | $V-b$ |  | $b$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Liq. | Vap. | Liq. | Vap. | Liq. | Vap. |
| $4 \cdot 23$ | 31.93 |  |  | $1 \cdot 01$ | $42 \cdot 50$ |  | $8 \cdot 27$ |  | $23 \cdot 66$ |  |
| $4 \cdot 59$ | 34.33 | $167 \cdot 4$ | $1 \cdot 37$ | $37 \cdot 1$ | $2 \cdot 87$ | $10 \cdot 27$ | $133 \cdot 0$ | $24 \cdot 06$ | $34 \cdot 4$ |
| $5 \cdot 19$ | $57 \cdot 72$ |  | $2 \cdot 26$ | $14 \cdot 95$ |  | $28 \cdot 86$ |  | $28 \cdot 86$ |  |

## III. Helium

From the previous discussion, the equation of state at the critical temperature becomes

$$
\left(p_{\mathrm{c}}+a / V_{\mathrm{c}}^{2}\right) \frac{1}{2} V_{\mathrm{c}}=R T_{\mathrm{c}}
$$

For helium $p_{\mathrm{c}}=2 \cdot 26 \mathrm{~atm}, \quad V_{\mathrm{c}}=57.72 \mathrm{~cm}^{3} / \mathrm{g}$ and $T_{\mathrm{c}}=5 \cdot 19^{\circ} \mathrm{K}$. This gives $a=4 \cdot 23 \times 10^{4}$, which is regarded as a constant.

The values of $b$ from the critical temperature down to the boiling point, are given in the last column of Table 1.
$b$ is plotted against $P\left(p+a / V^{2}\right)$ in Figure 1.
From the critical temperature to well below the boiling point, helium contracts in a manner normal to a homogeneous liquid. Approaching the $\lambda$ point, the rate of contraction falls off, the specific volume reaching a minimum at the $\lambda$ point. Following an initial expansion at the $\lambda$ point, the specific volume remains practically constant, apparently to the absolute zero. Particularly from its capacity to transmit a second sound wave, helium II, that is, helium below the $\lambda$ point, is generally regarded as a two-phase fluid, consisting of a normal component and a superfluid component, usually denoted by $\rho_{\mathrm{n}}$ and $\rho_{\mathrm{S}}$, the proportion of the $\rho_{\mathrm{S}}$ constituent increasing with fall of temperature. As the normal component is considered to contract in the usual manner for liquids, the superfluid must have a higher specific volume than the normal helium I.

It is proposed to show that an expanded form, conforming to the conditions set by the equation of state, is possible and the actual fluid is regarded as a mixture of these two phases, in proportions varying with the temperature and pressure.

In the expanded phase, the internal cohesion becomes less and the volume occupied by the atoms becomes greater, and, at the same time, potential energy within the volume occupied by the atoms is transformed into kinetic energy between the atoms.


Fig. 1.- $b$, atomic volume of atoms in $\mathrm{cm}^{3}$, versus $P, p+a / V^{2}$, in atmospheres.

Table 2 shows the mean values of $b$ calculated from the densities given by Keesom (1942, p. 207).

In the range from the $\lambda$ point, $2 \cdot 19^{\circ} \mathrm{K}$ down to $1 \cdot 1^{\circ} \mathrm{K}$, the external pressure is negligible and $P=a / v^{2}$. $b$ has expanded from $24 \cdot 13$ to $25 \cdot 91 \mathrm{~cm}^{3}$ under a mean internal pressure of 56 atm . The energy liberated as kinetic energy should, therefore, be

$$
\frac{(25 \cdot 91-24 \cdot 13) \times 56 \times 10^{6}}{4 \cdot 18 \times 10^{7}} \mathrm{cal} / \mathrm{mole} .
$$

This equals $2 \cdot 44 \mathrm{cal} / \mathrm{mole}$, or $0 \cdot 61 \mathrm{cal} / \mathrm{g}$.

From Keesom (1942, p. 246), the fall of entropy from $2 \cdot 2$ to $1 \cdot 1^{\circ} \mathrm{K}$ under its saturated vapour is from -0.45 to $-0 \cdot 82$, a difference of $0 \cdot 38$, at a mean temperature of $1 \cdot 6^{\circ} \mathrm{K}$. This represents a change of heat content equal to $0 \cdot 38 \times 1 \cdot 6=0.61 \mathrm{cal} / \mathrm{g}$. The view is taken that the kinetic energy liberated by the expansion of the atoms displaces an equal quantity of kinetic energy of heat origin and maintains the volume constant.

Table 2
EQUATION OF STATE DATA BELOW THE BOILING POINT

| Temperature $\left({ }^{\circ} \mathrm{K}\right)$ | Atomic Volume | $P$ | $V-b$ | $b$ |
| :---: | :---: | :---: | :---: | :---: |
| $1 \cdot 1$ | $27 \cdot 55$ | $55 \cdot 73$ | $1 \cdot 64$ | $25 \cdot 91$ |
| $1 \cdot 3$ | $27 \cdot 54$ | $55 \cdot 78$ | 1.94 | $25 \cdot 60$ |
| $1 \cdot 5$ | $27 \cdot 53$ | $55 \cdot 83$ | $2 \cdot 23$ | $25 \cdot 30$ |
| $1 \cdot 7$ | $27 \cdot 52$ | $55 \cdot 88$ | $2 \cdot 53$ | 24.99 |
| $1 \cdot 9$ | $27 \cdot 50$ | $55 \cdot 96$ | 2.82 | $24 \cdot 68$ |
| $2 \cdot 10$ | $27 \cdot 41$ | $56 \cdot 33$ | 3.10 | 24.31 |
| 2-19 | 27-36 | $56 \cdot 50$ | 3. 23 | 24-13 |
| $2 \cdot 27$ | $27 \cdot 42$ | $56 \cdot 30$ | 3.35 | $24 \cdot 07$ |
| $3 \cdot 27$ | $28 \cdot 81$ | $57 \cdot 60$ | $5 \cdot 27$ | $23 \cdot 54$ |
| $4 \cdot 24$ | $32 \cdot 04$ | $42 \cdot 20$ | $8 \cdot 35$ | $23 \cdot 69$ |

## IV. Helium II

Based on the experimental evidence, it is proposed to discuss the phenomena of helium II under two sections, the first from $2 \cdot 2^{\circ} \mathrm{K}$ down to $1 \cdot 1^{\circ} \mathrm{K}$ and the second from $1 \cdot 1^{\circ} \mathrm{K}$ down towards the absolute zero. The most reliable measurements have, of course, been made in the former section. It is obvious from the heat curves supplied by Keesom that the total heat content of helium II below $1 \cdot 1^{\circ} \mathrm{K}$ has become almost negligibly small, so that any further heat change from a denser form to a more expanded form would also be very small. The velocity of the second sound wave, after passing through a maximum at $1 \cdot 7^{\circ} \mathrm{K}$, decreases again to $1 \cdot 1^{\circ} \mathrm{K}$ and increases sharply from then on towards the absolute zero. The specific volume appears to remain constant down to the lowest temperatures, and helium II, apparently, is still a fluid at the absolute zero.

Regarding helium II as a mixture of the normal helium I and an expanded form, it is proposed to make the simplest assumption about the composition of the mixture, namely, that if $\rho_{\mathrm{n}}$ denotes the mass of the normal constituent and $\rho_{\mathrm{s}}$ the mass of the expanded form in $1 \mathrm{~cm}^{3}$ of helium II., then $\rho_{\mathrm{n}} / \rho_{\mathrm{s}}=T /\left(T_{\lambda}-T\right)$ from $2 \cdot 2$ to $1 \cdot 1^{\circ} \mathrm{K}$.

From $1 \cdot 1^{\circ} \mathrm{K}$ down to the absolute zero, $\rho_{\mathrm{n}} / \rho_{\mathrm{s}}$ differs little from unity.
These ratios will be justified by the calculations based upon them.

## Discussion of the Expanded Form

Though the denser and expanded forms can only exist in dynamic equilibrium with each other, they are each considered to have their own specific volumes. Any
ordinary liquid can only continue to exist in equilibrium with its saturated vapour. In Figure 2, atomic volumes are plotted against the absolute temperature. The line $A B_{1}$ represents the specific volume of the normal constituent. This line, produced, passes through the specific volume of helium I at the boiling point, and it is considered to represent with reasonable accuracy the specific volume of this constituent from $2 \cdot 2$ to $1 \cdot 1^{\circ} \mathrm{K}$. The point A is the $\lambda$ point and the line ABC represents the constant volume of helium II. In all calculations on helium II, the vapour pressure is neglected, the equation of state becoming

$$
\left(a / V^{2}\right)(V-b)=R T
$$

where $a=4 \cdot 23 \times 10^{4}$.


Fig. 2

$$
\left(a / V^{2}\right)(V-b)=\left(a / V_{\mathrm{n}}^{2}\right)\left(V_{\mathrm{n}}-b_{\mathrm{n}}\right)=\left(a / V_{\mathrm{s}}^{2}\right)\left(V_{\mathrm{s}}-b_{\mathrm{s}}\right)=R T .
$$

From $V$, the atomic volume of the fluid, and $V_{\mathrm{n}}$, the atomic volume of the normal constituent, $b$ and $b_{\mathrm{n}}$, the corresponding values of $b$ are obtained. At $1 \cdot 1^{\circ} \mathrm{K}$, where $\rho_{\mathrm{n}} / \rho_{\mathrm{s}}=1$, the specific volume of the expanded form must exceed that of the actual fluid, by the same amount as the actual fluid exceeds that of the normal constituent. In general, if $\rho_{\mathrm{n}}$ and $\rho_{\mathrm{s}}$ denote the mass of the normal constituent and the expanded constituent in $1 \mathrm{~cm}^{3}$ of the actual fluid and $\rho$ the mass of $1 \mathrm{~cm}^{3}$ of the actual fluid, so that $\rho_{\mathrm{n}}+\rho_{\mathrm{s}}=\rho$, then

$$
V_{\mathrm{n}} \rho_{\mathrm{n}}+V_{\mathrm{s}} \rho_{\mathrm{s}}=V \rho
$$

where $\rho_{\mathrm{n}}=\left(T / T_{\lambda}\right) \rho$ and $\rho_{\mathrm{s}}=\left\{\left(T_{\lambda}-T\right) / T_{\lambda}\right\} \rho . V_{\mathrm{s}}$, thus obtained, is a line parallel to $V_{\mathrm{n}}$. Also

$$
\left(a / V_{\mathrm{s}}^{2}\right)\left(V_{\mathrm{s}}-b_{\mathrm{s}}\right)=\left(a / V_{\mathrm{n}}^{2}\right)\left(V_{\mathrm{n}}-b_{\mathrm{n}}\right)=R T
$$

and

$$
\rho_{\mathrm{n}} b_{\mathrm{n}}+\rho_{\mathrm{s}} b_{\mathrm{s}}=\rho b
$$

The quantity $4 R T b / a(1+x)$ at $2 \cdot 2^{\circ} \mathrm{K}$ is 0.42 for the normal constituent and 0.49 for the expanded constituent. Both constituents are, therefore, physically real with the normal constituent the more stable of the two.

## V. Effects of Pressure on Helium II

The effect of pressure on helium I (Keesom 1942, p. 239) is to lower the temperature of the $\lambda$ point. Under sufficient pressure helium can be solidified. The lowering of the $\lambda$ point is to be expected. Pressure would oppose the formation of an expanded phase and thus lower the temperature at which a $\lambda$ point would appear. A very satisfactory quantitative analysis has been made of the effect of pressure on helium, but it is not proposed to reproduce it in this paper.

## Vl. Viscosity

The flow of helium II over the sides of vessels and through very fine capillaries, takes place as though the substance, or at least a part of it, had zero viscosity. The current explanation of these phenomena is that they are due to the presence in the mixture of a constituent with zero entropy. This explanation could still be pursued from the standpoint of this paper, but the author wishes to suggest a different explanation.

From either point of view, helium II seems to be a two-phase fluid, the composition of which changes with temperature and pressure. The anomalous viscosity may be an accompaniment of its two-phase character rather than the property of one constituent.

Consider the flow of a saturated vapour in contact with the parent liquid. This flow takes place, up to a certain critical velocity, as though the system had, practically, zero viscosity. Suppose we have an inverted " $J$ " tube (Fig. 3) with say water, in one arm A, at a higher level than in the other arm B. The tube is evacuated, but heat is allowed to flow in, to maintain $A$ and $B$ at the same temperature. The vapour pressure at $A$ will be the same as that at C, at the same level, but the vapour pressure at $B$ will be greater than that at $C$ by the weight of the column of vapour BC. Evaporation will take place from A to $B$. If now, we increase the length of the tube above $A C$ or alter its dimensions, this will not alter the equality of the pressure at C and A . The flow per unit area will be independent of the nature of the connecting tube. This is contrary to the nature of the flow of a single fluid through a tube under pressure. In the former case there is a transference of momentum between saturated layers, without a velocity gradient across the tube, in the latter the viscosity is due to this velocity gradient. Further, the pressure is an essential part of the viscosity equation as well as the
Fig. 3 dimensions of the tube. A saturated vapour, in contact with the liquid, will not sustain a pressure, so that for flows departing inappreciably from a state of equilibrium, an essential part of the viscosity equation is absent or indeterminate. If pressure were applied to disturb the natural rate of transference between the saturated layers a velocity gradient would appear and the fluid would show the property of viscosity. Because helium II is a two-phase fluid, the transference of momentum could take
place by a change of composition between the two phases, at low velocities, without an appreciable departure from a state of equilibrium and, apparently, without viscosity. Higher velocities would introduce velocity gradients and measurable viscosities. From this point of view, the property of zero viscosity is due to the property of a two-phase system, whose phases are a function of temperature and pressure, rather than to the peculiar property of one constituent in the mixture.

## VII. The Flow of Helium II

The phenomena connected with the anomalous flow of helium II can be given a simple explanation from the point of view outlined. Helium II has the property of spreading a surface film over the walls of a containing vessel. This film is considered to have a different composition from that of the bulk material. Approaching the surface of helium II, whether that surface is a free surface or a solid surface, the density and internal cohesion of the fluid would decrease. This would favour the formation of the expanded form and would be the seat of a greater proportion of kinetic energy, intrinsic to the system. It is understood that this kinetic energy is in equilibrium with the heat energy of the system. The flow is the flow of this phase.

Take first the flow from one vessel A to another B, the level in A being higher than that in B (Fig. 4). The fluid will attempt to restore equilibrium by flowing


Fig. 4 through the natural film provided by the connecting surface. In this case A tends to warm and B to cool. The flowing material carries with it an excess of kinetic energy intrinsic to the system, but of low actual heat content, and on reaching $B$ displaces actual heat from B back to A. A, therefore, warms and $B$ cools. It will be noticed that heat flows in one direction, and matter in the opposite direction. As B cools relative to A , it becomes the seat of a greater proportion of the expanded form due to the lower temperature, and an equilibrium would be established. If heat is given and received from the surroundings, B and A finally reach the same level.

If $B$ and $A$ are initially at the same level, but $B$ is cooler than $A$, then the fluid flows from $B$ to $A$. In the cooler liquid, there is a greater proportion of the expanded form. Only the expanded form can flow, which it does to restore equilibrium. In doing so, it carries matter with a low actual heat content from $B$ to $A$ and drives back actual heat from A to B. Again the heat and the matter are flowing in opposite directions.

If helium II is contained in three concentric cylinders, the level of the outer one being adjustable, so that the fluid can be made to flow into or out of the two inner cylinders, then the level of the two inner cylinders always remains the same. If the outflow from one cylinder is greater than that from the other, then its level will drop and, at the same time, its temperature will rise relative to the other. Both these factors immediately bring into play an increased flow from the cooler vessel with the higher pressure. It would therefore be impossible for the two levels to develop any real difference.

## VIII. The Entropy Diagram

In Figure 5, ABCD reproduces the entropy diagram of helium under its own vapour pressure (Keesom 1942, p. 246). Below $1 \cdot 1^{\circ} \mathrm{K}$, from Keesom's diagram, the entropy line would appear to descend sharply to the absolute zero and meet the straight line drawn through the values at the boiling point and the $\lambda$ point at that temperature. The entropy of the normal constituent can, therefore, be represented with reasonable accuracy by the line ABE . It is noticeable that in both the


Fig. 5
$T-V$ curve and the $T-E$ curve, a departure from normality takes place above the $\lambda$ point. This may indicate the commencement of a change over from potential energy, within the volume occupied by the atoms, to kinetic energy. At the $\lambda$ point, however, new properties appear in helium, particularly the propagation of a second sound wave. It is generally accepted that, at this point, the fluid separates into two phases. This change would, almost certainly, be accompanied by a loss of heat, indicated by a striking rise in the specific heat over a few hundredths of a degree at the $\lambda$ point; at the same time, a surface film, of great fluidity appears. Towards the surface of the bulk material, the internal cohesion would decrease, favouring the liberation of potential energy to kinetic energy. The surface film is regarded as having a lower density than the bulk material, with a greater proportion of the expanded form. The average kinetic energy would be the same as that of the bulk material, but a greater proportion of it would be intrinsic to the system. The formation of the film would lower the total heat content and contribute to the rise in the specific heat. It is pictured that the two phases, one condensed and the other
expanded, are in dynamic equilibrium. The former is the seat of excess potential energy and the latter of excess kinetic energy. This is typical of a dynamic system in equilibrium.

## IX. The "Apparent" Entropy and Specific Heat of Helium II

One of the striking anomalies of helium II is that the volume remains constant while the heat content falls continuously to the absolute zero. Actually, nearly all the heat is lost between $2 \cdot 2$ and $1 \cdot 1^{\circ} \mathrm{K}$. It was shown earlier in this paper that this heat loss is practically equivalent to the kinetic energy liberated by the mean expansion of the volume occupied by the atoms against the internal cohesion of the fluid. Calculation of the actual entropy of the system, on this basis, would indicate an entropy line along BD, Figure 5. This line is parallel to the actual line BCD over a considerable part of the distance, but does not take account of the abnormal specific heat in the immediate neighbourhood of the point. A definite departure from the normal helium along BE is, however, clearly indicated.

The entropy of the normal constituent, represented by the line BE, can be written as $A T$, where $A$ is a constant which from the figure is equal to $0 \cdot 2$. It is proposed to introduce terms called the "apparent" entropy and "apparent" specific heat to distinguish these quantities from the actual entropy and actual specific heat. As the actual heat disappears from the system, it is replaced by kinetic energy of intrinsic origin, functioning in the same manner as the actual heat energy and in equilibrium with it. This means that the "apparent" heat loss is zero and the apparent entropy remains constant, and equal to $A T_{\lambda}$, the entropy at the $\lambda$ point. It follows the line $\mathrm{BB}^{\prime}$. At $1 \cdot 1^{\circ} \mathrm{K}, \rho_{\mathrm{n}}$ and $\rho_{\mathrm{s}}$ are equal, so that the apparent entropy of the expanded form must be greater than that of the mixture by an amount equal to the difference between the normal component and the mixture, or $\mathrm{B}^{\prime} \mathrm{E}^{\prime}$ and $\mathrm{B}^{\prime} \mathrm{G}$. The entropy of the expanded form is assumed to increase proportionally to the absolute temperature so that it is equal to

$$
A T_{\lambda}+A T
$$

This also satisfies the relation that the sum of the apparent entropies of the constituents shall be equal to the apparent entropy of the mixture as

$$
\begin{aligned}
\rho_{\mathrm{n}} \cdot A T+\rho_{\mathrm{s}}\left(A T_{\lambda}+A T\right) & =\frac{T}{T_{\lambda}} \cdot A T+\frac{T_{\lambda}-T}{T_{\lambda}}\left(A T_{\lambda}+A T\right) \\
& =A T_{\lambda}
\end{aligned}
$$

The specific heat of helium II is one of its most marked anomalies. Over $0.01^{\circ} \mathrm{K}$ about the $\lambda$ point it moves up steeply from about $0 \cdot 6$ to $3 \cdot 0$, or even higher, and then moves down sharply so that at $1.8^{\circ} \mathrm{K}$ it is back to its normal value again. It has been suggested earlier in the paper that this marked loss of heat may be due to the sudden appearance of the second phase and to the formation of the surface film. Actually, the heat loss of helium II is such that at $1 \cdot 1^{\circ} \mathrm{K}$ the heat content is very small.

Helium is a monatomic substance, and from the point of view of this paper, this marked loss of actual heat is not accompanied by a corresponding loss of kinetic
energy from the system. Internally the number of atoms remains constant and their mean kinetic energy decreases proportionally to the absolute temperature. In the equation of state $\left(a / V^{2}\right)(V-b)=R T, V^{2}$ is constant, so that $(V-b)$ is proportional to $T .(V-b)$ is a measure of the mean kinetic energy of the atoms. It is considered therefore that the apparent specific heat is constant and equal to $0 \cdot 6$, the specific heat just above the $\lambda$ point.

## X. Second Sound Wave

Gogate and Pathak (1947) have derived Landau's expression for the velocity of the second sound wave in helium II, namely, $\mu^{2}=\left(\rho_{\mathrm{s}} / \rho_{\mathrm{n}}\right)(T / C) S^{2}$, from thermodynamical considerations.

The essential conditions for the propagation of a second sound wave through a fluid are that there should be two phases of different densities and different entropies, and that between the phases there should be, practically, zero viscosity. These general conditions are fulfilled by the type of fluid proposed in this paper. In their derivation of Landau's equation, Gogate and Pathak assumed that the entropy of the superfluid was zero. If we do not neglect $S_{\mathrm{s}}$ and use the arguments of the above paper, it is easy to show that there are two alternative expressions for the second sound wave, namely,

$$
\mu^{2}=\frac{\rho_{\mathrm{n}}}{\rho_{\mathrm{s}}} \frac{T}{C}\left(S-S_{\mathrm{n}}\right)^{2} \text { or } \frac{\rho_{\mathrm{s}}}{\rho_{\mathrm{n}}} \frac{T}{C}\left(S_{\mathrm{s}}-S\right)^{2}
$$

where $S_{\mathrm{n}}$ is the entropy of the normal constituent, $S$ the entropy of the mixture, and $S_{\mathrm{s}}$ the entropy of the superfluid, and $C$ the specific heat of the mixture.

In the present treatment, no constituent is assumed to have zero entropy, so that both expressions should give the velocity of the second sound wave. From $2 \cdot 2$ to $1 \cdot 1^{\circ} \mathrm{K}, \quad \rho_{\mathrm{n}} / \rho_{\mathrm{s}}=T /\left(T_{\lambda}-T\right), \quad S_{\mathrm{n}}=A T, S=A T_{\lambda}$, and $S_{\mathrm{s}}=A T_{\lambda}+A T$, where $A=0 \cdot 2$ and $C=0 \cdot 6$, as shown earlier in the paper, or

$$
\mu^{2}=\frac{T}{T_{\lambda}-T} \times \frac{T}{0 \cdot 6} \times(0 \cdot 2)^{2}\left(T_{\lambda}-T\right)^{2}
$$

also

$$
\mu^{2}=\frac{T_{\lambda}-T}{T} \cdot \frac{T}{0 \cdot 6} \times(0 \cdot 2)^{2}\left[\left(T_{\lambda}+T\right)-T_{\lambda}\right]^{2}
$$

$S$ and $C$ are heat terms and must be multiplied by $4 \cdot 2 \times 10^{7}$ to be expressed in ergs, and as $S$ is on the top line and squared and $C$ is to the first power on the bottom line, the expressions must be multiplied by $4 \cdot 2 \times 10^{7}$. Both expressions reduce to

$$
\mu^{2}=T^{2}\left(T_{\lambda}-T\right) \times 2 \cdot 80 \times 10^{6}
$$

or

$$
\mu=T \sqrt{ }\left(T_{\lambda}-T\right) \times 1 \cdot 67 \times 10^{3} \mathrm{~cm} / \mathrm{s}
$$

The result is in absolute units and no numerical quantities, other than those from the general argument, have been introduced. The usually accepted expression for the second sound wave is

$$
\mu=26 \sqrt{ }\left[\left(T / T_{\lambda}\right)\left\{1-\left(T / T_{\lambda}\right)^{5 \cdot 6}\right\}\right] \mathrm{m} / \mathrm{s} .
$$

The velocity of the second sound wave, calculated from the author's expression, is given in Table 3 together with the observed values (Atkins 1959) at the same temperature. Considering the simplicity of the expression and the obvious approximations at the extremes, the agreement is satisfactory.

Below about $1 \cdot 1^{\circ} \mathrm{K}$, the total heat content of helium II becomes very small. Any further appreciable change from $\rho_{\mathrm{n}}$ to $\rho_{\mathrm{s}}$ is, therefore, not to be expected, though there is no suggestion of discontinuity. From $1 \cdot 1^{\circ} \mathrm{K}$ down to absolute zero, the fluid is regarded as one of practically constant composition with $\rho_{\mathrm{n}} / \rho_{\mathrm{s}}=1$. This, of course, is only an approximate statement of the situation on either side of $1 \cdot 1^{\circ} \mathrm{K}$ as the exact equality of $\rho_{\mathrm{n}} / \rho_{\mathrm{s}}$ would not be reached above $0^{\circ} \mathrm{K}$. It is assumed that the normal constituent continues to lose entropy along the line $\mathrm{E}^{\prime} \mathrm{E}$, as the temperature

Table 3
velocity of second sound wave

| Temperature <br> $\left({ }^{\circ} \mathrm{K}\right)$ | Calculated <br> $(\mathrm{m} / \mathrm{s})$ | Observed <br> $(\mathrm{m} / \mathrm{s})$ |
| :---: | :---: | :---: |
|  |  |  |
| $1 \cdot 1$ | $19 \cdot 2$ | $18 \cdot 9$ |
| $1 \cdot 2$ | $20 \cdot 0$ | $19 \cdot 2$ |
| $1 \cdot 3$ | $20 \cdot 6$ | $19 \cdot 8$ |
| $1 \cdot 4$ | $20 \cdot 8$ | $20 \cdot 1$ |
| $1 \cdot 5$ | $20 \cdot 9$ | $20 \cdot 4$ |
| $1 \cdot 6$ | $20 \cdot 6$ | $20 \cdot 5$ |
| $1 \cdot 7$ | $20 \cdot 1$ | $20 \cdot 1$ |
| $1 \cdot 8$ | $19 \cdot 0$ | $18 \cdot 8$ |
| $1 \cdot 9$ | $17 \cdot 4$ | $16 \cdot 5$ |
| $2 \cdot 0$ | $14 \cdot 9$ | $12 \cdot 0$ |
| $2 \cdot 1$ | $11 \cdot 2$ | $7 \cdot 6$ |
| $2 \cdot 15$ | $7 \cdot 7$ | $0 \cdot 0$ |
| $2 \cdot 2$ | $0 \cdot 0$ |  |

falls and the heat lost is replaced by kinetic energy of intrinsic origin. In other words, as the normal constituent becomes more orderly, the expanded constituent becomes more disorderly. One constituent is regarded as the seat of excess potential energy, over the mean, and the other the seat of excess kinetic energy, and the two are considered to be in dynamic equilibrium. For this reason, while the entropy of $\rho_{\mathrm{n}}$ decreases along $\mathbf{E}^{\prime} \mathrm{E}$ and the entropy of $\rho_{\mathrm{s}}$ increases along GH, the apparent entropy of the mixture remains constant. This is the picture suggested, by this paper, to account for the fluidity and constant volume of helium II down to the lowest temperatures. The kinetic energy in the system, at the absolute zero, is intrinsic and cannot be removed. It will be noted that, as $\mathrm{d} s=\mathrm{d} Q / T$, a small change in the heat content of the system, at very low temperatures, produces large changes in the order or disorder of the system.

## XI. Second Sound Wave below $1 \cdot 1^{\circ} \mathrm{K}$

Below $1 \cdot 1^{\circ} \mathrm{K}$, on account of the very small heat content of the system, the fluid becomes a mixture of almost constant composition. Both $S-S_{\mathrm{n}}$ and $S_{\mathrm{s}}-S$ are now proportional to $T_{\lambda}-T$. The apparent specific heat becomes the same as the actual specific heat, which appears to obey a $T^{3}$ law down to a low temperature.

Table 4
VELOCITY OF SECOND SOUND FROM $1 \cdot 1$ TO $0 \cdot 3^{\circ} \mathrm{K}$

| Temperature <br> $\left({ }^{\circ} \mathrm{K}\right)$ | Calculated <br> $(\mathrm{m} / \mathrm{s})$ | Observed <br> $(\mathrm{m} / \mathrm{s})$ |
| :---: | :---: | :---: |
|  |  |  |
| $1 \cdot 1$ | $19 \cdot 2$ |  |
| $1 \cdot 0$ | $22 \cdot 8$ | $21 \cdot 0$ |
| $0 \cdot 9$ | $27 \cdot 5$ | $24 \cdot 0$ |
| $0 \cdot 8$ | $33 \cdot 3$ | $30 \cdot 8$ |
| $0 \cdot 7$ | $40 \cdot 9$ | $35 \cdot 0$ |
| $0 \cdot 6$ | $50 \cdot 9$ | $44 \cdot 0$ |
| $0 \cdot 5$ | $64 \cdot 9$ | $57 \cdot 0$ |
| $0 \cdot 4$ | $85 \cdot 7$ | $90 \cdot 0$ |
| $0 \cdot 3$ | $122 \cdot 9$ | $122 \cdot 0$ |

As $\rho_{\mathrm{n}} / \rho_{\mathrm{s}}=1$, the second sound wave expression becomes

$$
\mu^{2}=1 .\left(T / B T^{3}\right)\left(T_{\lambda}-T\right)^{2},
$$

where $B$ is a constant, or

$$
\mu=\frac{T_{\lambda}-T}{T} \cdot \frac{1}{\sqrt{B}} .
$$

At $1 \cdot 1^{\circ} \mathrm{K}$, where a minimum occurs, the two expressions should be equal, so that

$$
\frac{T_{\lambda}-T}{T} \frac{1}{\sqrt{B}}=16 \cdot 7 T \sqrt{ }\left(T_{\lambda}-T\right) \mathrm{m} / \mathrm{s}
$$

or

$$
1 / \sqrt{ } B=19 \cdot 2
$$

and

$$
\mu=\left(T_{\lambda}-T\right) / T \times 19 \cdot 2 \mathrm{~m} / \mathrm{s} .
$$

The values calculated from this expression from $1 \cdot 1^{\circ} \mathrm{K}$ down to $0 \cdot 3^{\circ} \mathrm{K}$ are given in Table 4 (see also Fig. 6). The observed values have been obtained from the curve given by Atkins and Osborne (1950); they do not claim great accuracy for their figures.

The equation would lead to an infinite value at the absolute zero, which is very improbable. The velocity of the second sound wave appears to be approaching that of the ordinary sound wave, which is probably between 200 and $300 \mathrm{~m} / \mathrm{s}$.

## XII. Heat Conductivity

Helium II is a remarkable conductor of heat, the conductivity increasing as the temperature gradient becomes less. When the conductivity for heat is plotted against the temperature, for a range of temperature gradients (Keesom 1942, p. 287), a family of curves is obtained. These curves all have the same general shape and all pass through a maximum at about $1 \cdot 92^{\circ} \mathrm{K}$.


Fig. 6


Fig. 7
Following the argument of this paper, the conductivity would depend on the rate of replacement of kinetic energy of heat origin by kinetic energy of cohesive origin. With low temperature gradients, this exchange would take place with little departure from equilibrium conditions. The effect of a heat gradient is to cause a pressure of kinetic energy of intrinsic origin from the cool end to the hot end and to displace the heat energy to the cool end. The rate of the reaction between the condensed and expanded phases might be expected to be proportional to the product
of their concentrations, that is, $T\left(T_{\lambda}-T\right)$ and also to the actual heat content of the substance. From $1 \cdot 1$ to $2 \cdot 2^{\circ} \mathrm{K}$, the heat content is proportional to $T^{6 \cdot 6}$. It is found that by plotting $T^{6.6} T\left(T_{\lambda}-T\right)$ or $T^{7.6}(T-T)$ against the temperature, the general slope of the conductivity curves is almost exactly reproduced. In Figure 7 the full line represents $T^{7 \cdot 6}\left(T_{\lambda}-T\right)$ while the crosses represent typical values taken from Keesom's data.

Table 5

| $\partial T / \partial x \times 10^{4}$ | $1 \cdot 93{ }^{\circ} \mathrm{K}$ |  | $1 \cdot 5^{\circ} \mathrm{K}$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $Q$ calc. | $Q$ obs. | $Q$ calc. | $Q$ obs. |
| 200 | 27-7 | $29 \cdot 0$ | $11 \cdot 0$ | $12 \cdot 0$ |
| 60 | $21 \cdot 3$ | 21.0 | $8 \cdot 4$ | $8 \cdot 5$ |
| 30 | $17 \cdot 7$ | $17 \cdot 0$ | $6 \cdot 9$ | $7 \cdot 0$ |
| 10 | $12 \cdot 0$ | $12 \cdot 0$ | $4 \cdot 7$ | $4 \cdot 9$ |
| 5 | $8 \cdot 4$ | $10 \cdot 0$ | $3 \cdot 3$ | $4 \cdot 0$ |

It was observed that when $Q$, expressed in watts per square centimetre (Keesom 1942, p. 287), was plotted against $\log (\partial T / \partial x)$, multiplied by $10^{4}$, the values fell, practically, on a straight line passing through the origin. Making use of the expression covering the general slope of the curves, this gave

$$
Q=\left(T_{\lambda}-T\right) T^{7 \cdot 6} \log (\partial T / \partial x) \times 0 \cdot 31 \mathrm{~W} / \mathrm{cm}^{2}
$$

where 0.31 is an arbitrary constant.
Values calculated from this expression, at different temperature gradients and temperatures are given in Table 5, together with the observed values.

## XIII. Helium ${ }^{3}$

Unlike helium ${ }^{4}$, helium ${ }^{3}$ does not have a $\lambda$ point. It apparently remains a fluid down to the lowest temperatures. The densities have been determined by Grilly, Hammel, and Sydorick (1949) between $1 \cdot 27$ and $2 \cdot 79^{\circ} \mathrm{K}$. While an analysis of the data given by these authors, in a manner similar to that adopted for helium ${ }^{4}$, indicates an increase in the volume of $b$ at lower temperatures, suggesting a change over from an overall attractive system to an overall repulsive system, there is no evidence of the formation of a two-phase system. Following the early analysis, the stability of a second phase was dependent on the quantity $4 R T b / a(1+x)$ being less than unity, that is, in part, on the ratio $b / a$. This ratio for helium ${ }^{4}$ at its critical temperature is $28 \cdot 86 / 4 \cdot 23$, whereas for helium ${ }^{3}$ it is $35 \cdot 7 / 3 \cdot 3$. The formation of a distinct expanded form is, therefore, less to be expected in helium ${ }^{3}$ than in helium ${ }^{4}$. The increase in the apparent volume of $b$ in helium ${ }^{3}$, could, however, liberate kinetic energy and account for the fluidity of helium ${ }^{3}$ down to lowest temperatures, without the formation of a two-phase system.

## XIV. Acknowledgments

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