ments from Professor M. E. Fisher and Professor H. A. Gersch. He is also indebted to Dr. G. H. Walker for his help in computer analysis.

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[1]M. E. Fisher, in Lectures in Theoretical Physics, edited by Wesley E. Brittin et al. (University of Colorado Press, Boulder, Colorado, 1965), pp. 1-159, and in Proceedings of the Centennial Conference on Phase Transition, University of Kentucky, 1965 (unpublished).

[2]This bound for τ is different from Fisher's (Ref. 1). Landau has shown that $\partial P/\partial V = \partial^2 P/\partial V^2 = 0$, at $t = T_c$, and therefore it is impossible for $\delta < 2$, hence, by Eq. (7), $2 < \tau < 2.5$ instead of $2 < \tau < 3$.

[3]A computer program has been made for Eq. (6) to calculate the value of τ with corresponding compressibility factor. We are able to get the accuracy of τ to 10^{-6}.

[4]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sons, Inc., New York, 1964).

[5]M. E. Fisher, Rept. Progr. Phys. 30, 615 (1967), Pt. II.

[6]M. E. Fisher, Phys. Rev. 136, A1599 (1964).

[7]From Ref. 2 we notice that the value of τ should be between 2 and 2.5 for the critical region; this means that the maximum possible change of τ is 0.5 for a substance which has a transition. In our calculations, the value of τ changes from 2.216 (CH_3CH) to 2.237 (He^4). Compared with the range of τ for the critical region, it is a significant difference.

ARE THERE THERMOELECTRIC EFFECTS IN SUPERCONDUCTORS?

Seth Putterman
Rockefeller University, New York, New York 10021

and

R. de Bruyn Ouboter
Kamerlingh Onnes Laboratorium, Leiden, The Netherlands

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A comparison between He II when the normal fluid is clamped and the superconducting state of metals leads to an extension of the two-fluid equations of London. The following consequences are discussed: (a) A nonstationary thermal emf (thermal electric effect) can exist in a superconductor, (b) a stationary potential difference (not an emf) can exist.

It is commonly accepted that there can be no thermoelectric effects in superconductors. This is based on the early experiments of Casimir and Rademakers on the Seebeck effect and of Daunt and Mendelssohn on the Thomson heat which show that in the usual stationary-state arrangement these effects vanish in the superconducting state.[1] Balazs[2] has in addition tried to show that in the macroscopic theory of London there is no room for any thermoelectric currents. In this Letter we will show that an extension of the two-fluid interpretation of the London theory leads to thermoelectric effects in nonstationary situations which are perhaps observable.

The motivation for the extension of the two-fluid model for superconductors comes from the comparison of superconductors with the superfluid state of helium (He II). It is well known that they have many similar properties (e.g., persistent currents), but it is perhaps not sufficiently realized that there is the following major difference. In He II both the normal and the superfluid components are in first approximation able to flow reversibly (that is, without dissipation) but in a superconductor the normal electrons are in first approximation clamped by the lattice.[3] Any flow of normal electrons involves dissipation. It seems therefore much better to compare the behavior of a superconductor with that of He II when the normal fluid is clamped (normal fluid velocity $\vec{v}_n = 0$) such as is experimentally realized in a superleak. This suggests that one has only one dynamical equation, namely for the superfluid component. For the superconductor this becomes in first approximation

$$\frac{D_s \vec{v}_s}{Dt} = -\vec{\nabla}\mu + \frac{e}{m}\left(\vec{E} + \frac{1}{c}\vec{v}_s \times \vec{B}\right) \quad (1)$$

which differs only by the $\vec{\nabla}\mu$ term (μ = chemical potential per gram) from the equation London proposed ($\vec{v}_s$ is the superfluid velocity).[4] This still leads for the analog of irrotational flow to the equation

$$\vec{\nabla}\times\vec{v}_s = -\frac{e}{mc}\vec{B} \tag{2}$$

which with $\vec{j}_s = e\rho_s\vec{v}_s$ and $\Lambda = m/\rho_s e^2$ (ρ_s = number density of superelectrons) is the first London equation. For such a flow (1) can be replaced by

$$\frac{\partial\vec{v}_s}{\partial t} = \frac{e}{m}\vec{E} - \vec{\nabla}\left(\mu + \frac{v_s^2}{2}\right). \tag{3}$$

In this approximation one has a continuity equation for ρ_s, the entropy is constant in time, and there is conservation of energy but not of momentum.

In the next approximation one can introduce the dissipative effects, again in a similar way as in He II,[5] and one is led to the following set of equations:

$$\frac{\partial\rho}{\partial t} + \vec{\nabla}\cdot(\rho_s\vec{v}_s + \vec{j}_n) = 0 \qquad (\rho = \rho_s + \rho_n), \tag{4}$$

$$T\left(\frac{\partial(\rho s)}{\partial t} + \vec{\nabla}\cdot\vec{q}\right) = R, \tag{5}$$

$$\frac{\partial\vec{v}_s}{\partial t} = \frac{e}{m}\vec{E} - \vec{\nabla}\left(\mu + \frac{v_s^2}{2}\right) - \vec{\nabla}h. \tag{6}$$

Here $\vec{j}_n$ is the normal-current density, T the temperature, s = entropy per electron, $\vec{q}$ = heat-current density, and R is the entropy production, which must be positive definite. The dissipative term $\vec{\nabla}h$ in the superfluid equation does not affect the validity of the London equation (2). To these equations must be added, besides the Maxwell equations, the phenomenological relations for the dissipative fluxes which become in the linear approximation

$$e\vec{j}_n = \sigma\left[\vec{E} - \frac{m}{e}\vec{\nabla}\left(\mu + \frac{v_s^2}{2}\right)\right] + \sigma\alpha\vec{\nabla}T, \tag{7}$$

$$\vec{q} = -\kappa\vec{\nabla}T - \sigma\beta\left[\vec{E} - \frac{m}{e}\vec{\nabla}\left(\mu + \frac{v_s^2}{2}\right)\right], \tag{8}$$

$$h = -\zeta\vec{\nabla}\cdot\rho_s\vec{v}_s, \tag{9}$$

where, in order that R be positive definite, σ, κ, and ζ must be positive and $(\alpha+\beta)^2 < 4\kappa/\sigma$. Finally $\alpha = \beta$ according to Onsager, so that there are four independent transport coefficients. Note that there is room for a thermoelectric current in $\vec{j}_n$. In fact, except for the term $v_s^2/2$, Eq. (7) has the same form as for a normal metal.[6] For the energy equation implied by the basic equations one obtains in the special case that $\vec{E} = -\vec{\nabla}\varphi$

$$\frac{\partial U}{\partial t} = -\vec{\nabla}\cdot\left[\left\{m\left(\mu + \frac{v_s^2}{2}\right) + e\varphi\right\}(\rho_s\vec{v}_s + \vec{j}_n) + T\vec{q} + m\rho_s h\vec{v}_s\right], \tag{10}$$

where U is given by

$$dU = \left\{m\left(\mu + \frac{v_s^2}{2}\right) + e\varphi\right\}d\rho + Td(\rho s) + m\rho_s\vec{v}_s\cdot d\vec{v}_s.$$

With regard to possible experimental verifications first note that in the stationary state (ignoring from now on possible contributions from the $\vec{\nabla}h$ term) the electrochemical potential $m[\mu + v_s^2/2] + e\varphi$ is a constant [as follows from (6)] so that there can be no emf even if there exists a $\vec{\nabla}T$ (no Seebeck effect). In this case $j_n \neq 0$ and one must say, following Ginsburg, that there is a stationary supercurrent which cancels $\vec{j}_n$ (in the usual case that the circuit may be considered open) so that the total current vanishes. Consider next the energy developed for the case in which we can consider ρ and $\vec{v}_s$ stationary. We find from (10), using (6) and (4),

$$\frac{\partial U}{\partial t} = \vec{\nabla}\cdot(\kappa T\vec{\nabla}T).$$

Unlike a normal metal there is no contribution to the energy developed which changes sign upon reversal of the current (i.e., no Thomson heat).

We now discuss three consequences of the equations presented here which may lead to an experimental verification:

(1) There can exist a nonstationary Seebeck effect as can be realized by incorporating (6) in (7) to obtain for the total electric current

$$\vec{J} = e\rho_s\vec{v}_s + \frac{m}{e}\sigma\frac{\partial\vec{v}_s}{\partial t} + \sigma\alpha\vec{\nabla}T. \tag{11}$$

Under conditions that $\vec{J} = 0$, (11) becomes a differential equation for $\vec{v}_s$ with $\vec{\nabla}T$ as the driving force. The line integral of $(m/e)\partial v_s/\partial t$ gives the nonstationary Seebeck emf and in the case that a temperature difference $(\delta T)\exp(i\omega t)$ exists in a superconducting circuit one finds an emf of the order $\omega\tau(\delta T)\alpha$ ($\tau \simeq m\sigma/e^2\rho_s$, and we have taken $\omega\tau \ll 1$) which lags the temperature by a phase $\omega\tau$. Note that, except near the transition temperature, $\tau < 10^{-10}$ sec so the effect may be small.

(2) There exists a longitudinal-wave solution to the complete set of equations which is analogous to fourth sound in He II. The dispersion law re-

lating wave number k and frequency ω is

$$\frac{\omega^2}{c^2} - \frac{1}{\lambda^2} = k^2 \frac{U_4^2}{c^2}, \qquad (12)$$

where $U_4^2 = \rho_s(\partial\mu/\partial\rho)_{\rho s}$ and depends on the equations of state of the electron fluid, and $\lambda = (mc^2/4\pi e^2\rho_s)^{1/2}$ is the penetration depth. Taking $\lambda = 10^{-5}$ cm one finds that the wave will decay over a distance $\lambda_4 = (U_4/c)\lambda$ unless ω is of the order of 10^{15} sec^{-1}. Such longitudinal fields may be very difficult to produce.

(3) Although the electrochemical potential is constant in the stationary state, there can be an electric field (analogous to the fountain pressure in He II)

$$\vec{E} = \frac{m}{e}\vec{\nabla}\mu$$

(where we have neglected contributions from v_s^2).

Experiments are under way in Leiden to try to observe this effect in niobium, where a temperature difference of the order of 1°K leads to a potential difference from 10^{-7} to 10^{-6} V.

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[2]N. L. Balazs, Physica 41, 393 (1969). Compare also the remarks by C. Kittel, Introduction to Solid State Physics (John Wiley & Sons, Inc., New York, 1957), 2nd ed., p. 460.

[3]Compare D. Pines, in Quantum Fluids, edited by D. F. Brewer (North-Holland Publishing Company, Amsterdam, The Netherlands 1966), p. 34.

[4]F. London, Superfluids (John Wiley & Sons, Inc., New York, 1954), Vol. I, p. 29. On p. 59 London discusses the possibility of supplementing the superfluid equation by a term $\vec{\nabla}\mu$, but he neglects it since the effects will be small. The term $\vec{\nabla}\mu$ was introduced by V. Ginsburg, Zh. Eksperim. i Teor. Fiz. 14, 177 (1944).

[5]See I. M. Khalatnikov, Introduction to the Theory of Superfluidity (W. A. Benjamin, Inc., New York, 1965), Chap. 9. Note that even in the case of He II in a superleak the dissipative equations do not follow from taking $\vec{v}_n = 0$ in the dissipative equations of unclamped He II. They must be derived independently from general principles. One finds that they are given by (4), (5), (6) with $e = 0$, so that even on the dissipative level the analogy between clamped superfluid and superconductor is valid.

[6]Equation (7) was proposed by Ginsburg (Ref. 4).