PHYSICAL REVIEW VOLUME 72, NUMBER 9 NOVEMBER 1, 1947

The Theory of Liquid Helium*

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(Received May 17, 1947)

A quasi-thermodynamic theory of liquid helium is developed based on very general assumptions regarding the energy spectrum of the liquid. Below the λ-point helium can be considered as a mixture of two fluids capable of two velocity fields. The macroscopic hydrodynamic equations of this system are derived. These are in the same relation to ordinary hydrodynamics as a two-body is to a one-body problem in point mechanics. The flow connected with the center of mass coordinate is associated with the transport of mass at constant entropy, the one connected with the relative coordinate (internal convection) is associated with an entropy transport at constant density. The results are in excellent agreement with experiment, in particular with the measurements of the temperature waves (second sound), the existence of which was predicted by the theory. The Bose-Einstein liquid introduced earlier is a possible molecular model consistent with the macroscopic results. Landau's theory is discussed.

I. INTRODUCTION

SEVERAL years ago F. London[1] brought forward evidence to support the idea that the peculiar phase transition of liquid helium at 2.19°K (λ-point) might be regarded as caused by the condensation mechanism characteristic of the ideal Bose-Einstein gas distorted by the presence of molecular forces which of course cannot be ignored in the case of a liquid. He showed that the various earlier attempts to explain the λ-transition by the familiar mechanisms of phase transitions of the second kind (order-disorder transition in ordinary space) are incompatible with the actual van der Waals forces of helium and with the requirements of quantum mechanics. In this situation the example of an order in momentum space, as presented by the Bose-Einstein condensation, seemed to offer a very welcome and suggestive new possibility. Moreover, the Bose-Einstein condensation demonstrated a very peculiar feature. It led to a kind of phase equilibrium of two phases inter-penetrating in ordinary space but separated in momentum space. There were good reasons to suspect that the "condensed" fraction of the atoms was the seat of a superfluid mass transfer.

Employing these ideas the present author was able to show[2] that the kinetic effects to be expected in an ideal Bose-Einstein gas revealed a close similarity to the well-known effects in helium II. Nevertheless, the theory did not seem very convincing since it was difficult to understand how the properties of a liquid could be interpreted, even qualitatively, in terms of a gas theory. The rigorous treatment of this problem would require the solution of the quantum-mechanical many-body problem. The mathematical difficulties involved have proved so far to be so tremendous that as yet it has been impossible to substantiate these ideas by the development of a rigorous molecular theory.

In view of this situation, the author has tried to avoid these difficulties by developing a somewhat more phenomenological theory of the various thermo-hydrodynamic effects in helium II.[3,4] (See also H. London.[5] For an account of the experiments, we refer to Keesom's monograph on helium.[6])

There are good reasons to expect that a quasi-thermodynamic method should be adequate to handle the problem of helium II. The peculiar properties of helium II are usually described by

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* The research reported in this paper was made possible in part through support extended the Massachusetts Institute of Technology, Research Laboratory of Electronics, jointly by the Army Signal Corps, the Navy Department (Office of Naval Research), and the Army Air Forces (Air Material Command), under the Signal Corps Contract No. W-36-039 sc-32037.

[1] F. London, Nature **141**, 643 (1938); Phys. Rev. **54**, 947 (1938).

[2] L. Tisza, Nature **141**, 913 (1938).

[3] L. Tisza, C. R. Paris **207**, 1035 and 1186 (1938).

[4] L. Tisza, J. de phys. et rad. **1**, 165 and 350 (1940).

[5] H. London, Proc. Roy. Soc. **A171**, 484 (1939).

[6] W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942).

the statement that this substance is superfluid and super-heat-conducting. Actually it is important to realize that the behavior of helium II cannot be characterized by assuming extremely small or large values of *kinetic coefficients* such as viscosity and heat conductivity. It is rather that the usual *differential equations* governing capillary flow and the transfer of heat have to be replaced by equations adapted to the particular mechanisms effective in helium II. This change in the differential equations rather than the assumption of an extreme value of the conductivity is characteristic also of superconductivity, as is apparent from the well-known theory of F. and H. London. While kinetic coefficients depend very sensitively on the nature of the molecular forces, this is usually not the case for the differential equations themselves.

The main point of the theory was the definition of the "Bose-Einstein liquid," uniting some properties of a liquid and some of a Bose-Einstein gas in a self-consistent scheme. Whereas the discussion of such a "hybrid" system could not be carried out with quantum-mechanical methods, it proved to be easily manageable from the much more schematic quasi-thermodynamic point of view. In particular, the notion of "condensation in momentum space" was extended to the Bose-Einstein liquid. Hence, below the condensation temperature, this system was supposed to have a heterogeneous character implying the existence of *two* velocity fields. The existence of two fields rather than one resulted in an "internal convection" carrying energy and entropy, but not associated with any net transfer of matter. Hence the macroscopic hydrodynamics of helium II proved to be of greater complexity than that valid for other substances and allowed the correlation of phenomena which appeared paradoxical from the point of view of ordinary hydrodynamics. The theory led also to various predictions which have been subsequently verified by experiment. The most important of these was the conclusion that inhomogeneities of the temperature would propagate according to a *wave equation* rather than the usual *parabolic equation* of heat conduction. The velocity of propagation of these "*temperature waves*" was computed as a function of the temperature. It was also indicated that an experimental verification could be obtained by exciting the temperature waves through periodic heating of helium II. A short report of these results appeared in 1938 in the form of preliminary notes,[3] but the detailed account[4] was, because of wartime conditions, not generally available until recently.

Landau, apparently unaware of these results, criticized the Bose-Einstein theory on the basis of the earlier note[2] and advanced instead a theory in which he maintained the assumption of the heterogeneous nature of helium II, but tried to justify it from a different molecular point of view based on quantum hydrodynamics.[7] As soon as the possibility of the two velocity fields was granted, the development of the macroscopic hydrodynamic equations had to proceed on the same lines as those based on the Bose-Einstein theory. In particular, Landau concluded that there should be two different modes of sound propagation in helium II with different velocities for the "first" and "second" sound. Landau did not discuss the physical meaning of this second sound wave. According to the recent account of Peshkov,[8] it was only after an attempt to excite the second sound by mechanical means had failed that the question was reconsidered by Lifshitz,[9] who concluded that the excitation of second sound could best be obtained by periodic heating of the liquid. Thus the second sound proved to be identical to the temperature waves predicted earlier on the basis of the Bose-Einstein theory. The existence of these temperature waves has been experimentally demonstrated by Peshkov[8] who measured also their velocity of propagation as a function of temperature. These results have been recently confirmed by an interesting indirect method suggested by Onsager.[10] The measurements of the temperature dependence of the velocity of propagation of second sound confirm the present author's prediction rather than that of Landau.[7, 9] It may be noted that the theoretical curves do not contain any adjustable constants but are

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[7] L. Landau, J. Phys. U.S.S.R. **5**, 71 (1941).

[8] V. Peshkov, J. Phys. U.S.S.R. **10**, 389 (1946); *ibid.* **8**, 381 (1944).

[9] E. Lifshitz, J. Phys. U.S.S.R. **8**, 110 (1944).

[10] C. T. Lane, H. Fairbank, H. Schultz, and W. Fairbank, Phys. Rev. **70**, 431 (1946); *ibid.* **71**, 600 (1947). My thanks are due Professor Lane and collaborators for communicating their results before publication.

evaluated with the empirical values of the entropy measured previously by Kapitza.[11]

The aim of the present paper is to clarify the relation between the theories and experiment, whereby it seems advantageous to proceed as far along phenomenological lines as possible. Such a procedure was adopted previously in reference 4, but the present paper is a further step in this direction. Thus it will be possible to avoid the pitfall of justifying any special molecular model by experimental results, which in reality can be also understood under broader assumptions.

Our procedure will then be to advance certain general assumptions regarding the energy spectrum of liquid helium, expressing the fact that this system unites in a peculiar way some characteristics of a liquid and of a gas (Section II). The lowest state of the system has liquid characteristics. The excited states can be classified into *compressional modes* which are also liquid-like (Debye phonons) and *shear modes* corresponding to the rearrangements of the molecules at constant density which are supposed to have a gas-like character. The technique of drawing conclusions from these assumptions will be essentially thermodynamic (Sections III and IV). Such an extension of classical thermodynamics seems to be an adequate method of dealing with second-order transitions. A discussion from the molecular point of view is, of course, of the greatest interest and will be outlined in Section V so far as it seems possible at present. Landau's theory will be discussed in Section VI.

II. THE FUNDAMENTAL ASSUMPTIONS

Let us consider a macroscopic system of helium atoms enclosed in a box of volume V. The characteristic values of the Schroedinger equation of the system, in particular the lowest energy E_0, are determined by the properties of the helium atoms and in addition depend on the volume V as a parameter. Two assumptions will now be made regarding the properties of this lowest state of the system. After a short discussion of the meaning of these assumptions, two others will follow regarding the excited states.

Postulate (*a*). *The function $E_0(V)$ has a minimum for some value $V=V_0$ of the volume:*

$$(dE_0/dV)^{V=V_0}=0, \quad (d^2E_0/dV^2)^{V=V_0}>0. \qquad (1)$$

Postulate (*b*). *The state $E_0(V)$ is characterized by a vanishing microscopic rigidity.*

Assumption (*a*) expresses the fact that at the temperature of absolute zero and with a vanishing external pressure $P=-dE_0/dV=0$, the system is in a condensed, and not in a gaseous, state. Assumption (*b*) specifies further that this state is liquid rather than solid. The postulate that a system should have a vanishing coefficient of rigidity at *absolute zero* is very far reaching. Indeed, according to classical statistics, one would expect every system which is in thermodynamic equilibrium at absolute zero to be in a crystalline state. Hence it is reasonable to define a system satisfying postulates (*a*) and (*b*) as a *quantum liquid.* Significant conclusions regarding the properties of such systems can be obtained from an analysis of the notion of "microscopic rigidity." This terminology was introduced[12,13] in order to account for the fact that ordinary (classical) liquids are in some way more reminiscent of solids than of dense gases. Even in liquids there are potential barriers opposing the rearrangements of the molecules at constant density. (Such rearrangements will be of importance for this theory; we shall refer to them briefly as *isopycnic rearrangements.*) The potential barriers constantly collapse under the impact of thermal agitation, hence no macroscopic rigidity results. There is, however, a so-called microscopic rigidity which manifests itself in various visco-elastic effects.

If a shearing stress is applied at a high frequency, the system will react as a solid and propagate transverse elastic waves. For liquids of low viscosity the frequency required for such a behavior is in the thermal range (hypersonic in contrast to ultrasonic waves). The specific heats of monatomic liquids near the freezing point show good evidence for their presence.[14]

At low frequencies, the microscopic rigidity gives rise to viscosity. This *liquid-type* viscosity should be distinguished from the *gas type* or *transport* viscosity well-known from the kinetic theory of gasses; we will call them *dynamic* and

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[11] P. Kapitza, J. Phys. U.S.S.R. **5**, 59 (1941).

[12] L. Brillouin, *Les tenseurs en mécanique et en élasticité* (Masson et Cie, Paris, 1938).

[13] J. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946).

[14] E. Bauer, M. Magat, and M. Surdin, J. de phys. et rad. **7**, 441 (1937). Also p. 349 of reference 11.

kinetic viscosity, respectively. The two viscosities give rise to the same type of macroscopic effects, but they can be clearly identified from their temperature dependences.

For the kinetic viscosity one has

$$\eta_{\mathrm{kin}} \sim \rho \bar{c} \bar{l}, \tag{2}$$

where ρ is the density, $\bar{c}$ the mean thermal velocity, and $\bar{l}$ the mean free path. η_{kin} increases slowly with the temperature.

For the dynamic viscosity one has a strongly negative temperature coefficient, since

$$\eta_{\mathrm{dyn}} \sim e^{A/kT} \tag{3}$$

where A is an activation energy clearly indicating the presence of potential barriers. The situation is illustrated in Fig. 1 where the dynamic viscosity of liquid hydrogen is compared with the kinetic viscosity of hydrogen gas. The case of hydrogen is typical of classical liquids.

The most spectacular effect of the *microscopic* rigidity is *freezing*. As the thermal agitation decreases with temperature, the potential barriers opposing molecular rearrangements organize into a crystalline pattern and give rise to the *macroscopic* rigidity of the solid.

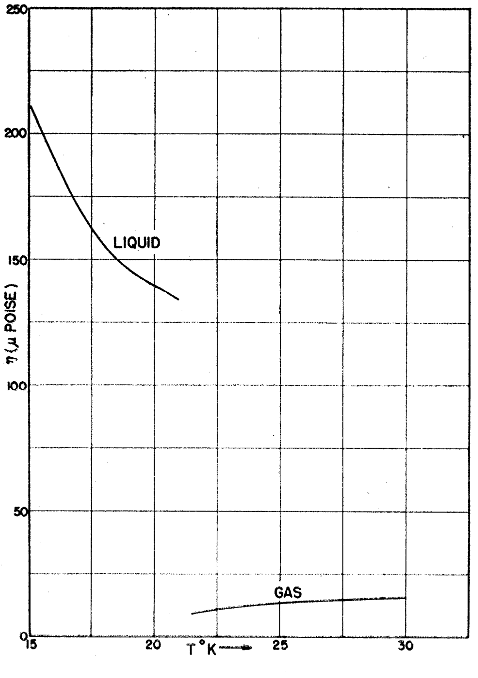

Fig. 1. Viscosity of liquid and gaseous hydrogen, from W. H. Keesom and G. E. MacWood, Physica 5, 745 (1938); A. Van Itterbeck and A. Claes, Physica 5, 938 (1938).

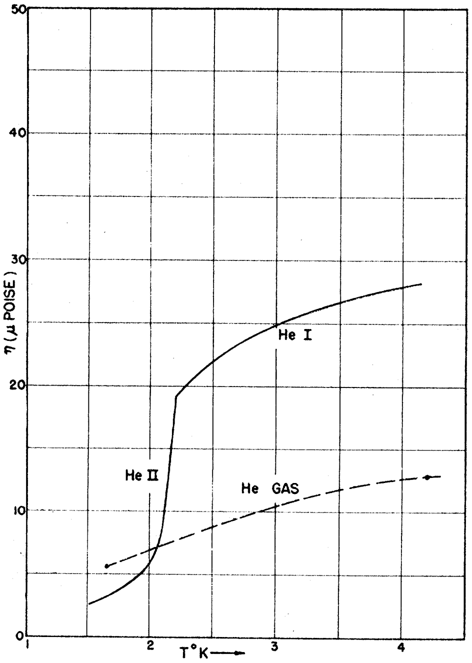

Fig. 2. Viscosity of liquid and gaseous helium from pp. 106 and 267–8 of reference 5.

The important point for the present purpose is that the propagation of transverse hypersonic waves, dynamic viscosity, and freezing are all due to the same factor, the microscopic rigidity. As helium does not solidify at low pressures, one concludes that the microscopic rigidity vanishes, as was postulated in (*b*). According to the above discussion this implies also the vanishing of the dynamic viscosity and the absence of transverse hypersonic waves. The first conclusion finds a striking verification in the measurement of viscosity. Figure 2, which shows the viscosity of helium, is to be compared with Fig. 1. Attention is drawn to the viscosity of helium gas and liquid helium I, since in the case of helium II additional complications arise which will be discussed below. It should be pointed out that in our terminology it is helium, not just helium II, that is a quantum liquid. This terminology is at variance with the rather generally adopted view that helium I is "classical" or a "normal" liquid.

A qualitative discussion of postulate (*b*) from the point of view of quantum mechanics will be found in Section V. At present we turn to the discussion of the excited states of the system.

The excited states of a continuum or quasi-continuum can be classified into compressional and shear modes of motion. (P. 277 of reference 12.) The density fluctuations connected with the first type can be analyzed into longitudinal waves. The elastic quanta, or phonons, obtained by quantization of these waves are the "elementary excitations" of the compressional modes of motion.

Regarding the shear modes, postulate (*b*) leads only to the negative statement that they cannot have the character of waves. This gap will be filled by the next assumption: Postulate (*c*). *The shear modes of motion of liquid helium (isopycnic rearrangements of the molecules) have a gaseous character. The "elementary excitations" correspond to translations of atoms (or groups of atoms) with definite values of mass momentum and energy.*

In accordance with the program formulated in the introduction, postulate (*c*) is kept in very general terms, since the macroscopic equations to be derived in the next two sections do not depend on the molecular interpretation of the "gas" introduced in (*c*). A molecular interpretation is, of course, important for the intuitive understanding of the theory and will be discussed in Sections V and VI. At present it will suffice to mention that a molecular model compatible with postulate (*c*) is the Bose-Einstein liquid. In this case the "elementary excitations" correspond to helium atoms in translational Bloch-type states.[1,4] In reference 4 the term "translational quanta" was used to emphasize that only the translational energy in excess over the zero-point energy is considered to be the energy of the "molecule."

Also a somewhat different molecular model could possibly be considered. In this case the "elementary excitations" of postulate (*c*) are groups of atoms possessing, besides their linear momentum, also an internal angular momentum. Thus, the monatomic "molecules" of the Bose-Einstein liquid are replaced by polyatomic "molecules." This difference is irrelevant for most of the thermo- and hydrodynamic phenomena considered in this paper.

The most important property of the Bose-Einstein liquid is its "condensation" in momentum space.[1,4] The essential features of this condensation phenomenon will now be postulated for our more general case.

While the elementary excitations introduced in (*c*) have the main attributes of molecules in the kinetic theory of gases (constant mass, momentum, and energy) this is true only if a definite quantum state is considered. At absolute zero no "molecules" are present, but they can be created by means of thermal excitation. In every quantum state one can distinguish the total mass of the corresponding "molecules" from the total mass of the system. On averaging over a canonical ensemble, the same kind of subdivision is obtained as a function of temperature. Hence the density of the system will be subdivided into two parts:

$$\rho=\rho_n+\rho_s \tag{4}$$

where ρ_n is the density connected with the "molecules" of the gas and ρ_s refers to the "background" in which the molecules are moving. The subscripts refer to "normal" and "superfluid," a terminology which will be explained below. The ratio ρ_n/ρ is a very important property of the system. The last postulate of the theory will be concerned with it: Postulate (*d*). *There exists a temperature T_0 such that*

$$\rho_n/\rho\begin{cases}=0 & \text{if}\quad T=0 \qquad \text{He II}\\ <1 & \qquad 0<T<T_0 \quad \text{He II}\\ =1 & \qquad T\geqq T_0 \qquad \text{He I}\end{cases}$$

with ρ_n/ρ monotonically increasing between $T=0$ and T_0. T_0 is to be identified with the lambda-point of helium.[15]

Let us consider now a volume element in helium II which is small compared to macroscopic dimensions but big enough to contain not only a large number of helium atoms but also a large number of "molecules." Averaging over the translational motion of the "molecules," one obtains a drift velocity $\mathbf{v}_n$ which will not in general coincide with the velocity of the "background" $\mathbf{v}_s$. In contrast with ordinary liquids and also with helium I, one has two densities and correspondingly two velocity fields. The

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[15] Actually ρ_n/ρ will also be a function of the pressure P and this would have to be taken into account in a refinement of the present theory.

total mass current density is

$$\mathbf{j}=\rho_n\mathbf{v}_n+\rho_s\mathbf{v}_s. \tag{5}$$

According to (*c*) every "molecule" has a momentum. Averaging over this momentum current one gets, through the procedure well-known from the kinetic theory of gases, a stress tensor. The diagonal elements will be equal to a pressure P_n (*which is to be distinguished from the liquid pressure* P) while the non-diagonal elements represent a viscous stress. This is, of course, of the kinetic type and is uniquely associated with the flow $\mathbf{v}_n$. No kinetic viscosity is associated with the flow of the background $\mathbf{v}_s$. Since the dynamic viscosity was found to be totally absent in helium, none of the mechanisms of viscosity is effective for the flow $\mathbf{v}_s$ which may hence be called *superfluid*. In particular at absolute zero at which $\rho_n=0$, $\rho_s=\rho$, helium II as a whole is superfluid.

The character of the two currents will be essentially different; this is reflected most clearly in the boundary conditions for the tangential and perpendicular components of the velocities at a solid wall at rest:

$$v_{n\parallel}=0, \quad v_{n\perp}=0 \quad \text{whereas only} \quad v_{s\perp}=0. \tag{6}$$

The kinetic viscosity of the gaseous component entails the "normal" boundary condition for the velocity, while no condition is obtained for the tangential component of the superfluid flow. The terminology "normal" and "superfluid" is thus explained.

The superfluid component can "slip" along a solid surface which is its most essential characteristic, more so than the absence of dissipation. Actually, according to experimental evidence, the superfluid flow may be associated with a dissipation of the turbulent type as soon as a critical velocity is exceeded.

The slip of the superfluid component of helium II is most effectively demonstrated in the well-known creeping of the Rollin film.[6] This is, however, a complex phenomenon for quantitative discussion, corresponding to the fact that the general hydrodynamic equations of helium II are most unwieldy. It is satisfactory that the boundary conditions (6) lead to some simple conclusions which can be quantitatively checked by experiment. This will be seen in the next section.

Finally, we have to consider the specific entropy s of the system. According to our classification of the excited states, s consists of two terms

$$s=s_n+s_{\text{phon}} \tag{7}$$

corresponding to the shear and compressional modes of motion. As indicated by the subscript, s_n is associated with the ***normal component*** ρ_n of the liquid while the contribution s_{phon} of the Debye phonons is associated with the *liquid as a whole*.

III. HELIUM II AS A MIXTURE

The proper understanding of the heterogeneous nature of helium II is made somewhat difficult by the fact that it does not conform to the terminology of the classical phase rule with its clean cut distinction between "phase" and "independent component." In one connection it is best to consider helium II as a two-phase system and in another rather as a two-component system. Both analogies have to be handled with certain qualifications.

The two-phase point of view has been emphasized by London[1] in connection with the ideal Bose-Einstein gas. Below the condensation temperature this system can be considered as a gas in equilibrium with a condensed phase, the phase separation taking place in momentum space rather than in ordinary space. The saturation gas pressure $P_n=P_n(T)$ is a function of the temperature alone. In the liquid the situation is complicated by the fact that in addition to the gas pressure P_n one has liquid pressure P. The relation between P and P_n can be better understood in terms of the second analogy: the pressure P_n appears then as an "osmotic pressure" of the normal component dissolved in the superfluid. Because of the existence of semi-permeable membranes, P_n is subject to direct observation and this analogy will serve us as a useful guide throughout this section. Two qualifying remarks have to be observed, however. In the theory of solutions the total amount of each component is constant. In helium II this is true only if adiabatic conditions are maintained. In case of heat transfer there is a transition of one component into the other which has no analogy in the case of ordinary solutions. This requirement of maintenance of adiabatic conditions is of importance also from the experimental point of view.

There is a second point in which P_n differs from the conventional osmotic pressure. A gradient of the osmotic pressure in a salt solution, for instance, gives rise to diffusion (second-order effect). In virtue of postulate (c), however, a gradient in P_n gives rise to a current (first-order effect) i.e., in this connection P_n has the character of a gas pressure. This idea will be developed in the next section.

The simplest and most direct experimental method for the verification of the heterogeneous nature of helium II and of the boundary conditions (6) consists in the measurement of the moment of inertia of a rotating vessel containing helium II. As the superfluid component will not take part in the rotation, the apparent moment of inertia of the liquid will be

$$I = I_0\rho_n/\rho,$$

where I_0 is the moment of inertia above the λ-point. This effect was first predicted by Landau,[7] and the decrease of the moment of inertia was experimentally demonstrated by Andronikashvilli.[16] This experiment constitutes the most direct, although not the most accurate determination of the important quantity ρ_n/ρ. The experimental results can be approximately represented in the form

$$\rho_n/\rho = (T/T_0)^r, \tag{8}$$

where r is a constant of value about 6. More precise methods discussed below give $r = 5.5$. It should be emphasized that *this is a purely empirical relation which cannot be derived within the framework of the quasi-thermodynamic theory.*

A related, though somewhat more involved, case is the measurement of the viscosity by means of the oscillating disk method. Although the discussion goes somewhat beyond the scope of the quasi-thermodynamic method, it should be given here because of the special interest of the problem.

As in the previous case, the presence of the superfluid component can be ignored. The results can be understood in terms of the elementary formula (2), valid for the kinetic viscosity provided the density ρ is replaced by ρ_n. In order to obtain the temperature dependence of η, one has to realize that $\rho_n\bar{l} = \text{const}$. This is equivalent to the statement that the "molecules" of the normal liquid collide only with each other. The justification and meaning of this assumption can be discussed only from the molecular point of view. (Compare Section V.) It should be mentioned also that in reference 4, the author has used at this point the ad hoc assumption $\rho\bar{l} = \text{const.}$, which is in conflict with the fundamental assumptions of the theory. This was pointed out to the author by Professor Onsager to whom he is indebted also for the correct interpretation of the experiments. The earlier discussion of the viscosity measurements has also been rightly criticized by Keesom.[6] The present assumption leads to the temperature dependence $\eta\sim\bar{c}\sim T^{\frac{1}{2}}$ for both helium I and II. This result seems to conflict with the measurements of Keesom and MacWood[17] reproduced in Fig. 2, according to which the temperature dependence of the viscosity of helium II is essentially given by $\eta\sim\rho_n/\rho = (T/T_0)^r$. An analysis of the experiment reveals, however (compare formula (1) in reference 17), that the quantity actually measured is the *viscosity multiplied by the density* which is $\eta\rho_n$ in the case of helium II. Keesom and MacWood have evaluated their measurement under the assumption of having obtained $\eta\rho$. Hence the curve in Fig. 2 has to be corrected by multiplication with the factor ρ/ρ_n, which is in agreement with the above result of the theory. Landau's interpretation of the viscosity measurement[18] is in line with the present discussion.

The next special case to be considered is that of a very thin capillary in which the flow velocity of the normal component is negligibly small. Such a capillary acts as a semi-permeable membrane, being permeable to the superfluid component alone; it can be used for the measurement of P_n in much the same way as the osmotic pressure of a salt solution is measured. The analogy with the osmotic cell leads to a qualitative understanding of the well-known fountain phenomenon in helium II.[6]

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[16] E. Andronikashvilli, J. Phys. U.S.S.R. **10**, 201 (1946).

[17] W. H. Keesom and G. E. MacWood, Physica **5**, 737 (1938); The theory of the measurement is given in G. E. MacWood, Physica **5**, 374 (1938).

[18] L. Landau, J. Phys. U.S.S.R. **8**, 1 (1944).

We proceed now to investigate the "osmotic cell" with quantitative thermodynamic methods. In order to avoid complications connected with the liquid-vapor interface (evaporation and consequently non-adiabatic transition of the normal component to the superfluid state) an osmotic cell will be constructed as follows: A small part of a long cylinder filled with helium II is compressed adiabatically by means of a semi-permeable piston. (This can actually be realized using a porous material.) During the compression the superfluid component flows across the piston, thus keeping the total density ρ constant while the values of ρ_n, P_n, and consequently also of the temperature T are increased over their values in the helium bath.[19] *Since ρ is constant such compressions will be called isopycnic.*

The basis for the application of thermodynamics to the isopycnic compression is the assumption that the flow across the piston *carries along no entropy and is reversible.* This assumption was first advanced by the author[2] who pointed out also its approximate nature.[4] In fact, as indicated above, the phonon contribution to the entropy s_{phon} is associated with the whole liquid and is carried along in particular also with the superfluid component. Hence the above assumption means that

$$s_{\text{phon}} \ll s_n, \quad s \approx s_n. \tag{9}$$

The following considerations depend essentially on this assumption which will prove to be correct for not too low temperatures.

The assumption of reversibility of the superfluid flow implies that the flow across the capillary should be slower than the so-called critical velocity marking the beginning of dissipation.

Let us now compress the cell adiabatically by applying the pressure dP on the semi-permeable piston until the osmotic pressure difference balances the external pressure $dP_n = dP$. The condition of equilibrium with respect to the superfluid mass transfer is the equality of the chemical potentials:[20]

$$\mu(T, P) = \mu(T + dT, P + dP).$$

Expanding the right-hand side and noting that $(\partial\mu/\partial T)_P = -s \approx -s_n$, $(\partial\mu/\partial P)_T = v = 1/\rho$ (v is the specific volume), one has

$$(\partial P_n/\partial T)_\rho = \rho s_n. \tag{10}$$

The fact that the temperature difference is associated with an osmotic pressure is referred to as the thermo-mechanical effect or fountain effect. Relation (10) was first derived by H. London.[5,21]

While the derivation of (9) was worded in the terminology of the two-component system, an interpretation from the two-phase point of view is equally possible: Eq. (10) is then the Clausius-Clapeyron relation. Clearly, it should contain the entropy *difference* of the two phases, i.e., s_n rather than s.

The experimental verification of (10) is rendered difficult because of the necessity of maintaining reversible conditions. This seems to have been achieved to a sufficient degree by Kapitza[11] who found the relation (10) to be valid within experimental error.

Another important relation can be derived in connection with the osmotic cell. In the course of the isopycnic compression the normal component of the fluid and the entropy associated with it are "trapped" within the cell. Denoting the volume of the cell by V, one is thus led to the following relations:

$$d(\rho_n V) = \rho_n dV + V d\rho_n = 0$$

and

$$d(\rho s_n V) = \rho(s_n dV + V ds_n) = 0.$$

Hence

$$d\rho_n/\rho_n = ds_n/s_n, \tag{11}$$

or, on integration,

$$\rho_n/\rho = s_n/s_0, \tag{12}$$

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[19] The small thermal expansion is neglected throughout this section.

[20] This follows from the principle of virtual work. It is somewhat unusual that the equality of chemical potentials is obtained for states at different temperatures. In the case of the true osmotic cell, the virtual process is the mass transfer of the solvent which is, of course, associated with transfer of energy (entropy). Hence, the equality of temperatures follows simultaneously with the equality of the chemical potentials. In the present case the superfluid flow carries no entropy or energy in excess over the zero-point value, thus the equality of the chemical potential does not imply the equality of temperatures.

[21] London's interpretation of Eq. (10) differs, however, in several respects from that of the present author. London did not distinguish between the pressures P_n and P, and assumed that the thermo-mechanical pressure depends essentially on the proximity of solid walls. The present interpretation is essential for the theory of second sound. to be discussed in the next section.

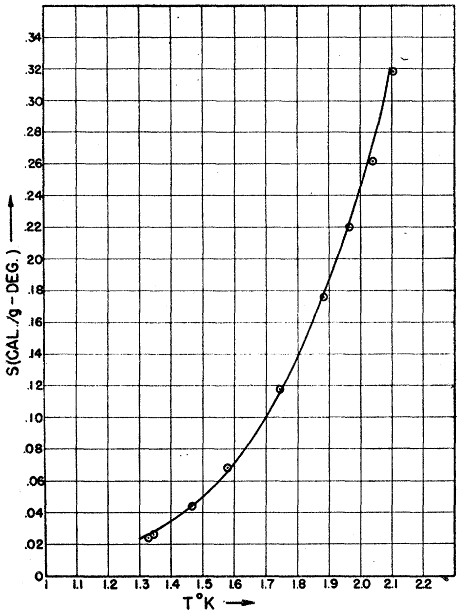

FIG. 3. Approximation of Kapitza's entropy measurements[11] (circles) with formula (13) (curve).

where $s_0 = s_n(T_0)$ is the entropy at the λ-point. This relation was obtained also by F. London.[22]

The function $s_n(T)$ plays the role of an equation of state for helium II and is of great importance for correlating its different properties. An analytic expression for this function will prove useful, we will use the expression

$$s_n = s_0(T/T_0)^r \tag{13}$$

with $s_0 = 0.405$ cal./g-deg., $r = 5.5$. It is seen from Fig. 3 that (13) represents to a good approximation the entropy measurements of Kapitza. The entropy values following from the Leyden specific heat measurements seem to be a few percent lower but have essentially the same temperature dependence. Equation (13) has certainly only a preliminary character and should be corrected when new measurements become available.

Equations (12) and (13) confirm the expression (8) for ρ_n/ρ with a more precise value for the exponent r.

We are now in a position to discuss the validity of the condition (9). The contribution of the phonons to the entropy can be tentatively represented by the Debye formula, hence $s_{\text{phon}} \sim (T/\theta)^3$. One sees that (9) would certainly fail at sufficiently low temperatures provided that (13) can be extrapolated to this region. The temperature for which $s_{\text{phon}} \approx s_n$ could be determined if the Debye temperature θ were known. The sound velocity ($\sim$240 m/sec.) leads in the usual way to $\theta \approx 18°$. Picard and Simon[23] have actually found an approximate T^3 law for the specific heat in the temperature range 0.2°–1.0° but their measurements correspond to $\theta \approx 11°$.[24] This value of θ may be too low, the specific heat too high; actually Keesom and Westmijze (p. 220 of reference 5) report a lower value for the specific heat. While new measurements of the specific heat at low temperatures are desirable, it seems that the two contributions to the entropy are of the same order of magnitude for temperatures somewhere between 0.6° and 1°K. In the extreme low temperature region one has $s_n \ll s_{\text{phon}}$; the effect of the normal component can be neglected and the liquid becomes essentially homogeneous. The main characteristic of this region is its superfluidity no longer complicated by the viscosity of the normal component and the thermo-mechanical effect.

IV. MACROSCOPIC HYDRODYNAMICS IN HELIUM II

We will now derive the general macroscopic (coarse-grained) hydrodynamical equations of helium II in the range of temperatures for which condition (9) is satisfied. Only the so-called first approximation will be considered and dissipation effects will be neglected.

The state of motion of the liquid will be described by two vector fields $\boldsymbol{\xi}_n$, $\boldsymbol{\xi}_s$ denoting the displacement of every elementary mass of the normal and superfluid liquids, respectively, from a standard state of constant densities ρ_{n0}, ρ_{s0}. The previously introduced velocities are $\mathbf{v}_n = d\boldsymbol{\xi}_n/dt = \dot{\boldsymbol{\xi}}_n$, $\mathbf{v}_s = d\boldsymbol{\xi}_s/dt = \dot{\boldsymbol{\xi}}_s$. Since we are considering processes in the first approximation, the densities ρ_n, ρ_s can change only by means of the *flow* of the components and non-adiabatic

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[22] F. London, Rev. Mod. Phys. **17**, 310 (1945).

[23] G. L. Picard and F. Simon, Abstr. of papers comm. to the Roy. Soc. London S21 (3 April, 1939); compare R. Bleaney and F. Simon, Trans. Faraday Soc. **35**, 1205 (1939).

[24] Picard and Simon claim that their measurements should be described by $\theta = 15.5°$. This value is $3^{1/3}$ times too high since they used the Debye formula valid for solids, assuming two transverse waves for every longitudinal one. The transverse waves are absent in helium.

transitions from one component to the other should be ignored. Hence separate equations of continuity are valid for the two components:

$$\Delta\rho_n/\rho_n+\nabla\cdot\xi_n=0, \tag{14a}$$

$$\Delta\rho_s/\rho_s+\nabla\cdot\xi_s=0, \tag{14b}$$

where $\Delta\rho_n=\rho_n-\rho_{n0}$ is assumed to be small compared to ρ_{n0} and similarly $\Delta\rho_s\ll\rho_{s0}$. If Eqs. (14) are differentiated with respect to the time, one gets the equations of continuity in the conventional form.

The Lagrangian of the system is an integral over the volume

$$\mathfrak{L}=\int LdV, \tag{15}$$

where L is the Lagrangian density; i.e., the difference of the kinetic and potential energy densities. The kinetic energy density is $\frac{1}{2}\rho_n\dot{\xi}_n^2+\frac{1}{2}\rho_s\dot{\xi}_s^2$. A potential energy arises because of fluctuations of the specific volume and entropy from their values in the standard state. According to well-known results of thermodynamics[25] this potential energy is equal to the minimum work required to bring forth the fluctuations Δv, Δs from the standard state. Its density is given by

$$\tfrac{1}{2}\rho[(\partial^2u/\partial v^2)(\Delta v)^2+2(\partial^2u/\partial v\partial s)(\Delta v)(\Delta s)+(\partial^2u/\partial s^2)(\Delta s)^2], \tag{16}$$

where u is the energy per unit mass.

New variables will now be introduced in terms of which both kinetic and potential energy will take a simple form:

$$\xi_1=(\rho_n\xi_n+\rho_s\xi_s)/\rho, \tag{17a}$$

$$\xi_2=\xi_n-\xi=(\xi_n-\xi_s)\rho_s/\rho. \tag{17b}$$

A simple calculation using (14), (17), and (11) leads to the equations of continuity in terms of ξ_1 and ξ_2:

$$\Delta\rho/\rho+\nabla\cdot\xi_1=0, \tag{18a}$$

$$\Delta s_n/s_n+\nabla\cdot\xi_2=0. \tag{18b}$$

The physical meaning of the new variables is apparent from (17) and (18). The "center of mass" coordinate ξ_1 corresponds to the net flow of matter at constant entropy and the "relative coordinate" ξ_2 to the flow of entropy at constant density. The possibility of the latter process distinguishes helium II from ordinary homogeneous liquids for which one would have $\xi_2=0$.

The three terms of the potential energy will now be rewritten by using simple thermodynamic transformations. One has

$$(\partial^2u/\partial v^2)_s(\Delta v)^2=(\partial P/\partial\rho)_s[(\Delta\rho)/\rho]^2, \tag{19a}$$

$$(\partial^2u/\partial v\partial s)(\Delta v)(\Delta s)=\alpha Ts/c_v[(\Delta\rho)/\rho][(\Delta s)/s], \tag{19b}$$

$$(\partial^2u/\partial s^2)(\Delta s)^2=-(\partial T/\partial(1/s))_\rho[(\Delta s)/s]^2, \tag{19c}$$

where α is the coefficient of thermal expansion, c_v the specific heat at constant volume. Remembering that $s\approx s_n$ and by using (18), the potential energy is expressed in terms of $\nabla\cdot\xi_1$ and $\nabla\cdot\xi_2$. Finally, expressing the kinetic energy in terms of ξ_1, ξ_2, one obtains for the Lagrangian:

$$\mathfrak{L}=\int\tfrac{1}{2}\rho[\dot{\xi}_1^2+(\rho_n/\rho_s)\dot{\xi}_2^2-(\partial P/\partial\rho)_s(\nabla\cdot\xi_1)^2+(\partial T/\partial(1/s_n))(\nabla\cdot\xi_2)^2-\alpha Ts_n/c_v(\partial P/\partial\rho)_T(\nabla\cdot\xi_1)(\nabla\cdot\xi_2)]dV. \tag{20}$$

An alternative form for (19b) and hence for $\mathfrak{L}$ is obtained by noting that from (10) and (11) one gets

$$-(\partial T/\partial(1/s_n))_\rho=(\rho_n/\rho)(\partial P_n/\partial\rho_n)_\rho. \tag{21}$$

The equations of motion corresponding to (20) are

$$\frac{d}{dt}\left(\frac{\partial L}{\partial\dot{\xi}_1}\right)+\nabla\left(\frac{\partial L}{\partial(\nabla\cdot\xi_1)}\right)-\frac{\partial L}{\partial\xi_1}=0 \tag{22}$$

and similar equations in ξ_2, or explicitly:

$$d^2\xi_1/dt^2-(\partial P/\partial\rho)_s\nabla(\nabla\cdot\xi_1)=((\alpha Ts_n)/c_v)(\partial P/\partial\rho)_T\nabla^2\xi_2, \tag{23a}$$

$$d^2\xi_2/dt^2+(\partial T/\partial(1/s_n))_\rho\nabla(\nabla\cdot\xi_2)=((\alpha Ts_n)/c_v)(\partial P/\partial\rho)_T(\rho_s/\rho_n)\nabla^2\xi_1. \tag{23b}$$

A numerical calculation based on the observed values of the quantities involved shows that the right-hand sides of (23) are very small. These terms representing a coupling between the ξ_1 and ξ_2 motions will hence be neglected. Equations (23) are then simply the Eulerian equations in first approximation for the two flows, respec-

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[25] Compare L. Landau and E. Lifshitz, *Statistical Physics* (Oxford University Press, New York, 1938), p. 100.

tively. In fact, by using (18) and (21) one gets:

$$d\dot{\xi}_1/dt=\partial\dot{\xi}_1/\partial t+(\dot{\xi}_1\cdot\nabla)\dot{\xi}_1=-(\nabla P)/\rho, \tag{24a}$$

$$d\dot{\xi}_2/dt=\partial\dot{\xi}_2/\partial t+(\dot{\xi}_2\cdot\nabla)\dot{\xi}_2 =-(\nabla P_n)(\rho_s/\rho\rho_n). \tag{24b}$$

By making use of the vector relation $\nabla(\nabla\cdot\xi)=\nabla^2\xi+\nabla\times(\nabla\times\xi)$, taking the divergence of the Eqs. (23) justified and replacing the total time derivatives by partials (justified for small velocities), one obtains two wave equations:

$$\partial^2(\nabla\cdot\xi_1)/\partial t^2-c_1^2\nabla^2(\nabla\cdot\xi_1)=0 \tag{25a}$$

$$\partial^2(\nabla\cdot\xi_2)/\partial t^2-c_2^2\nabla^2(\nabla\cdot\xi_2)=0 \tag{25b}$$

The value of the first wave velocity is

$$c_1=[(\partial P/\partial\rho)_s]^{\frac{1}{2}}, \tag{26}$$

and, by (21), the second wave velocity can be given in either of two alternative forms:

$$c_2=[(\partial P_n/\partial\rho_n)\rho_s/\rho]^{\frac{1}{2}}, \tag{27a}$$

$$c_2=[-(\partial T/\partial(1/s_n))_\rho\rho_s/\rho_n]^{\frac{1}{2}}. \tag{27b}$$

Finally, by using (12) and the empirical relation (13), one obtains c_2 as a function of temperature:

$$c_2=26[(T/T_0)(1-(T/T_0)^{5.5})]^{\frac{1}{2}}\text{ m/sec.} \tag{28}$$

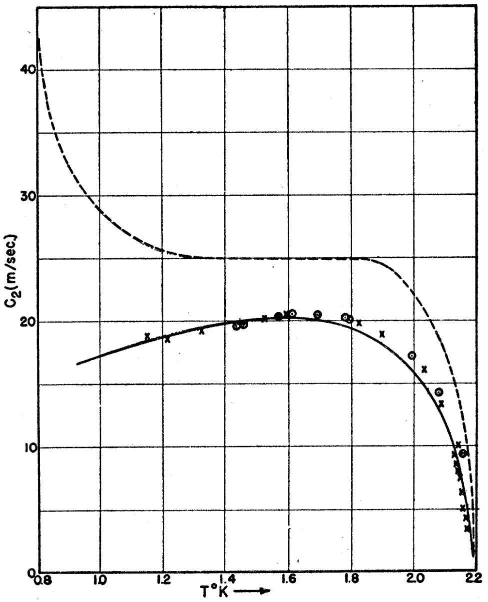

FIG. 4. Velocity of second sound. xxx-measurements of Peshkov.[8] ooo-measurements of C. T. Lane and collaborators.[10] —— formula (28) of present paper. - - - calculated by Lifshitz from Landau's theory.[9]

The physical meaning of the two waves is apparent from Eqs. (18), (8), (11). It is seen that $\nabla\cdot\xi_1$ is equal to the fluctuation of the density ρ and hence also of the pressure P. The corresponding wave has the properties of ordinary wound waves. The ξ_2 waves consist of fluctuations in s_n, ρ_n, P_n, and T. The two waves can be conveniently referred to as pressure and temperature waves,[4] or simply first and second sound.[7] The terminology of temperature waves is suggestive of the simplest way of generating these waves by periodic heating, which has actually been carried out by Peshkov[8] and by Lane and his collaborators.[18]

In the case of heat transfer between the liquid and its surroundings, the continuity equation (18b) has to be supplemented by "sources" for the normal component. If the heating occurs across a solid wall, this source can be conveniently accounted for by the boundary conditions for the perpendicular components of $\dot{\xi}_1$ and $\dot{\xi}_2$:

$$\dot{\xi}_{1\perp}=0,\quad \dot{\xi}_{2\perp}=W/Ts_n\rho, \tag{29}$$

where W is the amount of heat absorbed by the liquid across a unit area per unit time.

The very existence of the temperature waves bears out the fundamental assumptions of the theory.[26] A more quantitative check of the theories is obtained by comparison of the theoretical expressions of $c_2(T)$ with the observed values, as shown in Fig. 4. The agreement is seen to be very satisfactory. It should be noted that formula (28) contains no adjustable constants.

The figure also shows the function $c_2(T)$ computed by Lifshitz[9] on the basis of Landau's

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[26] Recently E. G. Richardson, Nature **158**, 296 (1946) expressed the view that the temperature waves might be explained within the ordinary theory of heat conduction simply by a large value of the coefficient of heat conductivity χ, and without assuming any wave equation for the temperature. Although the parabolic equation of heat conductivity actually possesses wave solutions, these waves are strongly damped (independently of the value of χ) and show a strong dispersion, their velocity of propagation being proportional to $\omega^{\frac{1}{2}}$ (ω is the frequency). The criterion of dispersion for distinguishing between the wave solutions of a parabolic and a hyperbolic differential equation has been pointed out previously.[4] The experiments[8] decide the question without ambiguity in favor of the hyperbolic equation. It may be also mentioned that the true heat conductivity in helium II is proportional to the viscosity and is of the same order of magnitude in helium II as in helium I. Its presence is completely masked by the presence of the internal convection.

theory. The reason for the discrepancy will be discussed in Section VI.[27]

The agreement between (28) and the experimental points is not complete. This is believed to be due mainly to inaccuracy of the empirical relation (13), rather than to any inadequacy of (27). It is true that the neglected dissipation effects will give an absorption and dispersion of the temperature waves and hence a modification of (27), but these effects seem to be small since Peshkov failed to find any dispersion from 30 to 10,000 c.p.s.

The discussion of the dissipation effects is beyond the scope of this theory, but the various effects should now briefly be listed.

In addition to dissipation caused by viscosity and the true heat-conductivity, there are effects characteristic of helium II. The first of these is due to non-adiabatic transitions between the two components which lead to deviations from (18b).

A second effect is due to the Debye phonons which should give rise to an absorption and dispersion of the relaxation type. This can be expected to be of importance for the second sound at low temperature ($T<1^\circ$K) and should eventually (at sufficiently low temperatures) lead to a complete attenuation of the temperature wave within one wave-length. In case the "molecules" of postulate (*c*) should have internal degrees of freedom (vortex model), another relaxation phenomenon should be expected. Considerable dissipation arises if the flow velocity exceeds the so-called critical value. This seems to be of a turbulent character.[28]

A quantitative refinement of this theory should take into account the small coupling between the ξ_1 and ξ_2 motions and also the fact that ρ_n/ρ and s_n/s_0 are functions of the pressure and not only of the temperature.

This section will be closed by a brief outline of the qualitative discussion of the experiments on heat conductivity and capillary flow.

Let us first consider the heat conductivity. Two heat reservoirs of temperatures T_1, T_2 are connected by a capillary completely filled with helium II precluding any net flow of the liquid. Hence $\xi_1=0$. The temperature difference $\Delta T=T_1-T_2$ gives rise to a difference of osmotic pressure ΔP_n and thus to a circulation in the capillary ($\xi_2\neq 0$), whereby the normal component flows towards the cold reservoir. The current is closed by a transition of the superfluid component into the normal at the warm reservoir while absorbing the heat given by (29). The reverse process takes place at the cold reservoir. The efficiency of this heat transport is about $T/\Delta T$ times larger than ordinary convection. This factor may reach very high values of the order of 1000. In the steady state the flow is limited by dissipation effects neglected in the above discussion. If the dissipation were due to the viscosity of the normal component alone, the heat current should be proportional to ∇P_n and hence to ∇T. Assuming *tentatively* Poiseuille's law for the internal convection, one gets for the heat flow

$$W=(\pi r^4 s^2 \rho^2 \rho_s)/(8\eta\rho_n)T\nabla T, \qquad (31)$$

where r is the radius of the capillary. Actually the heat current increases rather like $(\Delta T)^{\frac{1}{3}}$, (reference 5), which makes it likely that the dissipation is partly of a turbulent character. This is supported by a series of experiments carried out by Kapitza.[28]

The situation is even more complicated in the case of capillary flow. In the limiting case of very thin capillaries only the superfluid component can flow under the influence of a pressure head, say caused by gravity. Thus a temperature difference is set up between the two ends of the capillary, the outflowing liquid being colder than that staying behind.[29] The flow should thus be stopped by the osmotic pressure difference which arises. Actually the increased temperature will lead to vaporization of the liquid with a corresponding cooling and transition of the normal component to the superfluid with a continuation of the flow. In somewhat wider capillaries the

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[27] It may be noted that (27a) was first given by the author.[3] Also (28) was then given except for an undetermined constant of the order of unity. A formula similar to (27b) was derived by Landau,[7] but he obtained $s=s_n+s_{\text{phon}}$ in place of s_n. Expression (28) was first given by F. London in a review paper to be published in the Proc. Phys. Soc. The author is indebted to Dr. London for communicating his paper before publication.

[28] P. Kapitza, J. Phys. U.S.S.R. 4, 181 (1941).

[29] This was one of the first conclusions of the theory which was readily verified by experiment. J. G. Daunt and K. Mendelssohn, Nature **143**, 719 (1939). The outflowing liquid is never at absolute zero as it still contains the phonon entropy, and at least a small fraction of the normal component.

normal flow velocity also becomes appreciable and both flows are complicated by turbulence. Consequently, the thermo-mechanical pressure will be smaller than that expected from Eq. (10), which was derived under the assumption of strictly semi-permeable capillaries. In summing up, it is clear that the complexity of the results obtained with all but the narrowest capillaries is not surprising and the disentanglement of the various effects from these measurements is hardly feasible.

It would seem advisable to study the dissipative effects by measuring the absorption of first and second sound whereby the complications of turbulence are avoided. On the other hand, the study of turbulence could best be carried out at low temperatures, where the concentration of the normal component is negligible and the flow is no longer complicated by the thermo-mechanical effect and the viscosity of the normal component.

V. OUTLINE OF A MICROSCOPIC THEORY OF LIQUID HELIUM

The conclusions drawn from the postulates (*a*)–(*d*) are in good agreement with experiment; practically all the peculiar kinetic effects finding either a quantitative or at least a qualitative interpretation. Thus the task of a microscopic theory is reduced to providing a quantum-mechanical foundation for these postulates. There is at present no question of deriving the postulates from first principles, and the following discussion has only an intuitive character.

No special discussion is required for postulate (*a*) since the presence of van der Waals attractive and repulsive forces always assures its validity. In contrast to the universal nature of (*a*), the validity of postulate (*b*) is most exceptional. Systems satisfying both postulates have been called quantum liquids in Section II.

It would be desirable to find criteria for the interatomic forces which assure that the macroscopic system built of these atoms will be a quantum liquid. Although this does not seem possible at present, one can point out a peculiarity of the repulsive forces in liquid helium which seems to be at the root of this question. In an ordinary (classical) system both attractive and repulsive forces between the atoms are of the van der Waals type. In helium, however, an additional repulsive force appears which originates in the quantum-mechanical zero-point energy. It blows up the volume of the liquid to about three times the value one would expect from the atomic diameter. The importance of the zero-point energy was first recognized by F. Simon,[30] and the idea has been developed by F. London.[31] For further details we refer to these papers.

The inference from these considerations is that the absence of microscopic rigidity as postulated in (*b*) might be due to the quantum-mechanical nature of the repulsive forces. Whereas in an ordinary liquid the potential barriers opposing a shearing motion (isopycnic rearrangements of the molecules) break down under the impact of thermal agitation, in helium this happens as a result of the zero-point motion. No proof of this statement has been given so far but the following remark may prove relevant.

Consider a particle in a *cubic* box of volume V. The box is slightly deformed into a rectangular parallelepiped of volume $V+\Delta V$. The zero point energy appears here as the lowest eigenvalue E_0 of the particle. It can be easily shown that, neglecting quadratic terms in the deformation, one has

$$\Delta E_0/E_0 = -\Delta V/V. \tag{30}$$

Hence, for a shearing deformation ($\Delta V=0$), the energy is in first approximation unaffected. More generally, (30) holds for an energy level of the cubic enclosure if, and only if, the corresponding ψ function is invariant under the cubic rotation $x\rightarrow y\rightarrow z$.

Although this case is altogether too simple to be applicable to the many-body problem of liquid helium, it is hard to suppress the feeling that this selective behavior of the zero-point energy with respect to shear and compression might be of more general validity.

We turn now to the discussion of the postulates (*c*) and (*d*) from the point of the Bose-Einstein model.

As first suggested by London,[2] individual helium atoms might exist in liquid helium in

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[30] F. Simon, Nature **133**, 529 (1934).

[31] F. London, Proc. Roy. Soc. **A153**, 576 (1936); J. Phys. Chem. **43**, 49 (1939); compare also T. Nagamiya, Proc. Phys. Math. Soc. Japan (3), **22**, 492 (1940).

excited translational states associated with a definite energy and momentum in much the same way as the electrons in metals according to Bloch's theory. The Bose-Einstein statistics implies a "condensation in momentum space," hence postulate (*d*) appears as a theorem on the basis of this model.

The incorporation of London's hypothesis in the present theory considers only the shear modes of motion, and otherwise the system has the liquid characteristics as discussed above. Such a system can be conveniently called a *Bose-Einstein* liquid.[4] It is assumed that its ψ-function in a state of weak excitation can be written as

$$\Psi=\psi_0(1,2,\cdots,N)\psi_{\text{phon}}\psi_{\text{gas}},$$
$$\psi_{\text{phon}}=\textstyle\prod_i\psi_i(u_i), \qquad (31)$$
$$\psi_{\text{gas}}=\sum_P\prod_{j=1}^{N_{\text{exc}}}\exp[i\mathbf{k}_j\cdot\mathbf{r}_j].$$

The function $\psi_0(1, 2, \cdots N)$ is essentially the eigenfunction of the lowest state. *It depends on the coordinates of all the atoms.* The u_1 are the longitudinal normal modes of the system also involving the coordinates of all the atoms. In contrast to this situation ψ_{gas} depends only on the coordinates of the excited atoms. (The assumption of weak excitation implies $N_{\text{exc}}\ll N$.) The symbol $\sum_P$ represents the summation over all the permutations of the particles.

The form (41) for the ψ-function has not been derived from first principles, and it is hard to see how that could be done at present. All we intend to point out is that it is conveivable to think of a system of strongly interacting particles where the ψ-function corresponding to certain modes of motion can be factorized nevertheless. This is an important point in view of the numerous objections which had been brought up against the Bose-Einstein theory.

First, it should be pointed out that Keesom[5] was justified in rejecting the interpretation of the viscosity measurements given in reference 4. This objection concerned, however, only an erroneous application of the theory, not the theory itself. After removal of this error (see this paper, Section III and the discussion of the free path given below) the viscosity measurements of Keesom and MacWood give a particularly striking support of the theory. Apart from this instance, most of the criticism seems to stem from some misunderstanding the main source of which is in the failure to appreciate the difference between a real Bose-Einstein *gas* and a Bose-Einstein *liquid*. Several attempts have been made to replace the *ideal* by a *real* Bose-Einstein gas by introducing a self-consistent potential. This method fails to account for the correlations between the states of the individual particles which are all important in the case of a liquid. They are taken into account to a large extent by our postulates: the gaseous nature of the system is restricted to the shear modes of motion (isopycnic rearrangements), its compressibility is that of a liquid. This remark disposes of the numerous attempts which tended to prove or disprove the theory by means of the "critical opalescence" arising from the large density fluctuations in a condensed *Bose-Einstein gas*.[32] In a *Bose-Einstein liquid* the density fluctuations are determined by the liquid-type compressibility (observed, for example, in the first sound), which shows no significant anomalies around the λ-point.

The fact that the Bose-Einstein liquid allows one to take into account the correlations between the excited atomic states to a satisfactory degree is due to the artifice of formulating these correlations macroscopically rather than in quantum-mechanical terms. In other words, the difficulties of the quantum-mechanical many-body problem are not *solved*, but *by-passed* in the present theory.

Another source of misunderstanding is that in the Bose-Einstein liquid one has to distinguish "collisions" of the excited atoms from "interactions" of the atoms in general.

All atoms are strongly interacting through the mechanism of the zero-point energy precluding large fluctuations of density. In other words, the factor ψ_0 in (31) is not separable in the coordinates of the particles. In contrast to this interaction, one speaks of a "collision" if two or more atoms in definite translational states interact to make a transition into different states. In such processes translational energy

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[32] L. Goldstein, Phys. Rev. **57**, 241, 457 (1940); L. I. Schiff, Phys. Rev. **57**, 844 (1940); V. L. Ginsburg, J. Phys. U.S.R.R. **7**, 305 (1943).

and momentum are conserved. Obviously double collisions between excited and non-excited atoms are excluded by these conservation principles which assure an apparent independence of the two components. This is the basis for the assumption $\rho_n \bar{l} = \text{constant}$, which was advanced in Section III regarding the mean free path. The mechanism for the establishment of thermal equilibrium is given by multiple collisions. These tend to maintain the value appropriate to the temperature.

Finally, we conclude that the Bose-Einstein theory furnishes a self-consistent although hypothetical molecular model for the postulates (*a*)–(*d*). It is, of course, of importance to know whether there is another molecular model with the same properties. This will be discussed in the next section.

VI. DISCUSSION OF LANDAU'S THEORY

No attempt will be made here to analyze the logical connection between Landau's microscopic quantum hydrodynamics on the one hand and his macroscopic relations on the other. These relations will be considered rather from the point of view of our quasi-thermodynamic theory and the question to be answered is: What changes and additions have to be applied to the postulates (*a*)–(*d*) in order to obtain Landau's results?

Postulates (*a*) and (*b*) are made tacitly by Landau. In particular, the validity of (*b*) is essential if the Hamiltonian of the system should depend on the density alone as is implied by formula (1.10) of reference 6.

In Landau's theory, the excited atoms of the Bose-Einstein theory are replaced by "rotons." A divergence from the present theory arises in connection with postulate (*d*). There is agreement inasmuch as helium II has to be considered as a mixture of a normal and a superfluid component, but Landau defines the normal component as a "gas of phonons and rotons," leaving the superfluid component with rigorously vanishing entropy.

It is seen that the theories agree sufficiently closely to account for the similarity of the results. The difference in the role attributed to the phonons leads, however, to several observable discrepancies.

In the first place, Landau fails to get the condition of validity (9) for the thermo-mechanical effect. Accordingly Kapitza[11] suggested a cooling method which would *a priori* permit us to approach infinitely near to the absolute zero. The investigation of this effect at low temperatures should allow us to test the importance of condition (9).

A second point concerns the expression (27b) for the second sound velocity. The function $c_2(T)$ depends very sensitively on the manner ρ_n/s_n depend on temperature. Equation (12) implies generally $c_2 \sim T^{\frac{1}{2}}$ for $T \rightarrow 0$. Landau, in contrast, concludes that so far as phonons are concerned, $\rho_n \sim u_n \sim T^4$ where u_n is the phonon energy, while the corresponding entropy is $s_n \sim T^3$. This is a violation of (12) and leads in the limits of low temperatures to $c_2 \rightarrow c_1/3^{\frac{1}{2}} \approx 130$ m/sec. Thus the discrepancy between Landau's theory and the experiments (compare Fig. 4) originates in the violation of Eq. (12).[33]

Landau's discussion of phonons can be rejected already from the point of view of the quasi-thermodynamic theory. The question of rotons is more difficult since the macroscopic theory remains unchanged if the "elementary excitations" of postulate (*c*) are interpreted in terms of "rotons" rather than excited atoms. The merits of this interpretation have to be judged from more specific results. We find two results of this kind in Landau's theory. First, the exponential temperature dependence of ρ_n and s_n, and second, the high value of about 100 m/sec.

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[33] After this manuscript had been completed, Landau published a note (J. Phys. U.S.S.R. **11**, 91 (1947) where, in an attempt to account for this discrepancy, he suggested a new expression for the energy spectrum of helium. This expression was obtained by adjustment of three arbitrary constants. Apart from the unsatisfactory nature of this procedure, it tends to modify the theory in the wrong direction. Originally Landau failed to notice that every vortex element can be associated with a definite mass contained in the volume in which the vorticity is different from zero. It is a consequence of the hydrodynamic equations that this mass is an integral of the motion. In contrast to this situation, phonons are associated with the liquid as a whole.

Only elementary excitations associated with definite masses can make it understandable that the liquid breaks up into two components as required in postulate (*d*). Landau introduced such a mass by his device of the rotating vessel for rotons *and* phonons *indiscriminately.* This argument is not convincing as it tends to obtain information on a kinetic coefficient (viscosity) from equilibrium considerations. Thus Landau had ignored an important difference between phonons and rotons. In his latest paper this difference is even more blurred.

for the critical velocity. Both results are in conflict with experiment; they follow directly from Landau's assumption of a "gap" in the vortex spectrum. If this assumption is dropped, new difficulties arise, the discussion of which is beyond the scope of this paper.

Summing up, it may be said that the vortex model is in a rather unsatisfactory state. In some respects, however, the situation is not unlike that encountered in the Bose-Einstein theory. A rigorous proof or disproof of the theory seems equally difficult. Under such circumstances, it is of interest to see whether the question could be decided experimentally. Even this approach is rather difficult, since one has to consider *second-order* hydrodynamic effects which are at present little understood. A distinguishing feature of the vortices compared with the excited atoms of the Bose-Einstein theory is the existence of an internal rotational energy which should manifest itself in an absorption and dispersion of the relaxation type for first and particularly for second sound.

Interesting crucial experiments would be possible if the H^3 isotope obeying Fermi statistics would be sufficiently enriched to make flow experiments possible. Such experiments should show conclusively whether the Bose-Einstein statistics are of any fundamental importance for the phenomenon of superfluidity. If liquid He^3 should not be superfluid, this fact could be actually used for the enrichment of this isotope as has been recently suggested by J. Franck.[34]

VII. CONCLUSIONS

In the discussion of the properties of liquid helium, it is useful to distinguish three ranges of temperature in which the liquid shows essentially different characteristics. In addition to the well-known modifications helium I and II, separated by a sharp λ-point, there is a gradual transition between a low temperature and high temperature domain in helium II. The transition region is somewhat below 1°K, but its location needs further experimental study. In the low temperature region, the entropy is due mainly to the elastic phonons (elementary excitations of the compressional modes), whereas in the high temperature region the phonon contribution is negligible compared with that of the elementary excitations of shear modes (isopycnic rearrangements of the liquid). This contribution is responsible for the anomaly in the specific heat and has a "gaseous" nature. The main properties of the liquid are as follows:

Helium I

From the macroscopic point of view, this modification shows a "normal" hydrodynamic behavior; its coefficient of viscosity is, however, rather remarkable. In ordinary liquids the viscosity has a negative temperature coefficient because of the "microscopic rigidity." This type of viscosity can be called *dynamic viscosity*, to be distinguished from the *kinetic viscosity* which is observed in gases and which has a positive temperature coefficient. The qualitative understanding of the properties of liquids is greatly facilitated by the concept of *microscopic rigidity*. However, the difficulties of giving to this notion a quantitative formulation seem to be responsible in no small degree for the lack of a satisfactory kinetic theory of liquids. Hence it seems to be of interest that helium I has a kinetic and *no* dynamic viscosity revealing the complete absence of microscopic rigidity. The comparison of ordinary liquids with helium I should be useful for the disentanglement of the gas-like and solid-like properties of liquids.

Helium II. Low Temperature Regions
($0<T\lesssim 1°K$)

The main characteristic of the liquid in this temperature range is its superfluidity which implies that the liquid can slip along solid walls. This is demonstrated in the spectacular creeping phenomena. Beyond a certain critical velocity, the superfluid flow may be associated with dissipation, apparently of a turbulent character.

Helium II. High Temperature Region
($1°\lesssim T<2.19°K$)

In this "anomalous" region the liquid is a mixture of a normal component (like helium I) and a superfluid component (like the low temperature form of helium II). The main object of the present paper was to develop the macroscopic thermo-hydrodynamic properties of such a two-

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[34] J. Franck, Phys. Rev. **70**, 261 (1946).

fluid system. The results are in excellent agreement with experiment. Minor discrepancies may well be due to small inaccuracies in the caloric measurements, although the theory will have to be refined to include small effects neglected at present, like dissipation and the dependence of ρ_n/ρ on pressure. The formalism developed seems to furnish valuable criteria for the consistency of measurements and might possibly be used to establish the thermodynamic temperature scale.

The principal problems for further experimental and theoretical research seem to be as follows:

(1) The derivation of the postulates of the quasi-thermodynamic theory from first principles. In particular, establishing the correct molecular model which would lead to these postulates. At present the choice seems to be between the Bose-Einstein liquid and possibly the vortex model (modified Landau theory). The experimental approach to this problem has been briefly discussed at the end of Section VI.

(2) *The clarification of the nature of the pure superfluid liquid* (*helium II near absolute zero*). This problem has not been discussed in the present paper. According to Landau, the superfluid state is characterized by the condition curl$\mathbf{v}_s=0$. The question has been further discussed by F. London[18] and by Onsager.[35] So far, superfluidity (capillary flow and the creeping phenomenon) has been studied experimentally only above 1°K where the effects have been greatly complicated by the thermo-mechanical effect and the viscosity of the normal component. Experiments below 1°K where these effects practically vanish would be greatly desirable. Of particular interest is the investigation of the dissipation arising above the critical velocity. This seems to be of turbulent character; hence, a unique opportunity is offered for studying turbulence in the absence of viscosity (no boundary layer). On the other hand, this turbulence will be influenced by quantum effects.

The author wishes to extend his thanks to Dr. F. London for a long series of discussions extended over a period of years. They have led to the clarification of many of the questions considered in this paper. His thanks are also due Dr. Lars Onsager for stimulating discussions.

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[35] Private communication.

PHYSICAL REVIEW VOLUME 72, NUMBER 9 NOVEMBER 1, 1947

Theory of the Ferroelectric Effect and Clamped Dielectric Constant of Rochelle Salt

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(Received July 25, 1947)

Using the crystal structure determination of rochelle salt made by Beevers and Hughes, a theory of the ferroelectric effect and clamped dielectric constant has been worked out using the displacement of the hydrogen nucleus in the 1–10 hydrogen bond as the ferroelectric dipole. This theory has only one disposable constant, β, the factor of proportionality between the polarization and the Lorentz internal field. Taking the oxygen separation found by x-rays, the dielectric constant for electrons and atoms found by experiment, and the number of molecules per cubic centimeter found from the x-ray cell determinations, the value of β becomes 4.07 which agrees well with the theoretical value $4\pi/3$ for an isotropic substance. This theory accounts for the clamped dielectric constant at low field strengths, which as shown by measurements presented here, has maximum values at -18°C and $+24$°C, the Curie temperatures for the free crystal. This shows that the anomaly must lie in the clamped dielectric constant alone and not in the interaction of the clamped dielectric constant and the piezoelectric effect. This model also accounts for recent measurements of W. A. Yager which show that the dipole dielectric constant is relaxed at a frequency of about 5×10^9 cycles.

I. INTRODUCTION

ALL measurements of the properties of rochelle salt indicate that the piezoelectric and elastic properties are normal and that all the anomalies reside in the "clamped" dielectric constant, i.e., the dielectric constant measured in the absence of strain. The piezoelectric stress has been found to be directly proportional to the