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Reversible Flow Phenomena and Thermodynamic Properties of Liquid Helium and the Two-Fluid Hypothesis*

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The terms superfluid and normal fluid may be interpreted in various ways, and in Landau's theory the fraction of normal fluid given by flow experiments (e.g., second sound) is not a direct measure of the number of atoms involved in the excitations. Furthermore, the anomaly in the specific heat above the λ point indicates the continued existence of unexcited material above the λ point, probably in the form of (nonspherical) droplets or clusters, which does not actually contribute to the superfluidity. These rather complex relationships are considered in the introduction, and it is concluded that, in spite of the various possibilities of choosing the two components for the two-fluid theory, any pair can be considered as thermodynamic components. It is also concluded that it is probable that the normal fluid and superfluid are separated in ordinary space as well as momentum space. There follows a discussion of the equation for second sound, and a comparison of the values for x (mole fraction of normal fluid) obtained from second sound and from the Andronikashvili experiment. The values of x are also discussed in connection with the values of the roton part of the specific heat, c_r. It is shown that these are difficult to reconcile from a thermodynamic point of view on the basis of any of the usual theories, and it may be necessary to reinterpret the equation for second sound in the region where both phonon and roton excitations are of importance. At higher temperatures the apparent anomalies, and especially the rapid rise of c_r/x near the λ point, are readily explained with the aid of the unexcited droplets mentioned above. Finally a critical analysis is made of the assumption, inherent in the second-sound equation, that entropy is carried only by normal fluid and not by the superfluid, which is in apparent contradiction with the fact that the entropy of mixing of superfluid and normal fluid cannot be zero if they are separated in ordinary space. It is shown from two points of view that there is no actual contradiction. In the first procedure a pressure is introduced which arises from the forces tending to separate normal and superfluid, and the accompanying work is considered. It is shown that this pressure must be considered to reside in the superfluid. The second procedure starts directly with the energy equation. It is shown that H. London's equation for the fountain pressure follows directly.

1. INTRODUCTION

As is well known, many of the properties of liquid helium can be explained, or at least described, in terms of the two-fluid hypothesis, which supposes that superfluid and normal fluid exist together below the λ point. In actual fact, however, both theory and experiment indicate that the situation is more complicated than that. The fractions of superfluid and normal fluid can be estimated from certain flow experiments such as the Andronikashvili experiment and second sound. On the other hand, they can also be inferred from the thermodynamic properties, and these two estimates may not agree. In fact, different things have been meant by the terms, superfluid and normal fluid.

Let us first consider the roton excitations at low temperatures. As these excitations are presumably localized and do not change greatly in character over a range of temperatures, it seems quite natural to assume that the atoms involved in these excitations constitute the normal fluid. It is, however, quite possible that flow experiments will not measure the mass of these atoms. In the theory of Landau[1] and the theory of Feynman[2] the excitations are considered to behave like a Bose-Einstein gas. These excitations are assumed to be in equilibrium with the superfluid substrate regardless of whether they are drifting with respect to the latter or not. The excitations have various momenta, and their energy depends upon their momentum with respect to the substrate. Thus motion of the substrate affects their distribution in momentum, and the drift of mass relative to the substrate occurs because now some relative momenta are favored over others. Thus the apparent mass is only indirectly related to the actual mass of the atoms involved. Because of the peculiar relation between energy and momentum, the state of lowest energy can shift in such a way that its

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[1] L. Landau, J. Phys. U.S.S.R. **5**, 71 (1941); **11**, 91 (1947).
[2] R. P. Feynman, Phys. Rev. **94**, 262 (1954); *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955), Chap. 2.

momentum changes greatly. This results in a very large apparent mass at low temperatures, and in the 1947 theory of Landau and the theory of Feynman we have

$$\rho_n/\rho \sim n/NT, \tag{1}$$

where ρ_n/ρ is the ratio of the effective density of rotons to the total density, n is the number of rotons per N atoms, and $\sim$ stands for approximate proportionality. There remains the question whether equilibrium would actually be established in a second-sound experiment. Also, we have shown[3,4] that the roton excitations can be discussed by a more conventional type of statistical mechanics. This leaves some question as to whether the close tie-up between momentum and internal energy of the roton is actually necessary, and gives a picture more consistent with the idea that the rotons move through the superfluid with a mass closely related to the actual number of atoms involved.

Just below the λ point, in any event, it is the normal fluid which is the substrate, and we can hardly imagine that excitations of different momentum can be distinguished. Since the liquid behaves much like an ordinary fluid just above the λ point, we may infer that the normal fluid still behaves so just below. This suggests that in this temperature region at least the apparent fraction of normal fluid as obtained by flow experiments closely approximates the true fraction.

Nevertheless the possibility must be considered that, especially at low temperatures, the flow experiments will give a ratio ρ_n/ρ, which is different from the ratio for what we should like to think of as the components in a two-fluid theory, and this is certainly true in the case of phonons. Phonons are in any case not localized excitations, and it would be difficult to assign particular atoms to them.

The complications do not end here, however. Some years ago we made an attempt[5] to understand the behavior of the specific heat just above the λ point on the basis of the supposition that droplets of superfluid appeared in the liquid above the λ point. Whatever the details of the theory one may propose, it would appear that the sharp rise of the specific heat in this region is a pretransition phenomenon which implies fluctuations involving superfluid. However, the superfluid which appears above the λ point obviously does not contribute to the superfluid properties.

The appearance of superfluidity probably requires establishment of some kind of long-range order in the superfluid. We have supposed[5,6] that, while the superfluid is in the form of disconnected (though by no means necessarily spherical) globules above the λ point, below the λ point there are connections extending throughout the liquid, or at least over macroscopic distances. However, below the λ point an appreciable fraction may be expected still to be in the form of droplets which will appear to be part of the normal fluid in a flow experiment.

In view of this complicated situation we propose to distinguish between *superfluid* and *normal fluid*, as measured by a flow experiment, and *superfluid substance* and *normal substance* characterizing the actual parts of the fluid. Further we shall consider the droplets to be part of the normal substance, and shall consider in addition *excited* and *unexcited* components, with the relationships:

Normal fluid substance = excited component + droplets;
unexcited component = superfluid substance + droplets.

As is customary we shall write ρ_n and ρ_s for the apparent densities of normal fluid and superfluid obtained, say, from second sound, and we shall write $x=\rho_n/\rho$ (where ρ is the density of the liquid) for the apparent mole fraction of normal component.

Since all parts of the liquid are in equilibrium with each other, we can, in a two-fluid theory, choose either the normal substance and superfluid substance or the excited and unexcited components as the pair of thermodynamic components. In our previous work we have chosen the latter pair, although, unfortunately, we called them normal and superfluid.

Now $\rho_n \mathbf{v}_n$, where $\mathbf{v}_n$ is the velocity of normal fluid, is defined in terms of momentum in the Landau-Feynman theory [see, e.g., Feynman[2] (1955)], and hence represents a true mass flow. Also the composition of this material is independent of $\mathbf{v}_n$ if $\mathbf{v}_n$ is small. Thus it also is possible to consider whatever is transported with velocity $\mathbf{v}_n$ (i.e., the normal fluid, in the usual description) as one component, and whatever is transported with velocity $\mathbf{v}_s$ (i.e., the superfluid) as the other component. These components can be assigned proper partial molal quantities in the usual way and the standard procedures of thermodynamics can be applied. It is true that a certain conceptual difficulty may arise, since in the Landau-Feynman theory ρ_n and ρ_s are defined in terms of an equilibrium process, and a change in ρ_n/ρ implies a change in temperature, whereas the use of the partial molal quantities implies the addition of one of the components without change in temperature, and hence a slight departure from equilibrium between the two components, while equilibrium is established among the molecules of a single component. Since, however, we will be dealing with processes which never depart far from equilibrium, and which do not involve large temperature changes or sharp temperature gradients in the atomic sense, this difficulty is more apparent than real.[7]

[3] O. K. Rice, Phys. Rev. **96**, 1460 (1954).
[4] O. K. Rice, Phys. Rev. **98**, 847 (1955).
[5] O. K. Rice, Phys. Rev. **76**, 1701 (1949); **78**, 182 (1950).
[6] O. K. Rice, Phys. Rev. **93**, 1161 (1954).

[7] Equation (23) assumes that the transfer of material takes place at constant temperature, since the partial specific quantities are so defined. If equilibrium is maintained at any given point, however, change in the amount of normal or superfluid changes the temperature. Since the normal fluid presumably has an intrinsic specific heat, this would require a further change of normal fluid to superfluid, or vice versa, to effect the energy balance. Equation (24) excludes this particular change, giving only that which specifically interests us.

Whether ρ_n and ρ_s are equal to densities of normal and superfluid *substance*, or not, ρ_n and ρ_s are the appropriate quantities, and superfluid and normal fluid are the appropriate terms, to use when discussing flow experiments. This applies in the case of the present paper to Secs. 2, 4, and 5.

If we attempt to bring the phonons into the picture it becomes still more complicated, since the phonons cannot be considered to be localized excitations, and since their ratio of effective energy to mass appears to be much larger than that of the rotons. Fortunately, it does not appear to be necessary to consider the mass of the phonons if we confine our attention to temperatures above 0.8°K, since de Klerk, Hudson, and Pellam[8] estimated that the roton density is already 20 times the phonon density at that temperature. The phonon specific heat is appreciable, because of the phonons' large energy-mass ratio, but this can be at least approximately estimated by extrapolation from low temperatures and subtracted from the total.

The description of liquid helium just given implies a separation of superfluid and normal fluid in ordinary space as well as in momentum space, regardless of how the components are chosen. This means that there will be an entropy of mixing of the two fluids, and hence a nonzero partial entropy $\bar{s}_s$ of the superfluid. In dealing with second sound it is generally assumed that the superfluid carries no entropy, and there is good evidence to support this view. However, to say that it *carries* no entropy is not the same thing as to say that it *has* no entropy, despite a statement of London's[9] to the contrary, and one of the objectives of this paper will be to set up a consistent hydrothermodynamic formalism in which the entropy of transport of superfluid vanishes even though $\bar{s}_s$ does not.

2. RELATION BETWEEN THE ANDRONIKASHVILI EXPERIMENT AND SECOND SOUND

Second sound may be described as a wave motion in which the normal fluid and superfluid move with respect to each other. To compute the wave velocity u_{II} it is assumed that this motion is reversible and that all the entropy is carried by the normal fluid. It is then found that[10]

$$u_{\mathrm{II}}^2 = (\rho_s/\rho_n)(s^2T/c_p), \tag{2}$$

where s and c_p are respectively entropy and constant-pressure heat capacity per gram. Peshkov[11] measured u_{II} and concluded that the values of ρ_n/ρ which could be deduced from it were in good agreement with those of Andronikashvili.[12] They did not agree exactly, however; Andronikashvili[13] believed Peshkov's values were better than his own in the lower part of his temperature range, and he quoted them in connection with other work. The latter tabulation was apparently plotted by London[14] as Andronikashvili's own work. This is confusing, and it appears desirable to compare afresh Andronikashvili's values of ρ_n/ρ with those obtained from second sound and the new values[15] of c_p and s. We have used (see Table I) the second sound measurements of Pellam and of Maurer and Herlin[16] which agree very well with those of Peshkov and seem actually to lie between those of Peshkov and of Lane, Fairbank, Schultz, and Fairbank.[17] Also included are some results on the Andronikashvili experiment recently obtained by Dash and Taylor,[18] as calculated from an empirical formula given by them for the range 1.1° to 2.0°K, and some other data for later reference. It will be seen that the agreement between Andronikashvili and Pellam is very good, and Pellam's values would agree almost as well with the results of Hollis-Hallett[19] using Andronikashvili's method. However, below 1.7°K there appears a serious discrepancy between the results

TABLE I. Normal fluid density and roton specific heat.

T (°K)	$100x$ (References 15 and 16)	$100x$ (Reference 12)	$100x$ (Reference 18)	c_r (joules deg^{-1} g^{-1}) (Reference 15)	c_r/x (References 15 and 16)
0.8	0.094			0.0102	10.9
0.9	0.307			0.0339	11.0
1.0	0.715			0.0807	11.3
1.1	1.49		3.16	0.160	10.7
1.2	2.82		4.80	0.281	10.0
1.3	4.75		7.04	0.464	9.8
1.4	7.40	6.0	10.05	0.716	9.7
1.5	11.3	10.5	14.0	1.048	9.3
1.6	16.9	16.5	19.1	1.476	8.7
1.7	23.8	24.0	25.5	2.00	8.4
1.8	32.1	33.4	33.5	2.66	8.3
1.9	42.8	44.2	43.5	3.47	8.1
2.0	55.8	58.0	55.8	4.76	8.5
2.05	63.9	66.2		5.62	8.8
2.1	72.6	75.3		6.70	9.2
2.15	85.1	86.3		8.38	9.8
2.18	99.2	96		11.4	11.5

[8] de Klerk, Hudson, and Pellam, Phys. Rev. **93**, 28 (1954).

[9] F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1954), Vol. 2, p. 185.

[10] Reference 9, pp. 77 ff.

[11] V. P. Peshkov, J. Phys. U.S.S.R. **8**, 381 (1944); **10**, 389 (1946); J. Exptl. Theoret. Phys. U.S.S.R. **18**, 950 (1948); Report International Conference on Low Temperatures, 1946 (Physical Society, London, 1948), Part II, p. 19.

[12] E. Andronikashvili, J. Phys. U.S.S.R. **10**, 201 (1946); J. Exptl. Theoret. Phys. U.S.S.R. **18**, 424 (1948).

[13] E. Andronikashvili, J. Exptl. Theoret. Phys. **18**, 429 (1948).

[14] Reference 9, p. 67.

[15] Kramers, Wasscher, and Gorter, Physica **18**, 329 (1952).

[16] J. R. Pellam, Phys. Rev. **75**, 1183 (1949), for 1.5° to 2.18°. R. D. Maurer and M. A. Herlin, Phys. Rev. **76**, 948 (1949), for 0.9° to 1.4°. Reference 8 for 0.8°.

[17] Lane, Fairbank, Schultz, and Fairbank, Phys. Rev. **71**, 600 (1947).

[18] J. G. Dash and R. D. Taylor, Program of the National Science Foundation Conference on Low Temperature Physics and Chemistry, Baton Rouge, Louisiana, December 28–30, 1955 (unpublished). We may also note that at the same conference Pearce, Markham, and Dillinger presented data on the specific heat between 0.4° and 1.0° which apparently show roton contributions about 10% higher than those of Kramers, Wasscher, and Gorter. The data of G. R. Hercus and J. Wilks [Phil. Mag. **45**, 1163 (1954)] are also about 10% higher than those of Kramers, Wasscher, and Gorter, giving values of x from 10% (at 1.1°) to 5% (at 2.05°) higher.

[19] A. C. Hollis-Hallett, Proc. Roy. Soc. (London) **A210**, 404 (1952).

of Dash and Taylor and the earlier results. The discussion of Sec. 1 suggests that possibly such a discrepancy might arise if the Andronikashvili experiment allows true internal equilibrium to be established but that second sound does not. However, we shall not speculate further on this point.

To assess the significance of the agreement, insofar as it does exist (in any event near the λ point), we may consider what would be the effect of assuming that the superfluid and the normal fluid carry their partial entropies per unit mass, namely, $\bar{s}_s$ and $\bar{s}_n$, respectively, instead of assuming that only the normal fluid carries entropy. If entropy is carried only by normal fluid, the entropy, ρs per unit volume, moves with the velocity of the normal fluid, $\mathbf{v}_n$, the rate of transfer of entropy per unit time per unit cross section is $\rho s\mathbf{v}_n$ and the corresponding flow of heat is $T\rho s\mathbf{v}_n$. If, however, both fluids carry entropy, $\rho s\mathbf{v}_n$ would be replaced by $\rho_s\bar{s}_s\mathbf{v}_s+\rho_n\bar{s}_n\mathbf{v}_n$. Because superfluid and normal fluid are in equilibrium, we have the relation

$$\bar{h}_n-T\bar{s}_n=\bar{h}_s-T\bar{s}_s=h-Ts, \tag{3}$$

where $\bar{h}_n$ and $\bar{h}_s$ are the partial specific enthalpies, and h is the total enthalpy per gram. If there is no *heat* of mixing of normal and superfluid we can set $\bar{h}_s=0$ (neglecting any excitations in the superfluid) and we have the relation

$$\rho h=\rho_n\bar{h}_n. \tag{4}$$

Further, if we can suppose that the over-all density is constant and that there is no motion of the liquid as a whole,

$$\mathbf{v}_s=-\rho_n\mathbf{v}_n/\rho_s. \tag{5}$$

From Eqs. (3), (4), and (5) we find

$$\rho_s\bar{s}_s\mathbf{v}_s+\rho_n\bar{s}_n\mathbf{v}_n=\rho\mathbf{v}_nh/T. \tag{6}$$

The result of using this expression for the flow of entropy instead of $\rho s\mathbf{v}_n$ is that h/T is everywhere substituted for s, e.g., in Eq. (2). Since h/T is around 15 percent smaller than s for most of the temperature range, this would upset the good agreement between the results of Andronikashvili and Pellam, and the agreement between Dash and Taylor and Pellam above 1.7°.

If we assume that there is no entropy of mixing instead of no heat of mixing, we set $\bar{s}_s=0$; then Eq. (3) takes the form

$$\bar{h}_n-T\bar{s}_n=\bar{h}_s. \tag{3a}$$

(We cannot now set $\bar{h}_s=0$, so there is a heat of mixing.)[20]

[20] See reference 5. The situation is quite different in the case of the ideal Bose-Einstein gas, where both $\bar{h}_s$ and $\bar{s}_s$ (with subscript s referring to the condensed state) are zero. This is easily seen, since $\bar{h}_s-T\bar{s}_s=h-Ts=e+pv-Ts$ (where e is the energy per gram, p the pressure, and v the volume per gram), and $e+pv-Ts=0$ below the λ point (see e.g., reference 9, pp. 47 ff). This can be traced to the fact that in this case the transition is *first-order* (see, e.g., reference 6). Thus it is clear that $h-Ts$ is constant during an isothermal condensation, and regardless of the temperature the final state, in which all the gas is condensed, is one in which both enthalpy and entropy vanish.

We then have $\rho_s\bar{s}_s\mathbf{v}_s+\rho_n\bar{s}_n\mathbf{v}_n=\rho_n\bar{s}_n\mathbf{v}_n=\rho s\mathbf{v}_n$ and we recover Eq. (2). We shall return later to the question, whether this is the only way to obtain Eq. (2), or whether Eq. (2) can be reconciled with a nonzero value of $\bar{s}_s$.

3. THERMODYNAMICS

Under assumptions which are equivalent to supposing that the mixture of rotons and superfluid obeys Raoult's law, it can be shown[3] that at low concentrations of rotons the number n of rotons when there are N atoms is given by

$$n=Nme^{-\epsilon/kT}, \tag{7}$$

where m is the effective number of energy levels per roton (the intrinsic entropy of a roton being $k\ln m$) and ϵ is the energy (strictly the enthalpy) of formation of a roton from superfluid. We then have

$$d\ln n/dT=d\ln m/dT-(kT)^{-1}d\epsilon/dT+\epsilon/kT^2.$$

If a roton can be considered to have a fixed number of atoms then, since $k\ln m$ is an internal entropy term (or if both m and ϵ are fixed), we can write

$$kTd\ln m/dT=d\epsilon/dT$$

and

$$d\ln n/dT=\epsilon/kT^2. \tag{8}$$

If ϵ is constant, then

$$\ln n=-\epsilon/kT+\text{constant} \tag{9}$$

and the heat capacity per N atoms due to rotons is given by

$$C_r=\epsilon dn/dT=(\epsilon^2/kT^2)n.$$

Where we go from this point, depends upon whether we believe that the mass of normal fluid, as revealed by flow experiments, depends directly on the number of atoms in a roton, or is a more complicated function as in the Landau-Feynman theory. In the former case x is proportional to n, and we have

$$c_rT^2/x=\text{constant}. \tag{10}$$

In the latter case we apply Eq. (1) and obtain

$$c_rT/x=\text{constant}. \tag{10a}$$

Actually one would not expect ϵ to be entirely constant. If we suppose the internal energy of rotons to be simply the energy of normal fluid, we can make some estimate as to how ϵ may vary. Slightly above the λ point, the specific heat has a "normal" value for normal fluid of about 0.5 cal per gram per deg, and the total enthalpy is about 0.7 cal per gram. The specific heat of normal fluid substance would be expected to be less than this at 1°K, but orders of magnitude are such that the enthalpy of normal fluid substance, and hence inferentially ϵ, might be approximately proportional to T (though we have previously estimated[3] that the dependence on temperature is not this strong). Let us

suppose, then, that $\epsilon = bT$, where b is a constant; integrating Eq. (8) we find

$$n = aT^{b/k}, \tag{11}$$

where a is another constant. In this case,

$$C_r = d(\epsilon n)/dT = ba(1+b/k)T^{b/k},$$

and, again assuming x proportional to n,

$$c_r/x = \text{constant}. \tag{12}$$

In this case there would be no point in applying Eq. (1), since the Landau-Feynman theory definitely requires the approximate correctness of Eq. (9).

Values of x have been obtained over a wide range of temperatures from second-sound measurements, and we shall use these results to test the relationships which have just been found, recognizing that if the recent measurements of Dash and Taylor[18] are confirmed, our conclusions will need modification, especially in the low temperature range. The values of x obtained from second sound are plotted logarithmically against $1/T$ in Fig. 1 for temperatures from 0.8° to the λ point. Values of c_r may be obtained from the measured specific heat[15] by subtracting the extrapolated value of the phonon part, and values of c_r and c_r/x are given in Table I.

It will be observed from Fig. 1 that, between 0.8° and 1.4° Eq. (9) appears to hold, if we assume that x is proportional to n [but use of Eq. (1) would make little difference]. Above 1.4° the law changes; still Eq. (9), with a different set of parameters, seems better than Eq. (11). In spite of this, Eq. (12) is more nearly fulfilled than either Eq. (10) or Eq. (10a).

Above 1.4° this is not surprising since this is the region where the concentration of rotons becomes appreciable. There will be coalescence of rotons, they will lose their identity, and the relation between x and n appropriate to the lower temperature might break down. It is possible that the rotons entrain or drag some of the nearby unexcited atoms. As the density of normal fluid increased and some of the rotons coalesced there would be less exposed roton surface, and so fewer unexcited atoms would be included per atom of normal fluid. Thus c_r would increase relatively faster than x over a considerable range of temperatures, and this would be equivalent to a tendency for Eq. (10) to go over to Eq. (12).

If we assume that x is proportional to n, then the foregoing explanation of the preference for Eq. (12) over Eq. (10), despite the fulfillment of Eq. (9), must break down below, say, about 1.4°K, since in this region the rotons are separate and independent. On the other hand, if Eq. (1) holds it may be interpreted as a continually increasing drag of unexcited atoms (or material pushed through a "whirlpool"[2]) as the temperature decreases. This occurs in this case because of what may be regarded as a specific interaction between the excitations and the substrate, which, however, does not result in frictional forces because it operates reversibly. However, the predictions of the Landau-Feynman theory are specific and they, also, are not fulfilled. Possibly one should wait for further experimental data before drawing definite conclusions, in view of present uncertainties.[18] Tentatively, however, we suggest the possibility of a breakdown in Eq. (2) arising from a failure of the phonons to take part in the motion of the normal fluid under some circumstances. At the higher temperatures where the density of rotons is much greater than the effective density of phonons, the latter are probably dragged along with the former because of reflections, scattering, and other interactions; thus, although an appreciable part of the energy is phonon energy, since only a negligible fraction of the mass is phonon mass, all the excitations behave and move as though they were part of the roton excitation. Further, at the higher temperatures, the low-frequency phonons are not important. At temperatures between 0.6° or 0.8° and 1.4° where the roton density still predominates over the phonon density, but is itself small, low-frequency, long-wavelength phonons may move with a different velocity than the rotons due to weak and infrequent interaction. They might, in fact, produce a secondary wave or pulse of high velocity which would go unnoticed because of its low energy content. The values of s and c_p to be inserted in Eq. (2) should then not include all the phonon contribution. If we subtract all the phonon entropy and specific heat from s and c_p in Eq. (2), the calculated value of x changes in such a way as to considerably overcorrect the trend in c_rT^2/x.

At temperatures below 0.6° or 0.8° the roton excitations become completely unimportant, and then the waves or pulses characteristic of the low-frequency phonons predominate.

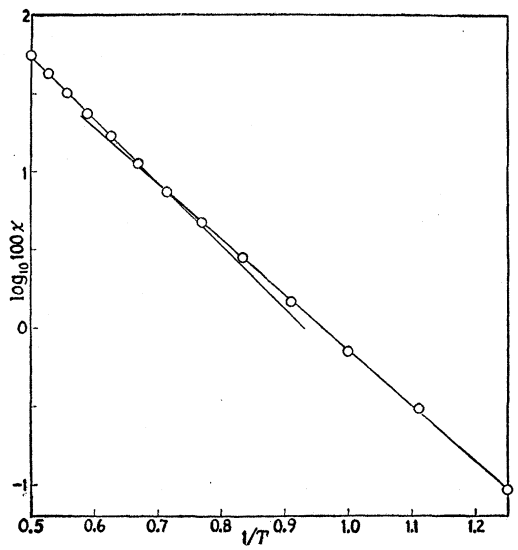

FIG. 1. Relation between mole fraction of normal fluid, by second-sound velocity, and temperature.

If the above discussion is correct, it means that the apparent straight line for $\log x$ against T^{-1} below 1.4° is to some extent spurious, for the values of x need to be corrected. The corrected values might not give such a straight line since ϵ probably varies. Above 1.4° (or perhaps only above 1.7°, considering the results of Dash and Taylor), the values of x are probably reliable. In this region the interpretation of the empirical results are complicated both by variation in ϵ and deviation from Raoult's law, and the straight-line segment in Fig. 1 is not readily interpreted.

The sharp rise of c_r/x above 2.1° is connected with a rise in each of the quantities separately, and it is seen that c_r increases less rapidly[20a] with T than does dx/dT. Thus, actually, a lowering of the intrinsic energy of the normal fluid is indicated. Above 2.1° the drag of unexcited atoms mentioned above is probably no longer important, and the regions of normal substance may now be large enough for the inclusion of unexcited droplets to begin, thus lowering the energy of the normal fluid. Close to the λ point this trend should reverse itself, due to increasing instability of the droplets, and their disappearance should cause a rise in the intrinsic specific heat of the normal fluid, continuing (as observed) above the λ point; however, no indication of such a rise below the λ point appears in the work of Dash and Taylor.[20a]

4. SECOND SOUND AND FOUNTAIN EFFECT

As already remarked, if the superfluid and normal fluid are separated in ordinary space, we expect there to be an entropy of mixing, and $\bar{s}_s$ will not be zero, even if the intrinsic entropy of superfluid vanishes. Equation (2), however, is valid if the superfluid carries no entropy when it moves with respect to the normal fluid. It has been widely believed[9] that this requires that $\bar{s}_s=0$. It will be shown that not only is this not true, but that the equations of motion which are used to derive Eq. (2) automatically provide for the possibility of a difference between the partial specific entropy and the entropy of transport.

The equation of motion which gives Eq. (2), relates the relative acceleration of the superfluid and the normal fluid to the temperature gradient, as follows[21]:

$$\partial \mathbf{v}_s/\partial t-\partial \mathbf{v}_n/\partial t=(\rho/\rho_n)s\ \mathrm{grad}T. \tag{13}$$

This equation leaves out the terms of the $(\mathbf{v}\cdot\mathrm{grad})\mathbf{v}$ type, but these are of higher order, since the velocity appears twice, and they may be neglected in setting up the wave equation for second sound. Other terms of higher order are also omitted.

The relative acceleration, $\partial \mathbf{v}_s/\partial t-\partial \mathbf{v}_n/\partial t$, may be considered to result from the gradient of a pressure P which exists within the superfluid, and which tends to move the superfluid relatively to the normal fluid. In ordinary hydrodynamics the negative gradient of the pressure is the force per unit volume, but in this case $-\mathrm{grad}P$ is the force per unit volume of superfluid, and the force per unit volume of the entire mass is $-(\rho_s/\rho)\mathrm{grad}P$. Equating this to the reduced mass of the two fluids in unit volumes times the relative acceleration (retaining only first order terms), we have

$$-(\rho_s/\rho)\ \mathrm{grad}P=(\rho_s\rho_n/\rho)(\partial \mathbf{v}_s/\partial t-\partial \mathbf{v}_n/\partial t). \tag{14}$$

Comparing this with Eq. (13), we find

$$-\mathrm{grad}P=\rho s\ \mathrm{grad}T. \tag{15}$$

Since $s=-\partial g/\partial T$, where g is the free enthalpy (Gibbs free energy) for a constant pressure, and since ρ is practically constant under such conditions, integration gives

$$P=\rho g=\rho(h-Ts). \tag{16}$$

The constant of integration is determined by setting h equal to zero at 0°K and assuming P is also zero at 0°K, which is necessary in order to obtain the correct results for the fountain effect. It is very interesting to note that if we had assumed the pressure P to reside anywhere other than in the superfluid we would have had some density other than ρ in Eq. (15) and could not have integrated it. This is, of course, connected with the form of Eq. (13), and throws some light on the meaning of that equation.

Let us now consider the rate at which the pressure P does work. The net rate at which the density of superfluid is increasing at any point, due to flow, is $-\mathrm{div}(\rho_s\mathbf{v}_s)$, and we suppose the normal fluid to be leaving at the same rate to keep the total density constant. The volume of superfluid which enters per unit volume per unit time is $-\rho^{-1}\,\mathrm{div}(\rho_s\mathbf{v}_s)$, since the intrinsic density of either superfluid or normal fluid is approximately that of the liquid. In calculating the rate, dW/dt, at which work is done by the pressure P on the entering superfluid, we note that, since the forces are forces tending to move superfluid with respect to normal fluid, they act through a distance equal to $\mathbf{v}_s-\mathbf{v}_n$, rather than $\mathbf{v}_s$, per unit time. Therefore we write

$$\begin{aligned} dW/dt&=-[(\mathbf{v}_s-\mathbf{v}_n)/\mathbf{v}_s]P\rho^{-1}\,\mathrm{div}(\rho_s\mathbf{v}_s)\\ &=-P\rho_n^{-1}\,\mathrm{div}(\rho_s\mathbf{v}_s), \end{aligned} \tag{17}$$

using Eq. (5). Then, from Eq. (16),

$$dW/dt=-(\rho/\rho_n)(h-Ts)\ \mathrm{div}(\rho_s\mathbf{v}_s). \tag{18}$$

If it is desired to restore the original temperature after the replacement of normal fluid by superfluid, it will be necessary not only to add enough heat to change the superfluid back to normal fluid, but in addition heat must be added at the rate $-dW/dt$. This quantity is

[20a] This has been discussed by Dash and Taylor in their definitive paper on the work of reference 18. I am indebted to Dr. Dash for a preprint of this paper, and have revised my conclusions in its light.

[21] For reviews see reference 9, pp. 83 ff.; J. G. Daunt and R. S. Smith, Revs. Modern Phys. **26**, 172 (1954), especially pp. 218 ff.

positive, since Ts is greater than h and since the rate of accumulation of superfluid is $-\mathrm{div}(\rho_s \mathbf{v}_s)$.

When a certain amount of superfluid enters a given volume an equal amount of normal fluid is displaced. To find the resultant *excess* of superfluid, the amount entering must be augmented by that which was originally associated with the departing normal fluid. Thus the rate of appearance of *excess* superfluid is

$$-(1+\rho_s/\rho_n)\,\mathrm{div}(\rho_s/\mathbf{v}_s) = -(\rho/\rho_n)\,\mathrm{div}(\rho_s \mathbf{v}_s).$$

To change this superfluid back to helium II it would be necessary to add heat at the rate $-h(\rho/\rho_n)\,\mathrm{div}(\rho_s \mathbf{v}_s)$, since h is the amount of heat required to change one gram of superfluid at 0°K to helium II at the appropriate temperature, besides the addition at the rate $-dW/dt$ to compensate the work term. The net rate of addition of heat per unit volume required i therefore

$$dq/dt = -Ts(\rho/\rho_n)\,\mathrm{div}(\rho_s/\mathbf{v}_s) = Ts(\rho/\rho_n)\,\mathrm{div}(\rho_n \mathbf{v}_n). \quad (19)$$

This neglects the effects of gradients of h or Ts, which are percentagewise negligible compared to the variations of $\mathbf{v}_s$ and $\mathbf{v}_n$, and therefore may be neglected, if $\mathbf{v}_s$ and $\mathbf{v}_n$ are small. Since the heat input dq/dt per unit volume is required to bring the system back to its original condition, we see that the entropy change per unit volume is $-T^{-1}dq/dt$ if no heat is added. From Eq. (19), then, we can say that entropy is being carried by the normal fluid at its velocity $\mathbf{v}_n$ and that the superfluid is carrying none.

If there is a heat of mixing of superfluid with the normal fluid, this can supply some of the heat required, and conceivably it could be just sufficient to compensate the work term.[22] This would mean that the pressure P was really the gradient of an internal potential energy, a situation which is easily visualized. This is essentially the assumption made by London.[9] It is, however, quite well known that osmotic pressures are often caused by differences in entropy. This is never as easy to visualize, but there is no reason to exclude this possibility. If there is no heat of mixing and if no heat is added then the work term will be compensated in the case where excess superfluid is entering a volume, by the conversion of some normal fluid to superfluid. It is for this reason that we have spoken of the rate of entry of superfluid $-\mathrm{div}(\rho_s \mathbf{v}_s)$ rather than the rate of increase of superfluid density $\partial\rho_s/\partial t$. It should be noted that this conversion of superfluid to normal fluid will not affect the derivation of the usual equations for second sound, since these depend only on Eq. (13) and the transport of entropy solely by the normal fluid.

Much the same discussion can be applied to the fountain effect. The only difference is that in this case the normal fluid cannot move down the capillary, so all the transport is done by the superfluid. No normal fluid enters into the end of the capillary when superfluid flows out. It flows out pushed by the pressure P and the volume which flows out is ρ^{-1} per gram. The work done by P on the superfluid is $h-Ts$ per gram, which must be subtracted from the heat h per gram necessary to change the superfluid back to helium II; thus the total heat absorbed in order to restore the system to its original temperature is Ts. With a temperature gradient in the capillary, when equilibrium, or more properly a steady state, is set up there will be a difference in hydrostatic pressure which just balances the change otherwise occurring in P. Eq. (16) then leads directly to London's[23] equation for the fountain effect and this has nothing to do[24] with the value of $\bar{s}_s$.

This reconciliation of the possibility of simultaneously having $\bar{s}_s \neq 0$ and a zero entropy of transport for superfluid is much more satisfactory than my previous essay in this direction.[25] In the latter paper we considered the possibility that there would be a pressure drop at the end of the capillary, but it appears necessary only to consider an effective internal pressure which regulates the relative rates of flow of superfluid and normal fluid, which must exist if their relative motions are to be explained at all. Further, we considered the possibility that there was a layer composed largely of superfluid near the wall in a capillary or a Rollin film, but the evidence that such a layer exists[26] is removed by later work[27] which indicates that there is no sudden change in the equilibrium thickness of a Rollin film at the λ point. No such special mechanism is required by the considerations of the present paper.

All the considerations of this section apply, of course, only to that region of temperature in which Eq. (2) is correct. If there is a region of temperature in which Eq. (2) fails, this presumably indicates that some of the energy excitations do not travel with the normal fluid. If Eq. (2) does not hold in any temperature range, it might well be expected that London's equation for the fountain effect would also break down, although this is perhaps not absolutely necessary since even excitations which do not travel with the normal fluid in the case of second sound might be stopped by a narrow capillary in the fountain effect. However, it is interesting in this connection that Bots[28] has indicated

[22] Superfluid is increasing effectively at the rate $-(\rho/\rho_n)\times\mathrm{div}(\rho_s \mathbf{v}_s)$. To restore this to helium II requires a rate of absorption of heat equal to $-(h-\bar{h}_s)(\rho/\rho_n)\,\mathrm{div}(\rho_s \mathbf{v}_s)$. But, if $\bar{s}_s=0$, then $\bar{h}_s = h-Ts$ at equilibrium, so comparing Eq. (18), the part of the expression involving $\bar{h}_s$ is just equal to $-dW/dt$. Therefore, if $\bar{s}_s=0$, the heat to compensate the work term is furnished by the heat of mixing. The expression $-(h-\bar{h}_s)(\rho/\rho_n)\,\mathrm{div}(\rho_s \mathbf{v}_s)$ is simply an alternative expression for $-h(\rho/\rho_n)\,\mathrm{div}(\rho_s \mathbf{v}_s) - dW/dt$.

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

[24] Compare reference 9, p. 73 (footnote 2).

[25] O. K. Rice, Phys. Rev. **89**, 793 (1953). Because we did not consider the pressure P in this paper, the derivation of Eq. (15) there is not correct. With the present value, Eq. (16), of P which is based only on the entropy of transport being zero, not on $\bar{s}_s=0$, only the London equation can result, and the equation of Gorter and de Groot, which substitutes $x_n(\partial S/\partial x_n)$ for S in London's equation, can be considered only as a special case, arising if $\bar{s}_s=0$.

[26] O. K. Rice and B. Widom, Phys. Rev. **90**, 987 (1953).

[27] A. C. Ham and L. C. Jackson, Phil. Mag. **45**, 1084 (1954).

[28] G. J. C. Bots, *Conference on Physics of Low Temperatures, Paris, September, 1955* (Supplément au Bulletin de l'Institut International du Froid, 177, Boulevard Malesherbe, Paris, 17e).

the possibility that London's equation does not hold below 0.8°K. He remarked that this may be an appearance only, since there may be some error in the entropy values in this region. If this proves to be the case some of the difficulties noted in Table I may also be eliminated, at least in part.

5. ENERGY EQUATION

The above results may be obtained from the energy equation

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\rho_n \mathbf{v}_n^2+\tfrac{1}{2}\rho_s \mathbf{v}_s^2+e)=-\operatorname{div}[\tfrac{1}{2}\rho_n \mathbf{v}_n^2\mathbf{v}_n+\tfrac{1}{2}\rho_s \mathbf{v}_s^2\mathbf{v}_s]-\operatorname{div}(\rho s T\mathbf{v}_n), \quad (20)$$

which states that the rate of change per unit volume of the sum of the internal energy (e per unit mass) and the kinetic energy is equal to the rate at which kinetic energy is carried in plus the rate at which heat passes in. It is assumed as before that the heat is bodily transported by the normal fluid, crossing unit surface at the rate $\rho s T\mathbf{v}_n$. This is the same as the equation given by London[29] except that we have omitted terms involving the bodily motion of the whole liquid as we assume it to be at rest, the total pressure which we assume to be constant, and external forces which we assume to be absent. We have also omitted a term in $(\partial e/\partial x)_{\rho,s}$. According to the theory of Zilsel,[30] $(\partial e/\partial x)_{\rho,s}=\frac{1}{2}(\mathbf{v}_n-\mathbf{v}_s)^2$, and the terms will be negligible if the velocities are small. The terms giving the flow of kinetic energy are also small since they involve the velocity to the third power. These terms are important in the Rayleigh disk experiment,[31] but are not needed to get the velocity of second sound. Carrying out the time differentiations, we thus obtain

$$\rho_n\mathbf{v}_n\cdot\partial\mathbf{v}_n/\partial t+\rho_s\mathbf{v}_s\cdot\partial\mathbf{v}_s/\partial t+\rho\partial e/\partial t=-\operatorname{div}(\rho s T\mathbf{v}_n)$$
$$=-\rho s\mathbf{v}_n\cdot\operatorname{grad}T-(\rho/\rho_n)sT\operatorname{div}(\rho_n\mathbf{v}_n)-\rho\rho_n T\mathbf{v}_n\cdot\operatorname{grad}(s/\rho_n) \quad (21)$$

[the last expression from application of $\operatorname{div}(a\mathbf{b})=a\operatorname{div}\mathbf{b}+\mathbf{b}\cdot\operatorname{grad}a$ to $\operatorname{div}\{(\rho/\rho_n)\rho_n sT\mathbf{v}_n\}$]. Using Eqs. (5) and (13), this reduces to

$$\rho\dot{e}=-(\rho/\rho_n)sT\operatorname{div}(\rho_n\mathbf{v}_n)-\rho\rho_n T\mathbf{v}_n\cdot\operatorname{grad}(s/\rho_n),$$

where the dot stands for $\partial/\partial t$. Now $\operatorname{grad}(s/\rho_n)$ will be a small quantity, and since it is multiplied by the small quantity $\mathbf{v}_n$ the last term may be neglected, so finally we have

$$\rho\dot{e}=-(\rho/\rho_n)sT\operatorname{div}(\rho_n\mathbf{v}_n). \quad (22)$$

The change of e is effected through transfer of normal fluid and superfluid. If the pressure and density of the whole liquid remain constant $\dot{e}=\dot{h}$, and since we are considering the case where $\dot{\rho}_s=-\dot{\rho}_n$ we have

$$\rho\dot{e}=(\bar{h}_n-\bar{h}_s)\dot{\rho}_n \quad (23)$$

Let us consider the case where there is no heat of mixing. If we can neglect any intrinsic energy of superfluid due to excitations in it, we may set $\bar{h}_s=0$ and $\rho h=\rho_n\bar{h}_n$, so that $\rho\dot{e}$ becomes equal to $(\rho/\rho_n)h\dot{\rho}_n$. Inserting this in Eq. (22) we find

$$\Gamma=(sT-h)h^{-1}\operatorname{div}(\rho_n\mathbf{v}_n), \quad (24)$$

where

$$\Gamma=\dot{\rho}_s+\operatorname{div}(\rho_s\mathbf{v}_s)=-\dot{\rho}_n-\operatorname{div}(\rho_n\mathbf{v}_n).$$

Γ gives the rate at which normal fluid must be changing into superfluid to maintain the energy balance, under the particular conditions noted, thus giving quantitative form to the ideas outlined in the preceding section.[7] There is no more difficulty in setting up equations for the energy balance if $\bar{h}_s=0$ than if $\bar{s}_s=0$. We can conclude that these equations offer no reason for believing that the entropy of mixing vanishes.

[29] Reference 9, p. 136.
[30] P. R. Zilsel, Phys. Rev. **79**, 309 (1950). See reference 9, pp. 126 ff.
[31] See reference 9, pp. 137 ff.