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The Macroscopic Theory of Superfluid He^3-He^4 Mixtures*

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The macroscopic hydrodynamic equations to the reversible linear approximation for mixtures are set up and analyzed, without making any assumptions beyond that of the traditional form of the two-fluid model. The equations of wave motion are derived and discussed. A novel feature of them is *appreciable* coupling between pressure and entropy-density fluctuations. It is shown how the constants appearing in the equations may be expressed partly in terms of the measured partial vapor pressures. Pomeranchuk's formula for the velocity of second sound appears as a possible special case; and it is shown how his assumption that the He^3 component is carried entirely with the normal velocity may be tested experimentally. The intervention of isotopic diffusion is briefly discussed.

I. INTRODUCTION

IN recent years experiments with liquid helium containing appreciable fractions of the He^3 isotope have shown that this mixture retains the properties characterizing a superfluid: a lambda transition,[1] superleak transfer of mass,[1] the fountain effect,[2] and "second sound" waves.[3] The study of these macroscopic properties in isotope mixtures may well become of importance to the progress of the microscopic (kinetic) theory of "quantum liquids." For pure[4] He^4 superfluid, an empirical macroscopic theory—the "two-fluid model"[5]—is a virtually indispensable intermediary between the dynamical experiments and microscopic theory: the principal theme of this paper is the construction of such a macroscopic dynamics for *mixtures*, analogous to and generalizing that for pure He^4. (The relation of this paper to other published work on the question is indicated below.)

On the basis of the experiments quoted, it is natural to assume that the two-fluid dynamics gives as correct a description for the superfluid mixtures as for pure He^4.[6] This assumption will be made throughout the present work. Accordingly, the density ρ is divided into two parts associated respectively with two velocity fields $\mathbf{v}_n$, $\mathbf{v}_s$; so that the mass flow $\mathbf{J}$ has two terms, of which the first alone is proportional to the entropy flow $\mathbf{N}$,

$$\rho=\rho_n+\rho_s,\quad \mathbf{J}=\rho_n\mathbf{v}_n+\rho_s\mathbf{v}_s,\quad \mathbf{N}=\rho S\mathbf{v}_n. \tag{1}$$

In the present case of a mixture, the density is also divided between the two chemical components; and we have to assign each of these isotope densities separately between the two velocity fields. Thus,

$$\begin{gathered}\rho=\rho_3+\rho_4,\quad \rho_3=\rho_{3n}+\rho_{3s},\quad \rho_4=\rho_{4n}+\rho_{4s},\\ \rho_n=\rho_{3n}+\rho_{4n},\quad \rho_s=\rho_{3s}+\rho_{4s}.\end{gathered} \tag{2}$$

The ratios ρ_{3n}/ρ_{3s}, ρ_{4n}/ρ_{4s}, will in general depend, like the total density and the other thermodynamic magnitudes, on the concentration of He^3.

We shall find that the precise partition of the He^3 component between the two velocity fields has far-reaching effects on wave propagation. The mass flow vector for the He^3 may be written

$$\begin{aligned}\mathbf{J}_3=\rho_{3n}\mathbf{v}_n+\rho_{3s}\mathbf{v}_s&=\rho_3\mathbf{v}_1+[(\rho_{4s}\rho_{3n}-\rho_{4n}\rho_{3s})/\rho]\mathbf{v}_2\\ &=\rho w\mathbf{v}_1+(\rho_s w_n-\rho_n w_s)\mathbf{v}_2,\end{aligned} \tag{3}$$

where

$$\rho\mathbf{v}_1=\mathbf{J}=\rho_n\mathbf{v}_n+\rho_s\mathbf{v}_s,\quad \mathbf{v}_2=\mathbf{v}_n-\mathbf{v}_s, \tag{4}$$

and

$$\rho_{3n}=\rho w_n,\quad \rho_{3s}=\rho w_s,\quad w_n+w_s=w=\rho_3/\rho. \tag{5}$$

The $\mathbf{v}_2$ term of (3) represents a flow of He^3 in the reference frame moving with the center-of-gravity velocity $\mathbf{v}_1$, in analogy with the $\mathbf{v}_2$ term in the entropy-flow equation

$$\mathbf{N}=\rho S\mathbf{v}_1+\rho_s S\mathbf{v}_2. \tag{6}$$

This flow of He^3 will give rise, in wave motion involving $\mathbf{v}_2$, to fluctuations of He^3 concentration and hence of the thermodynamic functions in their dependence on the concentration. The consequences of these fluctuations are: (a) an appreciable coupling between pressure and temperature waves, whereas for pure He^4 the coupling is negligible; and (b) a large influence on the dependence on He^3 concentration of the velocity of second sound.[7]

The flow represented by the $\mathbf{v}_2$ term of (3) has been isolated in the "heat flush" experiments of Lane *et al.*,[8] in which "normal" and "super" currents $\rho_n\mathbf{v}_n$ and $\rho_s\mathbf{v}_s$

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[1] Abraham, Weinstock, and Osborne, Phys. Rev. **76**, 864 (1949); J. G. Daunt and C. V. Heer, Phys. Rev. **79**, 46 (1950).

[2] Taconis, Beenakker, and Dokoupil, Phys. Rev. **78**, 171 (1950).

[3] E. A. Lynton and H. A. Fairbank, Phys. Rev. **80**, 1043 (1950).

[4] That is helium from natural sources, containing about one part in 10^7 of He^3.

[5] P. R. Zilsel, Phys. Rev. **79**, 309 (1950).

[6] E. F. Hammel and A. F. Schuch have recently (Schenectady conference, October 1952) described experiments on superleaks which are not obviously consistent with a two-fluid model for mixtures. However, a final interpretation of their results (which seem to contradict those of earlier experiments) must wait on further investigations.

[7] We shall see that $u_2(w)$ is analytic at $w=0$ only if the He^3 component is, like the entropy, carried entirely with the normal velocity $\mathbf{v}_n$.

[8] Lane, Fairbank, Aldrich, and Nier, Phys. Rev. **73**, 256 (1948).

exactly counterbalanced, and in which the He^3 component was found to be carried in the $\mathbf{v}_n$ direction—showing that the coefficient of $\mathbf{v}_2$ is *positive*. Koide and Usui assume,[9] however, that the coefficient of $\mathbf{v}_2$ is zero: that the average velocity of the He^3 atoms is the center-of-gravity velocity $\mathbf{v}_1$. Pomeranchuk's theory,[10] on the other hand, assumes the extreme values $\rho_{3s}=0$, $\rho_{3n}=\rho_3$: that the average velocity of the He^3 atoms is $\mathbf{v}_n$. The object of the present work, on the other hand, is to construct a general theory without making any assumptions beyond those of the traditional form of the two-fluid model (Appendix A). We shall see from the results obtained in Secs. III and IV that the ratios ρ_{3n}/ρ_3 and ρ_{4n}/ρ_4 may (like ρ_n/ρ for pure He^4) be determined empirically by suitable experiments.

Throughout this paper the equations of motion are restricted to their linear approximation, which represents those simpler dynamical effects whose study must be the first objective of the experimental program. We also exclude the linear *irreversible* effects, viscosity and heat conduction, which are known to introduce only inconsiderable refinements into the analysis of the superfluid He^4 phenomena and which may be considered second-level effects in the microscopic theory. Diffusion of He^3 relative to He^4, a linear irreversible effect peculiar to the mixtures, is introduced in a tentative way in the final Sec. V. It is shown there that the effect of diffusion on wave propagation is probably quite negligible, but that diffusion has an essential role in the *generation* of second sound in mixtures, and gives rise to a third mode of wave motion which is highly damped and confined to a thin "skin" round sources and absorbers of second sound.

The two previously published papers on this topic[9,10] make various restrictive assumptions, in addition to those mentioned above. Koide and Usui follow Gorter[11] in supposing that the division of the density between the two velocity fields may be treated as a Gibbsian equilibrium between two phases, and de Boer and Gorter[12] in setting the isotopic mixing term of the Gibbs function equal to that of an ideal solution with isotope densities ρ_3 and ρ_{4n}. Pomeranchuk, whose treatment is confined to dilute solutions ($w\ll 1$), seems to have assumed in his numerical predictions that

$$\rho_n(w)=\rho_n(0)+(m^*/m_3)\rho_3,\quad \rho_s(w)=\rho_s(0),$$

where $m^*/m_3>1$; which makes $\rho(w)>\rho(0)$, contrary to fact.[13]

II. THE REVERSIBLE EQUATIONS OF MOTION

The following equations for the mixture are proposed:

$$\partial\rho/\partial t+\operatorname{div}(\rho_n\mathbf{v}_n+\rho_s\mathbf{v}_s)=0, \tag{7}$$

$$\partial(\rho w)/\partial t+\operatorname{div}(\rho w_n\mathbf{v}_n+\rho w_s\mathbf{v}_s)=0, \tag{8}$$

$$\partial(\rho S)/\partial t+\operatorname{div}(\rho S\mathbf{v}_n)=0, \tag{9}$$

$$\rho_n\partial\mathbf{v}_n/\partial t+\rho_s\partial\mathbf{v}_s/\partial t+\operatorname{grad}P=0, \tag{10}$$

$$\partial\mathbf{v}_s/\partial t+\operatorname{grad}[g-w(\partial g/\partial w)_{P,T}] \\ +(w_s\rho/\rho_s)\operatorname{grad}(\partial g/\partial w)_{P,T}=0, \tag{11}$$

where $g=e+P/\rho-TS$ is the Gibbs function, e and S the internal energy and entropy, per unit mass of mixture. Equations (7), (8), and (9) are the conservation equations corresponding to the formulas (1) and (3) for $\mathbf{J}$, $\mathbf{J}_3$ and $\mathbf{N}$. Equations (10) and (11), the acceleration equations in linear approximation, are derived in Appendix A.

By (A3) and (A6) of the appendix, the energy flux vector $A_n\rho_n\mathbf{v}_n+A_s\rho_s\mathbf{v}_s$ is

$$\mathbf{Q}=(P+\rho e)\mathbf{v}_1 \\ +[\rho_s ST+(w_n\rho_s-w_s\rho_n)(\partial g/\partial w)_{P,T}]\mathbf{v}_2. \tag{12}$$

The $\mathbf{v}_2$ ("internal convection") term of (12), which generalizes to mixtures the corresponding term for pure He^4 found by Zilsel,[14] may be written:

$$[\rho_s S(\partial e/\partial S)_{\rho,w}+(\rho_s w_n-\rho_n w_s)(\partial e/\partial w)_{\rho,S}]\mathbf{v}_2,$$

when the exact analogy between the entropy-transport and He^3-transport parts becomes clear.

For pure He^4, the second and third terms of (11) reduce to an irrotational vector, grad$g$. Hence curl$\mathbf{v}_s$ is a constant of motion, and hence it is consistent with the equations of motion to set curl$\mathbf{v}_s=0$ identically. It is of interest to see if this result applies, on our equations, for mixtures. For Pomeranchuk's assumption ($w_s=0$), the third term of (11) vanishes and the result is still true. For the Koide-Usui assumption ($w_s\rho=\rho_s w$), $\partial(\operatorname{curl}\mathbf{v}_s)/\partial t$ is proportional to $\operatorname{grad}(\partial g/\partial w)\times\operatorname{grad}w$. But $\partial w/\partial t=-\mathbf{v}_1\cdot\operatorname{grad}w$ in this case, and hence if grad$w$ is ever zero everywhere (w constant) then it remains zero: and then curl$\mathbf{v}_s$ is constant. However, it is clear that in general, unless $w_s=0$, curl$\mathbf{v}_s$ is not constant and may not be supposed zero over all time.

III. WAVE MOTION

In this section we derive and discuss the wave equations governing macroscopic disturbances of small amplitude. For brevity we write:

$$\epsilon=(w_n\rho_s-w_s\rho_n)/w\rho_s,\quad (\epsilon\lessgtr 1) \tag{13}$$

and

$$\bar{S}=S-\epsilon\, w(\partial S/\partial w)_{P,T}. \tag{14}$$

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[9] S. Koide and T. Usui, Prog. Theor. Phys. **6**, 506 (1951).

[10] I. Pomeranchuk, J. Exptl. Theor. Phys. (U.S.S.R.) **19**, 42 (1949).

[11] C. G. Gorter, Physica **15**, 523 (1949).

[12] J. de Boer and C. G. Gorter, Physica **16**, 225 (1950).

[13] In reality, $\rho_4(w)\neq\rho(0)$. One would hence expect ρ_{4s} and ρ_{4n} each to depend on w, even if Pomeranchuk's assumption ($\rho_{3s}=0$, $\rho_{3n}=\rho_3$) is correct. Since the lambda-temperature—where $\rho_s=0$—depends on w,[1] it follows that more generally ρ_s is a function of w.

[14] Reference 5, Eq. (3.12).

Equations (7)–(11) give, in linear approximation:[15]

$$S\partial w/\partial t = \epsilon\, w \partial S/\partial t; \tag{15}$$

$$\partial^2 \rho/\partial t^2 = \nabla^2 P; \tag{16}$$

$$\partial^2 S/\partial t^2 = S(\rho_s/\rho_n)\{(1/\rho)\nabla^2 P - \nabla^2[g - w(\partial g/\partial w)_{P,T}] \\ - (1-\epsilon) w \nabla^2 (\partial g/\partial w)_{P,T}\}. \tag{17}$$

Equation (15) integrates to

$$S\delta w/\delta t = \epsilon\, w \delta S/\delta t; \tag{15'}$$

where the primes denote small deviations from the state at some arbitrary instant. Thus the fluctuations w' and S' are not independent; and hence (16) and (17) represent, as for pure He^4, a wave system with two degrees of freedom. To reduce (16) and (17) to separable form, it is most convenient to transform to the variables P', S'. By straightforward thermodynamics and substituting for w' by (15′), we find (Appendix B):

$$\rho' = \left(\frac{\partial \rho}{\partial P}\right)_{S,w} P' + \left[\bar{S}\left(\frac{\partial \rho}{\partial S}\right)_{P,w} + \epsilon\, w \left(\frac{\partial \rho}{\partial w}\right)_{P,T}\right]\frac{S'}{S}, \tag{18}$$

$$(1/\rho)P' - [g - w(\partial g/\partial w)_{P,T}]' \\ - (1-\epsilon) w[(\partial g/\partial w)_{P,T}]' \\ = \left[\bar{S}\left(\frac{\partial v}{\partial S}\right)_{P,w} + \epsilon\, w\left(\frac{\partial v}{\partial w}\right)_{P,T}\right] P' \\ + \left[\bar{S}^2\left(\frac{\partial T}{\partial S}\right)_{P,w} + \epsilon^2 w^2 \left(\frac{\partial^2 g}{\partial w^2}\right)_{P,T}\right]\frac{S'}{S}, \tag{19}$$

where

$$v = 1/\rho.$$

The wave equations derived from (15), (16), and (17) are hence

$$\begin{aligned} \partial^2 P/\partial t^2 - c_1^2 \nabla^2 P &= (\rho c_1^2 \mu/S)\partial^2 S/\partial t^2, \\ \partial^2 S/\partial t^2 - c_2^2 \nabla^2 S &= (S\rho_s/\rho\rho_n)\mu \nabla^2 P, \end{aligned} \tag{20}$$

where

$$c_1^2 = (\partial P/\partial \rho)_{S,w},$$

$$c_2^2 = (\rho_s/\rho_n)[(\bar{S})^2 T/C_{P,w} + \epsilon^2 w^2 (\partial^2 g/\partial w^2)_{P,T}], \tag{20'}$$

$$\mu = (\bar{S}/C_{P,w}) T \alpha_{P,w} + \epsilon (w/v)(\partial v/\partial w)_{P,T}$$

and where

$$C_{P,w} = T(\partial S/\partial T)_{P,w}, \quad \alpha_{P,w} = (1/v)(\partial v/\partial T)_{P,w},$$

as usual.

The equations (20) represent two wave motions, each of coupled pressure and entropy fluctuations, with velocities u_1 and u_2 given by the roots of

$$(u^2 - c_1^2)(u^2 - c_2^2) = (\rho_s/\rho_n)\mu^2 c_1^2 u^2. \tag{21}$$

The first term of Eq. (20′) for the coupling factor μ will be small, as it is for pure He^4, because α_P is small; but we would expect the second term to be appreciable when the concentration w is appreciable. The derivative $\partial v/\partial w$ has not yet been measured;[16] but we have the values for the pure liquids, $v_4 = v(0) = 6.9$ cm^3/g and $v_3 = v(1) = 12.7$ cm^3/g, from which we may take $(1/v)(\partial v/\partial w)$ to be of order unity, and hence

$$\mu \sim \epsilon w \sim w. \tag{22}$$

The factor $(\rho_s/\rho_n)\mu^2$ in (21) will always be finite, since $(\epsilon w)^2(\rho_s/\rho_n) \leqslant \epsilon w(1-w) \leqslant \frac{1}{4}$, but may be large enough at high concentrations for the actual velocities, u_1 and u_2, to deviate appreciably from c_1 and c_2. For small concentrations w, where we are looking for deviations of order w from the pure He^4 values, we may ignore the right-hand side of (21), which is of order w^2.

Appreciable coupling of thermal and acoustic disturbances will considerably complicate the wave phenomena. We set up here the equations needed for making calculations on the coupled waves: Equation (20) gives, for a wave motion of either mode, the equivalent formulas:

$$\begin{aligned} (u^2 - c_1^2)P' &= \mu\rho c_1^2 u^2 (S'/S), \\ \rho(u^2 - c_2^2)(S'/S) &= \mu(\rho_s/\rho_n)P', \end{aligned} \tag{23}$$

where $u = u_1$ or u_2, which are supplemented by the relation [Appendix B, Eq. (B3)],

$$T' = (T/C_{P,w})[\bar{S}(S'/S) + (\alpha_{P,w}/\rho)P']. \tag{24}$$

The mass and entropy flux vectors are given, for a general motion, by

$$\begin{aligned} -\partial \mathbf{J}/\partial t &= \operatorname{grad} P, \\ -\partial \mathbf{N}/\partial t &= \rho c_2^2 \operatorname{grad} S + \mu(\rho_s/\rho_n) S \operatorname{grad} P. \end{aligned} \tag{25}$$

From (24) and (25) we may write down an acceptance (inverted impedance) matrix,[17] for a plane traveling wave of either mode, according to:

$$\begin{pmatrix} \mathbf{u}\cdot\mathbf{J} \\ \mathbf{u}\cdot\mathbf{N} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ [\mu - \alpha_{P,w}(c_2^2\rho_n/\bar{S}\rho_s)]S(\rho_s/\rho_n) & \rho c_2^2 C_{P,w} S/T\bar{S} \end{pmatrix} \begin{pmatrix} P' \\ T' \end{pmatrix}, \tag{26}$$

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[15] In the equations which follow, the equals sign is to be understood as within this qualification, which will not be repeated.

[16] The curves of $v(w)$, when they are determined, will be of interest apart from the bearing indicated here on wave motion. For example, the limiting slopes of the curves will give the partial specific volumes, $v_{34} = (\partial V/\partial M_3)_{M_4,\, w\to 0} = v_4 + (\partial v/\partial w)_{w\to 0}$ and $v_{43} = (\partial V/\partial M_4)_{M_3,\, w\to 1} = v_3 - (\partial v/\partial w)_{w\to 1}$, which together with v_3 and v_4 provide four experimental measures which a realistic theory of the equilibrium state of quantum liquids should fit.

[17] J. R. Pellam, Phys. Rev. **76**, 872 (1949).

where $u=u_1$ or u_2. Equations (23) show that the second sound mode carries a pressure fluctuation

$$P_2' = -\mu \frac{\rho c_1^2 u_2^2}{c_1^2 - u_2^2}(S_2'/S), \tag{27}$$

while first sound carries an entropy fluctuation

$$S_1' = \mu \frac{(\rho_s/\rho_n)S}{\rho(u_1^2 - c_2^2)} P_1'. \tag{28}$$

However, these are not the only coupling effects which we may expect in practice. If, for example, we generate second sound in the conventional way, by a resistance strip carrying an alternating current, then the boundary conditions at the heater will be such that the first-sound *mode* must be generated at the same time. Picture the heater as a plane rigid wall, generating plane traveling waves by an oscillating outward entropy flux[18] $N(t)$: then, by the first of Eqs. (25), grad$P=0$ at the heater wall. Since the two wave modes generated have the same time variation, this means

$$P_1' = -(u_1/u_2)P_2', \text{ at the heater.} \tag{29}$$

Thus the coupling of modes at the wall leads to a bigger pressure component than does the coupling within the second mode. From (27), (28), and (29):

$$\frac{S_1'}{S_2'} = \mu^2 \frac{(\rho_s/\rho_n)c_1^2 u_1 u_2}{(c_1^2 - u_2^2)(u_1^2 - c_2^2)}, \tag{30}$$

and hence, by the second of Eqs. (25),

$$S_2' = \frac{u_2 N}{\rho c_2^2} \bigg/ \left[1 + \frac{\mu^2(\rho_s/\rho_n)c_1^2 u_2^2}{(c_1^2 - u_2^2)(u_1^2 - c_2^2)}\right], \text{ at the heater.} \tag{31}$$

If the oscillating flux N is periodic, then at increasing distances from the heater the pressure oscillations P_1' and P_2' will be alternately in and out of phase. If N_0 is the amplitude of N at the heater, then (neglecting μ^2) by (27), (29), and (31) the pressure amplitude will vary between the limits

$$P_0 = \frac{\mu N_0}{S}\frac{u_1^2}{u_1 + u_2}, \text{ and } P_0 = \frac{\mu N_0}{S}\frac{u_1^2}{u_1 - u_2}. \tag{32}$$

A rough estimate shows that amplitudes of grams per cm^2 should be readily produced in this way (indeed, for low temperatures and appreciable concentrations the cavitation threshold may be an effective limitation on second-sound amplitude†). It is suggested that measurements of this pressure effect be made to obtain an estimate of μ, and hence, when $\partial v/\partial w$ is determined, of ϵ.

The excitation of standing waves of second sound in a cavity requires a more complicated analysis, which is not attempted here. The Pellam disk experiment[19] registers a force proportional to

$$\rho_n v_n^2 + \rho_s v_s^2 = (\rho_n/\rho_s)[J^2/\rho_n - 2\mathbf{N}\cdot\mathbf{J}/S + N^2/S^2], \tag{33}$$

at the center of the cavity. It appears from the foregoing considerations that an analysis of this effect for mixtures,[20] as was attempted by Koide and Usui,[9] should take due account of the coupling measured by μ.

IV. EVALUATION OF RESULTS; DILUTE SOLUTIONS

The formulas (20′) are in terms of thermodynamic functions for mixtures, and their derivatives with respect to concentration, which are not known directly from practical measurements. This deficiency may be largely filled by combining the values of the functions for the pure He^3 and pure He^4 liquids with the extensive data on the partial vapor pressures of mixtures which have been obtained.[21] The link between the vapor pressures and the liquid functions is the equality of each of the chemical potentials in the two phases. This equality is expressed by the equations[22]

$$\begin{aligned} g - w(\partial g/\partial w)_{P,T} &= g_4 + (kT/m_4)\ln(p_4/p_4^0), \\ g + (1-w)(\partial g/\partial w)_{P,T} &= g_3 + (kT/m_3)\ln(p_3/p_3^0), \end{aligned} \tag{34}$$

where m_3 and m_4 are the atomic masses, p_3 and p_4 the partial pressures, and where g_3 and p_3^0 refer to pure He^3 liquid, g_4 and p_4^0 to pure He^4 liquid. (To allow for the nonideality of the vapor, the pressures p should be replaced by fugacities.[22]) In obtaining the other functions for the liquid from Eqs. (34), we have to remember that the latter are valid only on the saturation surface in the $P-T-w$ diagram. Thus, taking the difference of the two equations and differentiating along the line "$T=$constant" in the surface:

$$\left(\frac{\partial^2 g}{\partial w^2}\right)_{P,T} + \left(\frac{\partial v}{\partial w}\right)_{P,T}\left(\frac{\partial P_{\text{sat}}}{\partial w}\right)_T = kT\left[\frac{1}{m_3 p_3}\left(\frac{\partial p_3}{\partial w}\right)_T - \frac{1}{m_4 p_4}\left(\frac{\partial p_4}{\partial w}\right)_T\right].$$

Since the second term on the left may be neglected, this result gives the $w^2(\partial^2 g/\partial w^2)_{P,T}$ which occurs in the formula (20′) for c_2. $\bar{S}$ and $C_{P,w}$ are derived in the same way. Writing

$$\ln(p_3/p_3^0) = r_3, \quad \ln(p_4/p_4^0) = r_4 \tag{35}$$

for brevity, and neglecting terms in P_{sat} as before, we

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[18] There will necessarily also be a constant (dc) flux, which does not affect this analysis and which we ignore.

† *Note added in proof:*—With positive temperature *pulses*, rather than continuous ac, the tension tending to cause cavitation would have the smaller value given by (27).

[19] J. R. Pellam and W. B. Hanson, Phys. Rev. 85, 216 (1952).

[20] B. Weinstock and J. R. Pellam, Phys. Rev. 89, 521 (1953).

[21] H. S. Sommers, Jr., Phys. Rev. 88, 113 (1952).

[22] See E. A. Guggenheim, *Thermodynamics* (North-Holland Publishing Company, Amsterdam, 1949), Chap. 5. For the purposes of this paper, we express the formulas in terms of the concentration by mass w.

have altogether:

$$\bar{S}=S_4+(1-\epsilon)w(S_3-S_4)$$
$$-k\frac{\partial}{\partial T}\left[\frac{r_4T}{m_4}+(1-\epsilon)w\left(\frac{r_3}{m_3}-\frac{r_4}{m_4}\right)T\right],$$
$$C=wC_3+(1-w)C_4-kT\frac{\partial^2}{\partial T^2}\left[\frac{wr_3T}{m_3}+(1-w)\frac{r_4T}{m_4}\right], \quad (36)$$
$$\frac{\partial^2 g}{\partial w^2}=kT\frac{\partial}{\partial w}\left[\frac{r_3}{m_3}-\frac{r_4}{m_4}\right].$$

(To the approximation in which the P_{sat} term is neglected, C_P and C_v are not distinguished.) Thus, if the pure liquid data, the partial vapor pressures, and $\rho(P,T,w)$ are known, it is possible in principle to express ϵ and ρ_s/ρ_n in terms of u_1 and u_2.

The formulas (36) reduce to a more tractable and interesting form for the case of dilute solutions ($w\ll 1$), on which measurements of u_2 have actually been made and published.[3] It is known[21] that Henry's Law—the proportionality of solute vapor pressure to concentration—applies to sufficiently weak solutions of He^3.[23] We may then set

$$p_3=a(T)\cdot Xp_3{}^0+O(X^2), \quad p_4=(1-X)p_4{}^0+O(X^2), \quad (37)$$

where

$$X=\frac{m_4w}{m_3}\bigg/\left[1+\left(\frac{m_4}{m_3}-1\right)w\right] \quad (38)$$

is the concentration of He^3 by molar fraction, the measure commonly quoted in the literature. If the solution were ideal, we would have $a=1$. The second of Eqs. (37) necessarily follows from the first, by the Duhem-Margules equation.[24] Substitution of (37) into (36) gives:

$$\bar{S}=S_4+(1-\epsilon)\frac{m_3}{m_4}X(S_3-S_4)$$
$$+\frac{kX}{m_4}\left[1-(1-\epsilon)\frac{d(T\ln a)}{dT}-(1-\epsilon)\ln X\right],$$
$$C=C_4+X\left[\frac{m_3}{m_4}(C_3-C_4)-\frac{kT}{m_4}\frac{d^2(T\ln a)}{dT^2}\right], \quad (39)$$
$$w^2\left(\frac{\partial^2 g}{\partial w^2}\right)=\frac{kTX}{m_4},$$

+higher powers of X. Since $u_2{}^2-c_2{}^2$ vanishes as X^2 for dilute solutions, substitution of (39) in the second of (20′) gives $u_2{}^2$ as a function of ϵ, X, T, and ρ_s/ρ_n. If we assume with Pomeranchuk that the He^3 moves entirely with the normal fluid (i.e., set $\epsilon=1$), then we find

$$u_2{}^2=(\rho_s/\rho_n)[(S_4+kX/m_4)^2T/C(X)+kTX/m_4], \quad (40)$$

which is Pomeranchuk's result.[10] The above derivation of (40) shows that it is valid for just that range of concentrations for which Henry's Law is true. Corrections for higher concentrations, in terms of the deviations from Henry's Law, may be obtained from (36). We may expect ρ_s/ρ_n to be expandible as a power series in X,[25] so that according to (40)

$$[u_2(X)]^2=[u_2(0)]^2[1+XQ(T)+\cdots]. \quad (40')$$

If, on the other hand, $1-\epsilon$ does *not* vanish, then $u_2{}^2$ may not be expanded as a power series in X. We have instead an expansion of form

$$[u_2(X)]^2/[u_2(0)]^2=1$$
$$+XQ(T)+(X\ln X)R(T)+\cdots. \quad (41)$$

It follows that a sufficiently accurate examination of the dependence of u_2 on X for very small values of X (say 0.01 downward) would show whether or not $\epsilon=1$, i.e., whether or not $\rho_{3s}=0$, by the absence or presence of a $X\ln X$ term in the dependence. If such a term is present, then the determination of Q and R in (41) will serve to determine ϵ, and the dependence of ρ_s/ρ_n on X, separately. The numerical analysis depends on values of $a(T)$, Eq. (37), obtained from the vapor pressure data, and to a lesser extent on values of the entropy for pure He^3 liquid.[26] Q and R will increase very rapidly with decreasing temperature. For $\epsilon=1$, the part of Q not contributed by the variation of ρ_s/ρ_n with X is already of order 10^2 at 1.4°. It is therefore understandable that Lynton and Fairbank found a large increase of u_2 even for small concentrations, at such temperatures.

If $\epsilon\neq 1$, and varies with X, then for appreciable concentrations a knowledge of u_2, the vapor pressures, and the thermodynamic functions for the pure liquids, is not sufficient to determine ϵ and ρ_s/ρ_n separately. We need also (for example) the coupling factor μ and $v(X)$. In principle, μ might be found by comparing $u_1(X)$ with the values of $c_1(X)$ calculated from $P(\rho,T,X)$; but one would not expect the practical accuracy of this method to be good enough. However, as was remarked in Sec. III, μ might be found by measuring the pressure fluctuations in second sound; and there seems a reasonable hope that this method would be of tolerable accuracy.

V. DIFFUSION

In the preceding analysis we have ignored the possibility of *diffusion* of He^3 relative to He^4 [in addition to the reversible relative motion given by (3)] under a

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[23] Application of Nernst's Law to the expression for S derived from (34) (or equally to $\bar{S}$ in (36)) shows that Henry's Law must be violated at sufficiently low temperatures. The vapor pressure measurements only go down to 1.27°, and it seems unlikely that they can be carried much further.

[24] Reference 22, Eq. (5.20.3).

[25] This is not completely obvious. It would not be true if, for example, Tisza's relation $\rho_n/\rho=S/S_\lambda$ held for mixtures, because the expansion of S requires a term in $X\ln X$.

[26] Weinstock, Abraham, and Osborne, Phys. Rev. **89**, 787 (1953).

gradient of concentration and of the other thermodynamic variables. We shall see in this section that diffusion probably has a negligible influence on the propagation of free first- and second-sound waves. However, the *generation* of the waves at a solid surface cannot in general be consistently described without admitting diffusion.[27] At a solid wall the normal components of $\mathbf{J}$ and $\mathbf{J}_3$ must vanish separately; and consequently, if we did not allow diffusion, only for the Koide-Usui assumption ($\epsilon=0$) would the generation of second sound waves by the usual method be possible.

Beenakker *et al.*[28] have investigated the diffusion rate in very dilute solutions by measuring their thermal resistance. Arguing that thermal diffusion should be negligible[29] compared with concentration diffusion, they deduce from their measurements a concentration-diffusion coefficient D decreasing from about 2.5×10^{-2} cm²/sec at 1.2° to about 4×10^{-4} cm²/sec at 2.1°. Since the ratio of temperature gradient to concentration gradient is proportional to $(1/w)$ in second sound, whereas it is independent of w in the experiment quoted, the argument for neglecting thermal diffusion does not apply to second sound. However, we shall be concerned here simply with exploring qualitatively the consequences of diffusion, and accordingly use as a model the simplest equations which will serve this purpose—any particular model being, at this stage, provisional. We retain Eqs. (7), (9), (10), and (11), and replace (8) by

$$\partial(\rho w)/\partial t+\operatorname{div}[\rho w(\mathbf{v}_n+\mathbf{v}_3)]=0, \tag{42}$$

where

$$w\mathbf{v}_3=-D\operatorname{grad}w; \tag{43}$$

setting $w_s=0$, for simplicity, and neglecting thermal diffusion. We also neglect the coupling of entropy and pressure fluctuations, measured by μ of Sec. III, and solve the equations at constant pressure. If we define an operator

$$K=D\nabla^2\int dt\cdots, \tag{44}$$

then (to linear approximation as usual)

$$w\partial S/\partial t=S(1-K)\partial w/\partial t. \tag{45}$$

The wave equation for entropy and concentration fluctuations is hence

$$(1-K)\partial^2S/\partial t^2=[c_2^2-(\rho_s/\rho_n)(S\bar{S}T/C)K]\nabla^2S, \tag{46}$$

where $\bar{S}$ and c_2 are defined as in Sec. III, with $\epsilon=1$. If we now represent the time variation of S by the factor $\exp(2\pi ift)$, then the complex velocity of propagation u is given by substituting into (46):

$$K=2\pi iDf/u^2. \tag{44'}$$

Hence,

$$u^2[u^2-(c_2^2+ic_3^2)]=-i\alpha c_2^2c_3^2, \tag{47}$$

where

$$c_3^2=2\pi Df,\quad \alpha c_2^2=(\rho_s/\rho_n)S\bar{S}T/C. \tag{48}$$

The two roots of (47) correspond to a very slightly damped second sound and to a third very strongly damped "skin" mode. For the practical frequencies f and the Leiden values of D, $c_3^2\ll c_2^2$. Hence the roots are, to sufficient approximation,

$$u_2^2=[1+i(1-\alpha)(c_3/c_2)^2]c_2^2,\quad u_3^2=i\alpha c_3^2. \tag{49}$$

The extinction coefficient for second sound is thus at most of order Df^2/c_2^3 and hence will be negligible. In contrast, the mode corresponding to u_3 will be localized within a distance (from the source of the wave) of order $\sqrt{(D/f)}$: it will hence be confined in practice to a very thin skin around the source. There is thus a formal resemblance to the extra modes discussed by Kronig and Thellung.[30]

To satisfy the boundary conditions at the surface of a heater resistance, which is the conventional source of second sound, both second and third modes must be generated. By (45), the entropy and He³-mass currents, in either mode, are related by

$$\mathbf{N}^{(q)}=(S/w)(1-K^{(q)})\mathbf{J}_3^{(q)};\quad q=2,3, \tag{50}$$

where the superscripts label the mode. By (49) we may set

$$1-K^{(2)}\simeq1,\quad 1-K^{(3)}\simeq-(1-\alpha)/\alpha; \tag{51}$$

and hence, since the normal component of $\mathbf{J}_3=\mathbf{J}_3^{(2)}+\mathbf{J}_3^{(3)}$ vanishes at the heater surface, we have

$$N^{(3)}/N=1-\alpha \text{ at the heater.} \tag{52}$$

Equation (52) gives the fraction of the "signal" lost into the damped mode, on the present model. For dilute solutions we may write it:

$$\frac{N^{(3)}}{N}=\frac{X}{m_4}\left\{\frac{k}{S_4}\left[\ln X+\frac{C_4}{S_4}+\frac{d(T\ln a)}{dT}\right]+m_3\left(1-\frac{S_3}{S_4}\right)\right\}. \tag{52'}$$

Thus a fraction, of order X, of the signal is lost at the generator because of diffusion. An experimental study of this loss (or of the corresponding effect in the transimission of second sound through a thin conducting foil) might be complicated by the processes underlying the Kapitza temperature difference[31] at the boundary.[32] If the signal loss (52) is small, then we may expect that the formulas obtained in Sec. III for the pressure fluctuation in free second-sound waves will not be appre-

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[27] This remark (and the impetus thereby to the work in this section) is due to F. London.

[28] Beenakker, Taconis, Lynton, Dokoupil, and Van Soest, Physica 18, 433 (1952).

[29] Their argument for neglecting thermal diffusion in their experiment may at best be admitted provisionally, pending a realistic theoretical understanding of the magnitudes of the two coefficients; but their values for D are in any case presumably correct in order of magnitude, and will be used here as orders of magnitude.

[30] R. Kronig and A. Thellung, Physica 16, 678 (1950).

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

[32] I am indebted for this remark to J. R. Pellam.

ciably modified by diffusion; since (29) will still apply at a distance from the wall greater than the skin thickness but small compared with the wavelength.

It should be emphasized that the valid conclusions from the work in this section are qualitative and order-of-magnitude ones. In making the simplest possible modification, by (42) and (43), of the hydrodynamic equations, we have not taken account of the necessity for preserving the equations of conservation of energy and of momentum, and of "semi-conservation" (increase only) of entropy. It seems desirable that a study be made of the way in which the possible equations including diffusion are restricted by these conservation laws and the Onsager relations.[33] A detailed investigation—theoretical and experimental—of diffusion should be of some importance to the microscopic theory, in providing a clue to the way in which the He^3 component participates in the excitations of the liquid.

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APPENDIX A. THE EQUATIONS OF MOTION

Since

$$\delta(\rho e)=[g-w(\partial g/\partial w)_{P,T}]\delta\rho +(\partial g/\partial w)_{P,T}\delta(\rho w)+T\delta(\rho S), \qquad \text{(A1)}$$

we have by (7), (8), and (9):

$$-\partial(\rho e)/\partial t=[g-w(\partial g/\partial w)_{P,T}]\,\operatorname{div}(\rho_n\mathbf{v}_n+\rho_s\mathbf{v}_s) +(\partial g/\partial w)_{P,T}\,\operatorname{div}(\rho w_n\mathbf{v}_n+\rho w_s\mathbf{v}_s)+T\,\operatorname{div}(\rho S\mathbf{v}_n). \qquad \text{(A2)}$$

Limiting ourselves to terms quadratic and lower in the velocities, we may expect the two-fluid motion to satisfy as usual an energy-balance equation of form[14]

$$0=\partial(\tfrac{1}{2}\rho_n v_n^2+\tfrac{1}{2}\rho_s v_s^2+\rho e)/\partial t +\operatorname{div}(A_n\rho_n\mathbf{v}_n+A_s\rho_s\mathbf{v}_s), \qquad \text{(A3)}$$

where $A_n=A_n(\rho, S, w)$, $A_s=A_s(\rho, S, w)$. We choose A_n and A_s such that (A3) may be reduced to the form:

$$0=\partial(\tfrac{1}{2}\rho_n v_n^2+\tfrac{1}{2}\rho_s v_s^2)/\partial t-\rho_n\mathbf{v}_n\cdot\mathbf{F}_n-\rho_s\mathbf{v}_s\cdot\mathbf{F}_s, \qquad \text{(A4)}$$

where $\mathbf{F}_n$ and $\mathbf{F}_s$ are linear combinations of gradients of the thermodynamic functions:—i.e., with the terms remaining, in $\operatorname{div}(\rho_n\mathbf{v}_n)$ and $\operatorname{div}(\rho_s\mathbf{v}_s)$, cancelled identically. Equation (A4) may be written

$$0=\tfrac{1}{2}(v_n^2\dot{\rho}_n+v_s^2\dot{\rho}_s) +\rho_n\mathbf{v}_n\cdot(\dot{\mathbf{v}}_n-\mathbf{F}_n)+\rho_s\mathbf{v}_s\cdot(\dot{\mathbf{v}}_s-\mathbf{F}_s); \qquad \text{(A4}'\text{)}$$

and hence—since the first term of (A4′) belongs to the higher powers of the velocities which we are neglecting—the form (A4) implies equations of motion:

$$\dot{\mathbf{v}}_n=\mathbf{F}_n, \quad \dot{\mathbf{v}}_s=\mathbf{F}_s. \qquad \text{(A5)}$$

Thus our choice of A_n and A_s is just that designed to preserve the conventional form of the two-fluid dynamics. Substituting (A2) in (A3), we find that (A4) implies

$$\left.\begin{aligned} A_n&=g+(\partial g/\partial w)_{P,T}(w_n\rho_s-w_s\rho_n)/\rho_n+TS\rho/\rho_n,\\ A_s&=g+(\partial g/\partial w)_{P,T}(w_s\rho_n-w_n\rho_s)/\rho_s, \end{aligned}\right\} \qquad \text{(A6)}$$

and

$$\left.\begin{aligned} \mathbf{F}_n&=-\operatorname{grad}A_n+(\partial g/\partial w)_{P,T}\operatorname{grad}(\rho w_n/\rho_n) +T\operatorname{grad}(\rho S/\rho_n),\\ \mathbf{F}_s&=-\operatorname{grad}A_s+(\partial g/\partial w)_{P,T}\operatorname{grad}(\rho w_s/\rho_s). \end{aligned}\right\} \qquad \text{(A7)}$$

From (A5), (A6), and (A7) we obtain (10) and (11), which are evidently the only linear equations consistent with the forms of (A3) (energy flux vector) and (A5) (d'Alembert forces).

APPENDIX B. TRANSFORMATION FORMULAS

Expand ρ and S as functions of P, T and w, and substitute for w' by (15′):

$$\rho'=\left(\frac{\partial\rho}{\partial P}\right)_{T,w}P'+\left(\frac{\partial\rho}{\partial T}\right)_{P,w}T' +\epsilon w\left(\frac{\partial\rho}{\partial w}\right)_{P,T}\left(\frac{S'}{S}\right), \qquad \text{(B1)}$$

$$S'=\left(\frac{\partial S}{\partial P}\right)_{T,w}P'+\left(\frac{\partial S}{\partial T}\right)_{P,w}T' +\epsilon w\left(\frac{\partial S}{\partial w}\right)_{P,T}\left(\frac{S'}{S}\right). \qquad \text{(B2)}$$

Equation (B2) gives

$$T'=\left(\frac{\partial T}{\partial S}\right)_{P,w}\bar{S}\left(\frac{S'}{S}\right)+\left(\frac{\partial T}{\partial P}\right)_{S,w}P', \qquad \text{(B3)}$$

which, substituted into (B1), yields (18). Similarly expanding g and $(\partial g/\partial w)_{P,T}$, we have

$$[g-w(\partial g/\partial w)_{P,T}]'+w(1-\epsilon)[(\partial g/\partial w)_{P,T}]' =[v-\epsilon\, w(\partial v/\partial w)_{P,T}]P'-\bar{S}T' -\epsilon^2 w^2(\partial^2 g/\partial w^2)_{P,T}(S'/S). \qquad \text{(B4)}$$

Substituting (B3) into (B4) yields (19).

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[33] For Onsager relations see S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951).