

# Planck's Constant and Low Temperature Transfer

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## 1. INTRODUCTION

IT is generally considered rather certain that the peculiar low temperature transfer processes which occur in the superconducting state characteristic of certain metals and in the superfluid state of liquid helium below 2.19°K (liquid He II) cannot be understood on the basis of classical physics, or rather on the basis of that familiar mixture of quantum statistics and classical mechanics applied to certain energy surfaces ("Brillouin-Zones")—which procedure, as one knows, has found numerous successful applications in the theory of metals. As an admission of ignorance it has become customary to say that these "super-transfer" phenomena must be caused by some elementary mechanisms in which quantum mechanics plays an essential role. But up to the present, it has not been possible to substantiate the alleged quantum nature of the supertransfer mechanisms by a satisfactory molecular theory. As a first step in the direction towards such a future theory, one might expect to see, at least, that the occurrence of these low temperature phenomena is conditioned by something of the order of magnitude of Planck's constant. In fact it is surprising that nothing of this sort is known thus far.

Daunt and Mendelsohn<sup>1</sup> recently assembled some evidence for an interesting analogy between the surface flow of liquid helium II and the electric surface currents in a superconductor. In particular they stressed the fact that there are in both cases upper limits for the current densities, which considered as functions of temperature are known to have in either case a similar character; namely, they both start with a finite slope at the temperature at which the superfluid state begins, and they both become temperature independent near absolute zero. The authors suggested that these critical current densities

<sup>1</sup>J. G. Daunt and K. Mendelsohn, *Nature* **150**, 604 (1942).

might indicate the number of particles per cm<sup>3</sup> which are involved in the superfluid or superconducting transfer. However, they gave no hint why such a connection should exist; nor did they give any support to their view by presenting empirical evidence concerning the number of superfluid or superconducting particles.

While this so far quite qualitative analogy may appear rather accidental, it might be of interest to draw attention to the fact that the parallelism goes possibly further than at first suspected. It can be given the form of an *inequality* in which a quantity of the order of Planck's constant actually appears as a kind of limiting surface transfer velocity and which in fact expresses a connection between the critical rate of transfer and the number of superfluid or superconducting particles.

In order to show this, we shall refer both kinds of surface current, the supercurrents as well as the helium surface currents, to the same units. Both currents will be described by the rate of transfer,  $R$ , which we define as the mass in grams transferred per sec. through one cm width of surface. Since in reality a current is never confined to a strictly mathematical surface,  $R$  is the integral

$$R = \int j dx, \quad (1)$$

where  $j$  is the density of the three-dimensional mass current. The direction of the current is assumed to be parallel to the surface,  $x$  is the direction perpendicular to the surface, the integration being taken across the more or less extended region to which the "surface" current actually is confined, sharp curvatures of the surface being excluded. Obviously  $R$  is of the dimension ( $\text{g cm}^{-1} \text{sec}^{-1}$ ). If we now compare this quantity with the number of superfluid particles per cm<sup>3</sup>,  $n$ , we notice that the ratio  $R/n$  has the dimension ( $\text{g cm}^2 \text{sec}^{-1}$ ), i.e., the same dimension as an angular momentum. In the

following we shall show that in the few cases in which sufficient data are available the maximum value of  $R$  is of the order  $nh/2\pi$ , possibly just reaching this value at absolute zero.

A comparison with the quantum conditions (commutation rules) of quantum hydrodynamics indicates that by this relation the supertransfer processes are placed precisely within those limits in which classical hydrodynamics is indeed no valid approximation and actual consideration of quantum theory is indispensable.

2. SUPERCONDUCTIVITY

Considering first the case of superconductivity, one may express the mass current density  $j$  by the density  $J$  of the electric current,  $j = -mJ/e$ , and  $J$  in turn by the magnetic field  $H$  by means of  $J = (c/4\pi) \text{curl } H$ . Thus one obtains for the rate  $R$  of the mass transfer per cm surface cross section of a sufficiently large superconductor:

$$R = -\frac{m}{e} \int J dx = -\frac{mc}{4\pi e} \int \frac{\partial H}{\partial x} dx = \frac{mc}{4\pi e} H_s. \quad (2)$$

Here  $H_s$  = magnetic field at the surface and the integration is to be directed, as in (1), perpendicularly to the surface of the superconductor into its interior. The superconductor is supposed to be sufficiently large, i.e., large enough so that in some depth the magnetic field can, for all practical purposes, be assumed as zero. We will in addition assume the specimen as cylindrical and oriented parallel to the magnetic field, so that considerations of demagnetizing reactions by the specimen on its surroundings can be dispensed with. Then  $H_s$  is simply identical with the external field.

The realization of the superconducting state of a superconductor as assumed above is restricted by the condition

$$H_s \leq H_c, \quad (3)$$

where  $H_c$  is the so-called critical (or threshold) field strength, which is a certain function of temperature,  $H_c(T)$ , and has been measured for most known superconductors over a wide range of temperature. The quantity  $H_c$  according to (2) defines a critical value  $R_c$  for the surface mass-transfer  $R$ :

$$R_c = (mc/4\pi e)H_c. \quad (4)$$

In Fig. 1 we have drawn  $R_c$  as a function of temperature for Hg, the critical magnetic field strength being taken from measurements of A. D. Misener.<sup>2</sup>

As to the number of superconducting electrons per cm<sup>3</sup>,  $n$ , we have only some indirect information, which is derived from measurements of the so-called penetration depth,  $\lambda$ , that is the depth to which magnetic fields ( $H_s < H_c$ ), and currents are confined in a superconductor. This  $\lambda$  is defined by the relation

$$\text{curl } \lambda^2 J = -(c/4\pi)H, \quad (5)$$

which is assumed as the basic relation between magnetic field and electric current density in the electrodynamic of the superconductor.<sup>3</sup> The connection between this  $\lambda$  and  $n$  is then given by

$$\lambda^2 = (1/4\pi)(mc^2/ne^2). \quad (6)$$

It is at present not yet clear how  $n$  is to be interpreted in terms of an "effective" number of free electrons as used in the electronic theory of metals. We may consider (6) as the definition of that number  $n$  of electrons which would produce a magnetic screening as described by (5) if the electrons were perfectly free.

Measurements of  $\lambda$  are so far available only for Hg and, though on a somewhat less reliable basis, for Sn. In Fig. 1 we have plotted the values

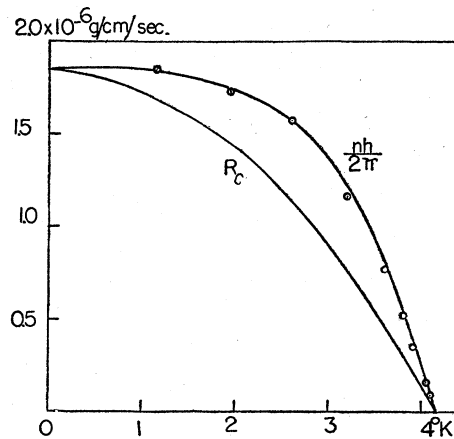


FIG. 1. Number of superconducting particles,  $n$ , and critical rate of superconducting mass transfer,  $R_c$ , for mercury as functions of temperature.

<sup>2</sup> A. D. Misener, Proc. Roy. Soc. A174, 262 (1940).

<sup>3</sup> F. London and H. London, Physica 2, 341 (1935); Proc. Roy. Soc. A149, 71 (1935).

for  $nh/2\pi = mc^2h/8\pi^2e^2\lambda^2$ , for Hg along with those of  $R_c$ , using the same scale  $10^{-6}$  g sec. $^{-1}$  cm $^{-1}$  for both quantities. The values of  $\lambda$  are based on measurements of the magnetic susceptibility of a very fine preparation of colloidal mercury ("HgA") by Shoenberg<sup>4</sup> which values agree well with those obtained by a quite different method by Appleyard, Bristow, H. London, and Misener<sup>5</sup> with fine mercury films. The numerical evaluation of  $\lambda$  from Shoenberg's measurements requires the knowledge of the average radius  $r$  of the colloidal particles. The value for  $\langle r \rangle_{Av}$  given by Shoenberg is  $\langle r \rangle_{Av} = 5 \times 10^{-6}$  cm which value has been determined by measuring the polarization of scattered light. Plotting  $nh/2\pi$  in Fig. 1 we have assumed  $\langle r^2 \rangle_{Av} = (4.63 \times 10^{-6})^2$ , which assumption is certainly quite within the range of the precision of such a measurement. This value has been chosen because it leads to an exact equality of  $R_c$  and  $nh/2\pi$  at  $T=0^\circ$  abs. However this choice is quite arbitrary, and one cannot at present say much more than that  $R_c$  and  $nh/2\pi$  are, for Hg, of the same order of magnitude,  $R_c$  differing from  $nh/2\pi$  nowhere by more than a factor between  $\frac{1}{2}$  and 1.

For tin the constant  $\lambda$  has so far been determined only by means of a quite different and somewhat more indirect method, namely by measuring the heat produced within a superconductor in a high frequency field.<sup>6</sup> The numerical evaluation of these measurements with respect to the quantity  $\lambda$  is, however, dependent on some special assumptions concerning the existence and the behavior of normal conducting electrons in a superconductor, and it appears that the final evaluation of these experiments still requires further discussion.<sup>7</sup> At any rate the available values also fulfill the inequality  $R_c \lesssim nh/2\pi$ . In actual fact  $R_c$  is found to be by a factor of about  $\frac{1}{6}$  smaller than  $nh/2\pi$ . At present it seems, however, not justified to attribute particular significance to this detail.

<sup>4</sup> D. Shoenberg, Proc. Roy. Soc. **A175**, 49 (1940).

<sup>5</sup> E. T. S. Appleyard, J. R. Bristow, H. London, and A. D. Misener, Nature **143**, 433 (1939); Proc. Roy. Soc. **A172**, 540 (1939).

<sup>6</sup> H. London, Nature **133**, 497 (1934); Proc. Roy. Soc. **A176**, 522 (1940).

<sup>7</sup> The difficulty in evaluating these results is connected with the fact (reference 6) that already the normal conductivity of tin becomes anomalously small for high frequencies and low temperatures.

### 3. THE NUMBER OF SUPERFLUID PARTICLES IN LIQUID HELIUM

Many properties of liquid helium II indicate that at a given temperature only a *fraction* of the atoms is actually responsible for the superfluid transfer processes:

1. There is no transition heat at the transition point into the superfluid state (" $\lambda$ -point"); only a discontinuity of the specific heat occurs accompanied by a rapid change of entropy over an extended temperature interval below the transition temperature (transition of "second kind") which indicates a *gradual* transformation, not a simultaneous change of state of all atoms at a certain temperature.

2. Liquid helium II shows a quite normal viscosity of the same order ( $\eta \sim 10^{-5}$ ) as liquid helium I (above the  $\lambda$ -point) if measured, not by the flow through narrow capillaries or slits, but rather by the motion, say, of a disk immersed in the liquid.<sup>8</sup> In apparent contradiction to the latter, flow experiments show an immeasurably small viscosity (or rather a peculiar "super-fluid" transfer, which cannot be described in terms of ordinary viscosity). It had been proposed<sup>9</sup> to resolve this contradiction by assuming that the superfluid transfer is not necessarily carried out by all atoms, but possibly only by a certain fraction of them, say, by those which are in some special quantum state. The remainder of the atoms might be subject to dissipation of momentum and thus account for the frictional work done on the disk, whereas in the flow experiments with very narrow channels, these atoms would be almost completely immobilized and consequently not be involved in the transfer.

3. It is impossible to empty entirely a thermally isolated container of liquid helium II by means of superfluid transfer processes alone.

This latter property will be discussed presently since it has apparently not yet received due attention.

Without reference to a specific molecular model, it is necessarily somewhat arbitrary how one defines, for a given quantity of He II, and for given temperature and pressure, the fraction

<sup>8</sup> W. H. Keesom and G. E. MacWood, Physica **5**, 737 (1938).

<sup>9</sup> L. Tisza, Comptes rendus **207**, 1186 (1938).

of particles considered as superfluid. However, each of the three properties named above leads actually to about the same result, and so we probably shall not be very far from the truth if we define the superfluid fraction as the maximum amount of liquid which can be separated from a given thermally isolated quantity of He II solely by means of superfluid transfer processes. In the following we will calculate this fraction.

The experiments of Kapitza<sup>10</sup> show very conclusively that the entropy current of helium II flowing through a very narrow channel must be very nearly zero, a result which was first predicted by Tisza<sup>11</sup> on the basis of a kinetic model of He II proposed by the present author.<sup>12</sup> If the helium leaving the channel actually had an entropy of exactly zero, its temperature would be also exactly 0° abs. Kapitza's experiments cannot, of course, exclude the possibility that a very small amount of entropy is being transmitted through the channel. In reality, with channels of a finite size there will certainly be at least some ordinary viscous transfer. Possibly also the small amount of entropy proportional to  $T^3$  observed by Simon and Pickard<sup>13</sup> below 0.8°K might not be separated by even the finest channels. In this case the temperature of the helium leaving the channel would be appreciably different from zero. In order to simplify matters we shall, however, assume that the entropy current through a sufficiently fine capillary is exactly zero.

From simple thermodynamics<sup>14</sup> it follows that two containers ( $A$  and  $B$ ) of liquid He II connected by a fine capillary are in equilibrium if the pressures  $p_A$ ,  $p_B$  and the temperatures  $T_A$ ,  $T_B$  in the two containers fulfill the condition

$$g(p_A, T_A) = g(p_B, T_B), \quad (7)$$

where  $g(p, T)$  is Gibbs' thermodynamical potential per gram. We assume that according to Kapitza or Tisza no entropy is being transferred through the capillary, which statement, by the way, is *not* a consequence of (7) but implies a

<sup>10</sup> P. L. Kapitza, *J. Phys.* **5**, 59 (1941).

<sup>11</sup> L. Tisza, *Nature* **141**, 913 (1938).

<sup>12</sup> F. London, *Nature* **141**, 643 (1938); *Phys. Rev.* **54**, 947 (1938).

<sup>13</sup> G. L. Pickard and F. Simon, *Proc. Roy. Soc.* **A173**, 21 (1939).

<sup>14</sup> H. London, *Nature* **142**, 612 (1938); *Proc. Roy. Soc.* **A171**, 484 (1939).

separate hypothesis as to the absence of a "Thomson heat"<sup>14</sup> along the capillary where there is a temperature gradient. If we take care that the container  $A$  is thermally isolated during any process in which  $M$  grams of He II initially at pressure  $p$  and temperature  $T$  are reduced to  $M_A$ ,  $p_A$ ,  $T_A$  then we have no change of entropy in  $A$ :

$$M_A s(p_A, T_A) = M \cdot s(p, T). \quad (8)$$

Here  $s$  is the entropy per gram.

Let us now consider a process in which, by applying a suitable pressure difference, the liquid He is pressed from  $A$  to  $B$ . Suppose that during the process the pressure in  $B$  is kept zero and that in the beginning  $B$  was empty. If actually no entropy can go through the capillary and  $B$  is thermally isolated, it follows that  $T_B = 0$  and we may write (7)

$$g(p_A, T_A) = g(0, 0). \quad (7')$$

This equation gives the equilibrium pressure  $p_A$  for any temperature  $T_A$ . Accordingly the process does not start at the initial temperature  $T$  in  $A$  unless the pressure in  $A$  is a little larger than that given by the equation

$$g(p, T) = g(0, 0). \quad (9)$$

With gradually increasing pressure in  $A$ , more and more helium will be pressed through the capillary, while at the same time the temperature rises. Equation (7') permits one to express  $p_A$  as function of  $T_A$ ,  $p_A = f(T_A)$ , which substituted in (8) gives  $M_A$  as function of  $T_A$  and the initial values,  $M$ ,  $T$ ,  $p$ :

$$M_A = M \frac{s(p, T)}{s(p_A, T_A)} = M \frac{s(f(T), T)}{s(f(T_A), T_A)}. \quad (10)$$

The process comes to a standstill when the helium in  $A$  reaches the  $\lambda$ -line, i.e., the line in the  $p$ - $T$ -plane which separates the superfluid state from the ordinary liquid state. Above the  $\lambda$ -line only viscous flow is possible, which we disregard anyway. If  $M_\lambda$ ,  $p_\lambda$ ,  $T_\lambda$  are the values for which our process reaches the  $\lambda$ -line the fraction of helium that has passed through the capillary is given by

$$\frac{M - M_\lambda}{M} = 1 - \frac{s(f(T), T)}{s(p_\lambda, T_\lambda)}. \quad (11)$$

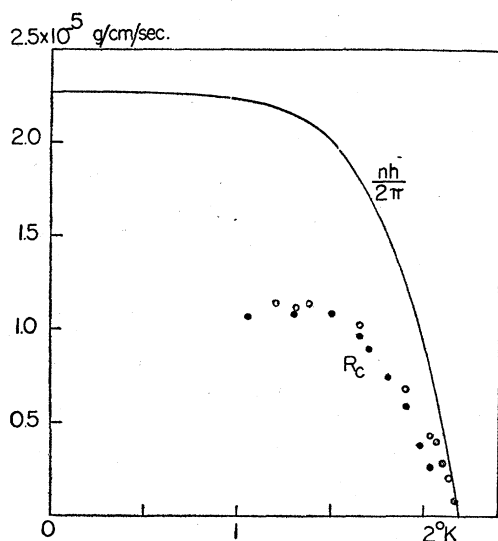


FIG. 2. Number of superfluid particles,  $n$ , and critical rate of superfluid transfer,  $R_c$ , for liquid helium II as functions of temperature.

We may determine this fraction numerically by using for  $g(p, T)$  the following empirical expression:

$$g(p, T) = 6.9p - 0.0205p^2 - 0.0317T^{6.6} \times (1 + 0.0175p + 0.00117p^2) \text{ cm}^3 \text{ atmos./g}, \quad (12)$$

( $p$  in atmospheres), which has been obtained by interpolating and integrating the values of  $s = -\partial g/\partial T$  and  $\rho = (\partial g/\partial p)^{-1}$ , given by Keesom and Keesom.<sup>15</sup> The values used are confined to the region between 1.2°K and the  $\lambda$ -line; they do not account for the fact that for temperatures below 0.8°K the specific heat has been found to follow a  $T^3$ -law.<sup>13</sup> However, in this region the entropy is already very small anyhow. Between 1.2° and the  $\lambda$ -line formula, (12) represents the experimental data fairly well.

With (12) one obtains for Eq. (7):

$$6.9p_A - 0.0205p_A^2 - 0.0317T_A^{6.6} \times (1 + 0.0175p_A + 0.00117p_A^2) = 0, \quad (13)$$

or for small pressure within sufficient accuracy:

$$p_A = 0.0046T_A^{6.6}. \quad (14)$$

<sup>15</sup> W. H. Keesom and Miss A. P. Keesom, *Physica* **1**, 128, 161 (1933-4); *Leiden Comm.* 240 (1936).

The  $\lambda$ -line is reached for  $T_\lambda = 2.18^\circ\text{K}$  and  $p_\lambda = 0.79$  atmos. Thus we have always  $p_A \leq 0.79$  atmos., and we were justified in neglecting the higher terms in  $p_A$  of Eq. (13).

The entropy given by (12) is

$$S = -\frac{\partial g}{\partial T} = 0.005T^{5.6}(1 + 0.0175p + 0.00117p^2) \text{ cal./}^\circ\text{K g}. \quad (15)$$

According to (11) we thus obtain for the fraction  $(M - M_\lambda)/M$  of helium that has passed the capillary:

$$(M - M_\lambda)/M = 1 - (T/T_\lambda)^{5.6}. \quad (16)$$

Here again the terms in  $p$  and  $p^2$  have been neglected. If we had preferred to keep the pressure in  $A$  constant and correspondingly had lowered the pressure in  $B$ , according to (7), we would have obtained the same result (16) even without neglecting the terms in  $p$  and  $p^2$ . The same would be the case if we had used the mechanism of the helium-pump of Allen and Jones<sup>16</sup> in order to empty container  $A$ .

So far we have not concerned ourselves with determining the *maximum* fraction which could be transferred by any adiabatic superfluid process. According to (11) this maximum will be reached if the process ends at such values ( $p, T$ ) for which the entropy per g of liquid He II has its maximum value. The measurements of Keesom show that this entropy maximum is located at the lower end of the  $\lambda$ -line (i.e., for  $p = 0.05$ ,  $T = 2.19^\circ$ ). The above considered processes all end very close to this point; they therefore yield just this maximum. Since the total number of atoms per  $\text{cm}^3$ ,  $n_0$ , for He II is for small pressure about  $2.2 \times 10^{22}$ , we obtain as the number of superfluid atoms per  $\text{cm}^3$ ,  $n$ :

$$n = n_0 \left( 1 - \frac{s(p, T)}{s(0.05, 2.19)} \right) \text{ cm}^{-3}, \quad (16')$$

or for not too large pressure approximately:

$$n \approx 2.2 \times 10^{22} (1 - (T/2.19)^{5.6}) \text{ cm}^{-3}. \quad (16'')$$

<sup>16</sup> J. F. Allen and H. Jones, *Nature* **141**, 243 (1938).

#### 4. THE CRITICAL FLOW VELOCITY IN HELIUM II

Most available data concerning the flow of liquid helium II do not permit a numerical determination of the critical flow velocity of the superfluid transfer. In fact it is not yet entirely certain whether the superfluid transfer is generally confined to the neighborhood of the solid surfaces. There seems, however, to be consent that there is a critical transfer velocity independent, within certain limits, of pressure. One difficulty in interpreting the measurements is caused by the fact that unless one uses extremely narrow channels, the supertransfer appears usually mixed with ordinary viscous flow so that special devices had to be invented in order to exclude or reduce the viscous flow. It is the nature of such devices (as Allen's and Misener's tubes filled with compressed fine wires or packed with a fine powder) that they are geometrically not so well defined as to permit speaking of the width of surface. In addition, the sharp curvatures of those surfaces bring a new element into the matter which might affect the mechanism as it does in the case of very small superconductors. Another difficulty, but one which can in principle be dealt with, is connected with the existence of the thermo-hydrodynamical effect. This necessitates a very careful control of any temperature changes, eventually brought about by the transfer itself, since even very small temperature differences are according to Eq. (7) connected with relatively large pressure differences which have to be taken into account. This excludes the discussion of older measurements where such precautions have not been observed. The measurements of Kapitza<sup>10</sup> are probably the ones which have been done under the most closely defined conditions. Unfortunately, his measurements have not yet been extended into the region where the existence of a critical flow velocity can be expected.

The measurements of Daunt and Mendelssohn<sup>17</sup> with the mobile helium films appear at present to be the only data of which we can reasonably make use. They fit well with Allen's and Misener's measurements<sup>18</sup> with the very

<sup>17</sup> J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. **A170**, 423 (1939).

<sup>18</sup> J. F. Allen and A. D. Misener, Proc. Roy. Soc. **A172**, 467 (1939).

narrowest channels in tubes filled with compressed fine wires ("tube C"), which shows that the estimated geometric surface area of the channels cannot be very far from correct. In Fig. 2 we have plotted, as functions of  $T$ , the quantity  $nh/2\pi$  as given by Eq. (16'') and on the same scale the values for the critical surface transfer  $R_c$ . The values of Daunt and Mendelssohn are marked by dots, those of Allen and Misener by circles. Below 1.5°K the former values appear somewhat erratic and might still be considered with due reserve. At any rate it is evident again that here also, in the case of liquid helium II, the ratio  $R_c/n$  differs from  $h/2\pi$  nowhere by more than a factor between  $\frac{1}{2}$  and 1.

#### 5. GENERALIZATION

The experimental evidence we could assemble is evidently too scant to permit any safe generalization. Indeed it would be very desirable to have more data available. Yet the cases discussed so far are conclusive enough to demonstrate that they fall under the jurisdiction of quantum kinematics. We shall show that the inequality

$$R \lesssim nh/2\pi, \quad (17)$$

which we have encountered in the previous empirical discussion has a close relationship to the commutation rules of quantum hydrodynamics. In order to show this we shall first write (17) in a somewhat different form.

A current which is confined to the neighborhood of a surface must show a decrease of current density  $j$  towards the interior perpendicular to the transfer direction or  $j$  must have a curl. If  $\lambda$  is the "depth" of the surface current and if we assume that

$$\lambda |\text{curl } j| \simeq |j|, \quad (18)$$

then the rate of surface transfer,  $R$ , can be written:

$$R = \int j dx \simeq \lambda j_{\max},$$

and the inequality (17):

$$\lambda j_{\max} \lesssim nh/2\pi. \quad (17)$$

Making use of (18) once more we may eliminate

$\lambda$  and obtain:

$$j_{\max}|j| \lesssim (nh/2\pi)|\text{curl } j|,$$

or *a fortiori*:

$$j^2 \lesssim (nh/2\pi)|\text{curl } j|, \quad (19)$$

or also:

$$j^2/2mn \lesssim (h/4\pi m)|\text{curl } j|. \quad (19')$$

In this form (19') the inequality (17) simply expresses a restriction for the hydrodynamical energy density  $j^2/2mn$  of the supertransfer. The curl of the current density times  $h/4\pi m$  appears as the upper limit for the hydrodynamical energy density. This restriction, by the way, has nothing to do with the thermodynamical stability condition of the superfluid or superconductive state though it must, of course, be compatible with this condition.

#### 6. COMMUTATION RULES OF QUANTUM HYDRODYNAMICS

In an interesting paper Landau<sup>19</sup> recently tried to develop general principles of a hydrodynamics on a quantum-mechanical basis. Though many details of his theory are open to criticism, there seems to be little doubt that this paper points to the right direction.

The fundamental quantities of quantum hydrodynamics are the operators  $\rho(R)$  of mass density and  $\mathbf{j}(R)$  of mass current density at a given point in space characterized by its radius-vector  $R$ . If  $r_1, r_2, \dots, r_\alpha \dots r_N$  are the radius vectors of  $N$  particles of the mass  $m$  and charge  $e$ , if  $\delta_{\alpha R}$  is an abbreviation of the three-dimensional Dirac-function  $\delta(r_\alpha - R)$  and if  $\mathbf{p}_\alpha$  is the usual momentum vector operator of the particle  $\alpha$ ,

$$\mathbf{p}_\alpha = \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial x_\alpha}, \frac{\hbar}{2\pi i} \frac{\partial}{\partial y_\alpha}, \frac{\hbar}{2\pi i} \frac{\partial}{\partial z_\alpha} \right),$$

then the non-relativistic operators of mass density and mass current density are given by

$$\rho(R) = m \sum_\alpha \delta_{\alpha R} = m \cdot \mathbf{n}(R), \quad (20)$$

$$\mathbf{j}(R) = \sum_\alpha \left[ \delta_{\alpha R} \left( \mathbf{p}_\alpha - \frac{e}{c} A(r_\alpha) \right) + \frac{\hbar}{4\pi i} \text{grad } \delta_{\alpha R} \right]. \quad (21)$$

Here  $A(r_\alpha)$  is the magnetic vector potential at the point  $r_\alpha$ . The quantity

$$\sum_\alpha \delta_{\alpha R} = \mathbf{n}(R)$$

<sup>19</sup> L. Landau, J. Phys. 5, 71 (1941).

is evidently the operator of the number of particles per  $\text{cm}^3$  in the neighborhood of the point in space  $R$ .

These operators are understood in the usual sense of non-relativistic quantum mechanics, i.e., that, for instance,

$$j(R) = \int \psi^*[\mathbf{j}(R), \psi] d\tau_1 d\tau_2 \dots d\tau_\alpha \dots d\tau_N, \quad (22)$$

gives the quantum-mechanical mean value of  $j$  at the point in space  $R$  if the whole system is in a state represented by the wave function  $\psi(r_1, r_2, \dots, r_\alpha, \dots, r_N)$ .

These four operators do not commute with each other. Thus for the commutator of  $\rho$  and  $\mathbf{j}$  one easily calculates:

$$\begin{aligned} \rho(R)\mathbf{j}(S) - \mathbf{j}(S)\rho(R) + \rho(S)\mathbf{j}(R) - \mathbf{j}(R)\rho(S) \\ = -\frac{\hbar}{2\pi i} \delta_{RS} \text{grad } \rho(R). \end{aligned} \quad (23)$$

(See Landau<sup>19</sup> Eq. (1.4).) Similarly, for the components of  $\mathbf{j}$  one obtains:

$$\begin{aligned} [j(R) \times \mathbf{j}(S)] + [\mathbf{j}(S) \times \mathbf{j}(R)] \\ = -\frac{\hbar}{2\pi i} \delta_{RS} \left( \text{curl } \mathbf{j}(R) + \frac{2ne}{c} H(R) \right), \end{aligned} \quad (24)$$

Here  $H(R) = \text{curl } A(R)$  is the magnetic field at the point in space  $R$ . The proof of this formula will be given in the appendix. Note that especially for superconductors, because of Eqs. (5) and (6), the right-hand side of this relation (24) is just equal to  $+(\hbar/2\pi i)\delta_{RS} \text{curl } j$ , i.e., except for an irrelevant sign of  $i$ , just the same as for uncharged particles like helium. This might be significant in connection with the fact that in both cases, superconductivity as well as liquid helium, we found the same upper limit (19),  $(nh/2\pi) \text{curl } j$ , for the mass transfer per cm width of surface per sec.

In actual fact Landau<sup>19</sup> merely mentions, without proof, a commutation rule of this kind for the operator

$$\mathbf{v}(R) = \frac{1}{2}(\rho^{-1}\mathbf{j} + \mathbf{j}\rho^{-1})$$

which he calls the "velocity operator at the point in space  $R$ ." I must confess that I have been unable formally to verify his result. Moreover, it is to be noted that the assumption of the existence of a linear operator which would rep-

resent the *local* velocity vector  $v(R)$  of hydrodynamics at a given point  $R$  is in contradiction to first principles of quantum mechanics. The uncertainty restrictions preclude such a possibility. This fact can also directly be ascertained if one considers the trivial case of a single particle only. If this special case and for  $A=0$  Landau's operator  $\mathbf{v}$  turns out to be the operator

$$\mathbf{v} = \frac{1}{2m} \left\{ \frac{1}{\delta_{1R}} \left( \delta_{1R} \mathbf{p}_1 + \frac{h}{4\pi i} \text{grad } \delta_{1R} \right) + \left( \delta_{1R} \mathbf{p}_1 + \frac{h}{4\pi i} \text{grad } \delta_{1R} \right) \frac{1}{\delta_{1R}} \right\} = \frac{1}{m} \mathbf{p}_1,$$

which is independent of  $R$  and actually represents the mean value of  $v$  (taken over the whole space) but not the *local* velocity itself.—On the other hand one may consider the quantity

$$\frac{h}{4\pi i m} \frac{\psi^*(R) \text{grad } \psi(R) - \psi(R) \text{grad } \psi^*(R)}{\psi(R)\psi^*(R)},$$

as giving the local mean velocity of the particle in a state  $\psi(r_1)$ . However, this quantity can certainly not be represented as a quantum mechanical mean value by whatever *linear* operator, say  $\mathbf{v}$ , in the form  $\int \psi^*[\mathbf{v}, \psi] d\tau$ , analogous to (22). The concept of the "velocity field" of classical hydrodynamics has apparently no simple counterpart in quantum hydrodynamics and Landau's operator  $\mathbf{v}(R)$  is merely a formal construction devoid of the physical significance attributed to it. It is rather the current density field,  $j$ , not the velocity field,  $v$ , which is to be considered as the appropriate basic quantity of quantum hydrodynamics.

#### 7. FINE-GRAINED AND COARSE-GRAINED CURRENT

The operator curl  $\mathbf{j}(R)$  which appears on the right-hand side of (24) is the operator

$$\begin{aligned} \text{curl } \mathbf{j} &= \sum_{\alpha} \text{grad } \delta_{\alpha R} \times (\mathbf{p}_{\alpha} - (e/c)A(r_{\alpha})) \\ &\equiv \sum_{\alpha} \text{curl } \mathbf{j}_{\alpha}. \end{aligned} \quad (25)$$

It is necessary to make clear that the quantum mechanical mean value of curl  $j$ ,

$$\begin{aligned} \text{curl } j &= \int \psi^*[\text{curl } \mathbf{j}, \psi] d\tau_1 \cdots d\tau_N \\ &= \sum_{\alpha} \text{curl } \int \psi^*[\mathbf{j}_{\alpha}, \psi] d\tau_1 \cdots d\tau_N, \end{aligned} \quad (26)$$

is in general *not even qualitatively* what is meant by the curl of the macroscopic current in hydrodynamics. This becomes evident if one observes that (26) (like (25)) is a sum of terms each of which refers to a single particle only. Each particle  $\alpha$  contributes a certain curl  $j_{\alpha}$ , we may call it the "self-curl" of that particle, a concept which has no analog in classical mechanics where a *single* particle can be endowed with a velocity but evidently not with a current density nor with a curl. In classical hydrodynamics the curl of  $j$ —characterizing the variation of current density between different though closely neighboring places—essentially implies *different* particles. Such a contribution must evidently also exist in quantum hydrodynamics in addition to the self-curl; but it is certainly not yet contained in (26).

The appropriate way to deal with this situation is to introduce a "coarse-grained" current density,  $\langle j \rangle_{Av}$ , by averaging the "fine-grained"  $j$  of (22) over a volume  $V_R$  around a point  $R$ , large compared with the mean volume per particle,  $1/n$ , but small enough to allow speaking of "coarse-grained" differentials. Thus we define:

$$\langle j(R) \rangle_{Av} = \frac{1}{V_R} \int_{V_R} j d\tau, \quad (27)$$

where the integration covers a volume element as described above around the point  $R$ .

It is this coarse-grained current,  $\langle j \rangle_{Av}$ , which plays the role of the ordinary current density in hydrodynamics. What appears in the commutation rules (24), is evidently the fine-grained current,  $j$ , and its curl, the self-curl. In order to appraise the importance of the commutation rules for hydrodynamics it is accordingly most decisive to know in what measure the self-curl contributes to the curl of the coarse-grained current.

1. So far as the particles can be represented by wave packets which do not essentially overlap (i.e., for packets small compared with the integration volume in (27)) the process (27) levels the fine-grained structure of the currents within each packet completely,<sup>20</sup> so that no coarse-grained contribution owing to the self-curls is left. In this case there is, of course, no trace of incom-

<sup>20</sup> This directly follows from the regularity properties of  $\varphi$  and Stokes' theorem.



mutability of the hydrodynamical current components however strong the vortex field might be.

2. Let us now consider the opposite limiting case, which might be here of special interest: If the wave packets are so large that they greatly overlap, that is to say, if the wave function of the system does not permit, even approximately, a localization of particles at distinct places in space, then the self-curly will have an extension over regions in space much larger than that of the integration volume in (27), they will actually cover the whole available volume, and the process (27) does not entirely level out the self-curly. In this case the fine-grained and the coarse-grained current fields are not essentially different from each other, and quantum effects due to the non-commutability (24) are to be expected. This situation is well known to be realized by the electrons within an atom and by the nuclear particles within the atomic nuclei, and there is all indication that this is also the case of the superfluid and superconductive states.

Here is not the place to expatiate on this point and to repeat arguments given in detail elsewhere<sup>21</sup> which support the idea that the superfluid and superconducting states represent arrangements of *approaching order in momentum space* (with approaching 0° abs.) with corresponding *loss of localizability in coordinate space* (necessitated by quantum-mechanical uncertainty). Indeed this would mean that these states realize the second of the two cases mentioned above.

### 8. PERMUTATION RULES OF THE COARSE-GRAINED CURRENT

The two operations (22) and (27) of quantum-mechanical and coarse-grained averaging are evidently commutable operations. We may directly introduce the operator  $\mathbf{j}$  of the coarse-grained current itself,

$$\langle \mathbf{j}(R) \rangle_{Av} = \frac{1}{V_R} \int_{V_R} \mathbf{j}(R') dR',$$

and derive its commutation rules. We have only to apply the above operation two times independently on both sides of (24). On the left-hand side we thus obtain the commutator of the

coarse grained current components. On the right-hand side we calculate first

$$\int_{V_S} \delta_{RS'} dS' = \begin{cases} 1 & \text{if } R \text{ within } V_S \\ 0 & \text{otherwise} \end{cases}$$

for which function of  $R$  we will use the abbreviation  $\Delta(R, V_S)$ . The coarse-grained average of the first term of the right-hand side of (24) can then be written in the following form:

$$\begin{aligned} & -\frac{\hbar}{2\pi i} \frac{1}{V_R V_S} \int_{V_R} \int_{V_S} \delta_{R'S'} \text{curl}(\mathbf{j}(R')) \\ & = -\frac{\hbar}{2\pi i} \frac{1}{V_R V_S} \int_{V_R} \Delta(R', V_S) \text{curl} \mathbf{j}(R') dR' \\ & = -\frac{\hbar}{2\pi i} \frac{V_{RS}}{V_R V_S} \langle \text{curl} \mathbf{j}(R) \rangle_{Av}. \end{aligned}$$

Here  $V_{RS}$  denotes the volume of space covered jointly by  $V_R$  and  $V_S$ , i.e., in particular,  $V_{RS} = 0$  if  $V_R$  and  $V_S$  do not overlap, whereas  $V_{RS} = V_R = V_S$  if  $V_S$  is identical with  $V_R$ . Thus we finally obtain:

$$\begin{aligned} & [\langle \mathbf{j}(R) \rangle_{Av} \times \langle \mathbf{j}(S) \rangle_{Av}] + [\langle \mathbf{j}(S) \rangle_{Av} \times \langle \mathbf{j}(R) \rangle_{Av}] \\ & = -\frac{\hbar}{2\pi i} \frac{V_{RS}}{V_R V_S} \left( \langle \text{curl} \mathbf{j}(R) \rangle_{Av} \right. \\ & \quad \left. + 2\langle \mathbf{n}(R) \rangle_{Av} \frac{e}{c} H(R) \right). \quad (28) \end{aligned}$$

Since  $V_R > n^{-1}$  and  $V_{RS} \leq V_S$  we have  $(V_{RS}/V_R V_S) < n$ . If we further realize that from the coarse-grained point of view two points,  $R$  and  $S$ , are indistinguishable if they lie within the same grain, we may also write:

$$\begin{aligned} \langle \mathbf{j}(R) \rangle_{Av} \times \langle \mathbf{j}(R) \rangle_{Av} & < -\frac{n\hbar}{4\pi i} \left( \langle \text{curl} \mathbf{j} \rangle_{Av} + 2\langle \mathbf{n} \rangle_{Av} \frac{e}{c} H \right) \\ \langle \mathbf{j}(R) \rangle_{Av} \times \langle \mathbf{j}(S) \rangle_{Av} + \langle \mathbf{j}(S) \rangle_{Av} \times \langle \mathbf{j}(R) \rangle_{Av} & = 0 \\ & \text{for } R \neq S. \quad (28a) \end{aligned}$$

Here the sign  $<$  is used in order to express simply that we have replaced the factor  $V_{RS}/V_R V_S$  in (28) by its upper limit  $n$ .

### 9. CONCLUDING REMARKS

A general theory of quantum hydrodynamics would have to develop the statistics of a canonical or microcanonical ensemble of many systems, each system, like that we had assumed so far,

<sup>21</sup> Reference 12, Section 2; F. London, Proc. Roy. Soc. A152, 31 (1935); J. Phys. Chem. 43, 49 (1939).

being represented by its wave function  $\psi(r_1 r_2 \cdots r_\alpha \cdots r_N)$ . However it can be foreseen that this statistical theory should be dispensable at least as far as one aspires primarily to an understanding of solely the hydrodynamics of the supertransfer processes. It should for this purpose be sufficient to consider the situation merely at  $0^\circ$  abs., since there is no reason to believe that superconductivity as well as superfluidity of He should not persist down to  $0^\circ$  abs.

This reduces the problem of the supertransfer hydrodynamics essentially to one of pure quantum mechanics, namely that of constructing the *one* wave function of the ground state of a many body system and of developing its *hydrodynamics as adiabatic transformations* of this single state under varying external conditions. While such a reduced theory cannot, of course, say anything about the *thermal* transition points into the superfluid states nor about the thermo-hydrodynamical effects, it should account not only for

the super-hydrodynamics at  $0^\circ$  abs. but, moreover, also for the *transitions at absolute zero* of superfluid helium under a certain pressure into solid helium and of the superconducting state in a sufficiently strong magnetic field into the normal state.

One can further anticipate that the restrictions we have discussed here in some detail concerning the rate of surface transfer must have a particularly simple basis within this reduced theory. Since the inequalities (17) or (19) evidently do not express any reference to any kind of forces, but only contain the constant  $\hbar$  and this, moreover, in the form of the product  $\hbar \cdot \text{curl } j$ , it appears plausible that one should be able to account for these inequalities within the bounds of *pure kinematics* in close connection with the commutation rules (28), which contain the same product  $\hbar \cdot \text{curl } j$ . The dynamical properties of the mechanism should in this matter be entirely irrelevant.

#### APPENDIX. PROOF OF THE COMMUTATION RULES FOR THE CURRENT COMPONENTS (24)

We shall use the following abbreviations for the vector components:

$$R = (x_R, y_R, z_R), \quad S = (x_S, y_S, z_S), \quad r_\alpha = (x_\alpha, y_\alpha, z_\alpha), \quad \frac{e}{c} A(r_\alpha) = (a_\alpha, b_\alpha, c_\alpha), \quad \mathbf{p}_\alpha = (\xi_\alpha, \eta_\alpha, \zeta_\alpha)$$

and for the derivatives of the  $\delta$ -function:

$$\delta_{\alpha R^x} = \frac{\partial}{\partial x_\alpha} \delta(r_\alpha - R) = -\frac{\partial}{\partial x_R} \delta(r_\alpha - R), \quad \text{etc.}$$

Further note the identity

$$\delta_{\alpha R} f(r_\alpha) \equiv \delta_{\alpha R} f(R), \quad (\text{I})$$

for any function  $f(R)$ .

Then we may write, according to (21), the commutator of  $\mathbf{j}_x(R)$  and  $\mathbf{j}_y(S)$  in the following form:

$$\begin{aligned} \mathbf{j}_x(R) \mathbf{j}_y(S) - \mathbf{j}_y(S) \mathbf{j}_x(R) &= \sum_{\alpha, \beta} \left\{ \left[ \delta_{\alpha R} (\xi_\alpha - a_\alpha) + \frac{\hbar}{4\pi i} \delta_{\alpha R^x} \right] \left[ \delta_{\beta S} (\eta_\beta - b_\beta) + \frac{\hbar}{4\pi i} \delta_{\beta S^y} \right] \right. \\ &\quad \left. - \left[ \delta_{\beta S} (\eta_\beta - b_\beta) + \frac{\hbar}{4\pi i} \delta_{\beta S^y} \right] \left[ \delta_{\alpha R} (\xi_\alpha - a_\alpha) + \frac{\hbar}{4\pi i} \delta_{\alpha R^x} \right] \right\} \\ &= \frac{\hbar}{2\pi i} \sum_\alpha \left\{ \delta_{\alpha R} \frac{\partial}{\partial x_\alpha} \left[ \delta_{\alpha S} (\eta_\alpha - b_\alpha) + \frac{\hbar}{4\pi i} \delta_{\alpha S^y} \right] - \delta_{\alpha S} \frac{\partial}{\partial y_\alpha} \left[ \delta_{\alpha R} (\xi_\alpha - a_\alpha) + \frac{\hbar}{4\pi i} \delta_{\alpha R^x} \right] \right\} \\ &= -\frac{\hbar}{2\pi i} \left\{ \frac{\partial}{\partial x_S} \sum_\alpha \delta_{\alpha R} \left[ \delta_{\alpha S} (\eta_\alpha - b_\alpha) + \frac{\hbar}{4\pi i} \delta_{\alpha S^y} \right] \right. \\ &\quad \left. - \frac{\partial}{\partial y_R} \sum_\alpha \delta_{\alpha S} \left[ \delta_{\alpha R} (\xi_\alpha - a_\alpha) + \frac{\hbar}{4\pi i} \delta_{\alpha R^x} \right] + \sum_\alpha \delta_{\alpha R} \delta_{\alpha S} \left( \frac{\partial b_\alpha}{\partial x_\alpha} - \frac{\partial a_\alpha}{\partial y_\alpha} \right) \right\}. \end{aligned}$$

Here we may make use of a special case of the above identity (I),

$$\delta_{\alpha R} \delta_{\alpha S} \equiv \delta_{RS} \delta_{\alpha S},$$

and of its derivative, say, with respect to  $y_\alpha$ ,

$$\delta_{\alpha R} \delta_{\alpha S^y} \equiv \delta_{RS} \delta_{\alpha S^y} - \delta_{\alpha R^y} \delta_{\alpha S}, \quad \text{etc.}$$

Note further that because of (I)

$$\sum_{\alpha} \delta_{\alpha R} \left( \frac{\partial b_{\alpha}}{\partial x_{\alpha}} - \frac{\partial a_{\alpha}}{\partial y_{\alpha}} \right) = \sum_{\alpha} \delta_{\alpha R} \frac{e}{c} H_z(r_{\alpha}) = \left( \sum_{\alpha} \delta_{\alpha R} \right) \frac{e}{c} H_z(R) = \mathbf{n}(R) \frac{e}{c} H_z(R).$$

Thus we obtain

$$\mathbf{j}_x(R) \mathbf{j}_y(S) - \mathbf{j}_y(S) \mathbf{j}_x(R) = -\frac{h}{2\pi i} \left\{ \frac{\partial}{\partial x_S} [\delta_{RS} \mathbf{j}_y(S)] - \frac{\partial}{\partial y_R} [\delta_{RS} \mathbf{j}_x(R)] + \delta_{RS} \mathbf{n}(R) \frac{e}{c} H_z(R) \right\}.$$

If here we commute  $R$  with  $S$  and add the result to the original expression and then everywhere replace  $\delta_{RS} \mathbf{j}(S)$  by  $\delta_{RS} \mathbf{j}(R)$ , we obtain

$$\begin{aligned} & \mathbf{j}_x(R) \mathbf{j}_y(S) - \mathbf{j}_y(S) \mathbf{j}_x(R) + \mathbf{j}_x(S) \mathbf{j}_y(R) - \mathbf{j}_y(R) \mathbf{j}_x(S) \\ &= -\frac{h}{2\pi i} \left\{ \left( \frac{\partial}{\partial x_S} + \frac{\partial}{\partial x_R} \right) [\delta_{RS} \mathbf{j}_y(R)] - \left( \frac{\partial}{\partial y_R} + \frac{\partial}{\partial y_S} \right) [\delta_{RS} \mathbf{j}_x(R)] + 2\delta_{RS} \mathbf{n}(R) \frac{e}{c} H_z(R) \right\} \\ &= -\frac{h}{2\pi i} \delta_{RS} \left\{ \frac{\partial \mathbf{j}_y(R)}{\partial x_R} - \frac{\partial \mathbf{j}_x(R)}{\partial y_R} + 2\mathbf{n}(R) \frac{e}{c} H_z(R) \right\}, \end{aligned}$$

or generally

$$[\mathbf{j}(R) \times \mathbf{j}(S)] + [\mathbf{j}(S) \times \mathbf{j}(R)] = -\frac{h}{2\pi i} \delta_{RS} \left\{ \text{curl } \mathbf{j}(R) + 2\mathbf{n}(R) \frac{e}{c} H(R) \right\},$$

which is the commutation rule (24) as given in the text.