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Time Variation of the Ginzburg-Landau Order Parameter*

ELIHU ABRAHAMS AND TOSHIHIKO TSUNETO†
Physics Department, Rutgers University, New Brunswick, New Jersey

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We use a nonequilibrium form of the Green's-function formulation of the BCS theory of superconductivity to investigate the circumstances under which differential equations in space and time, i.e., "time-dependent Ginzburg-Landau equations," give a valid description of the space and time variation of the order parameter Ψ in superconductors. We find that if the variations are sufficiently slow, time-dependent Ginzburg-Landau equations exist near absolute zero and near the transition temperature. In the former case the equation has wave-like character, and in the latter case it is of diffusion type, with the restriction that either the characteristic frequency of the time variation of Ψ is greater than the gap frequency or the ratio of the Fermi velocity to the product of the characteristic wavelength and frequency of the space-time variation of Ψ is greater than unity. Under all other circumstances and at general temperatures, there are no differential equations to describe the variations of Ψ. We discuss also the influence of slowly varying time-dependent fields and derive the dependence of charge and current densities on the variations of Ψ. Local electrodynamics are assumed. The necessary modifications for the case of dilute superconducting alloys are described. Applications are made to the questions of collective modes, nucleation, and London's theory near absolute zero.

I. INTRODUCTION

THE phenomenological theory of Ginzburg and Landau[1] (GL) describes the equilibrium properties of a superconductor in a spatially varying magnetic field. The GL equations are differential equations which relate the spatial variation of the order parameter Ψ to the vector potential and the current.

Gor'kov[2,3] was able to show that the GL equations are a consequence of the microscopic theory of superconductivity[4,5] when the temperature T is close to the transition temperature T_c. The order parameter of the GL theory is identified with the energy-gap function of the microscopic BCS theory. Subsequently, the ideas of Gor'kov were extended to lower temperatures by others[6–8] and corresponding GL equations were derived from the microscopic theory. A common feature of all this work is the requirement that the order parameter and vector potential vary slowly over distances of the order of the coherence length and that the electrodynamics be local (London limit).

In this paper, we investigate the question of whether or not it is possible to extend the Gor'kov formulation to the nonequilibrium situation in order to discuss the time variation of the order parameter by means of time-dependent GL equations. These would be differential equations in space and time relating the variations of the order parameter to space and time-varying fields and the charge and current densities. In the case of a pure superconductor, we find time-dependent GL equations only when T is near absolute zero and when T is near T_c. In the former case, the equation for the order parameter is wave-like and in the latter case it is of diffusion-type.

In a recent note, Stephen and Suhl[9] addressed themselves to the same question and used a formulation which is in many respects similar to the one with which we begin our discussion. We differ with them in our methods of analysis and we defer relevant remarks to the concluding Sec. VII of this paper.

We mention two limitations to our development here. Firstly, we take the thermal excitations (normal fluid) in the superconductor to be always at rest and in equilibrium with the local value of the energy-gap parameter and the external fields. This presupposes that the characteristic time for interaction between the heat bath (lattice vibrations) and the thermal excitations is short compared to the characteristic time for normal to superfluid conversion. Secondly, in anticipation of the case of the charged superconductor where density fluctuations are suppressed due to the long-range nature of the Coulomb interaction, we do not, even in the neutral case, solve simultaneously for the motion of the order parameter and the motion of the density. That is, we take the variation of the order parameter to be the sole driving term. More detailed remarks on these points will be made at appropriate places in the text.

We devote the greater part of the paper to the neutral pure superconductor. In the charged case, we restrict

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† On leave from (and present address) Department of Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Japan.

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ourselves to the London limit and give only the leading terms in the external fields. We discuss briefly the effect of impurities on some of the results. In Sec. II, we develop the formalism for treating the nonequilibrium case and apply it to the situation that the order parameter has sufficiently small time and space variations. In Sec. III, we use the formalism to extend the Gor'kov expansion procedure[2] when the order parameter varies slowly to the case of time as well as space variations and we derive time-dependent GL equations. In Sec. IV, we show that the expansion procedure of Sec. III is valid only at $T=0$ and we derive the correct time-dependent GL equation near T_c by analyzing the wave number and frequency-dependent response to space and time variations of the order parameter. Section V is devoted to the charge and current expressions and the influence of external electromagnetic fields. The modifications required for dilute alloys are discussed in Sec. VI. In the concluding Sec. VII, we discuss the results and their applications.

II. NONEQUILIBRIUM EQUATIONS

Our general purpose is to derive equations for the order parameter $\Psi(\mathbf{r},t)$. This quantity is proportional to the local self-consistent pair field or energy-gap function $\Delta(\mathbf{r},t)$ and we shall restrict ourselves to cases where the space and time variations of Δ are small and occur only over distances greater than the coherence length ξ_0 and over times greater than $\hbar/kT_c$. We begin by deriving integral equations relating the energy gaps at different space-time points. The procedure is an extension to the nonequilibrium, time-dependent case of previously used methods[6–8] which were based on Gor'kov's original derivation[2] of the equilibrium GL equations for temperatures near T_c. We employ Green's function methods[3,10] throughout and restrict ourvelves to the BCS model of superconductivity.

In the equilibrium case, one gets the energy gap from a calculation of the quasiparticle self-energy[11] by means of equilibrium thermal Green's functions. In the present case, when time-varying fields and interactions are present, we construct nonequilibrium one-particle Green's functions as follows. We imagine that in the distant past ($t=-\infty$), the system is in thermodynamic equilibrium with Hamiltonian H and chemical potential μ. We let time-dependent interactions occur which we describe by the Hamiltonian $H'(t)$ which includes external time-dependent fields and the time-dependent energy gap through the self-consistent pair potential as described below. We work in the interaction representation for $H+H'$ so that states develop in time according to the time-development operator U:

$$U(t,t')=T\exp\left[-i\int_{t'}^{t}H'(t_1)dt_1\right], \qquad (2.1)$$

where the symbol T is the usual time-ordering operator. The single-particle Green's function is then defined as

$$\begin{aligned}G(1,2)&=-i\langle\langle T\psi(1)\psi^\dagger(2)\rangle\rangle\\&=-i\,\mathrm{Tr}e^{-\beta(H-\mu N)}T[U(-\infty,t_1)\psi(1)U(t_1,t_2)\\&\qquad\times\psi^\dagger(2)U(t_2,-\infty)][\mathrm{Tr}e^{-\beta(H-\mu N)}]^{-1}, \qquad (2.2)\end{aligned}$$

$$F(1,2)=\langle\langle T\psi(1)\psi(2)\rangle\rangle. \qquad (2.3)$$

In Eq. (2.3), we have defined the "anomalous" Green's function.[5] The electron field operators ψ, $\psi^\dagger$ are in the interaction representation. The space-time point $\mathbf{r}_1$, t_1 is denoted by the symbol 1. Time-dependent properties of the system are determined by the Green's functions G and F which are thermal averages over the equilibrium grand canonical ensemble at $t=-\infty$. For example, the order parameter at $\mathbf{r}_1$, t_1 is proportional to $F(1,1)$.

In the equilibrium case one can proceed to find the energy gap by adopting a simple form for that part of the Hamiltonian density which gives the superconducting interaction, which, following Gor'kov,[5] we take to be local in space and time:

$$\begin{aligned}H(1)&=g\psi^\dagger(1)\psi^\dagger(1)\psi(1)\psi(1)\\&=-\Delta(1)\psi^\dagger(1)\psi^\dagger(1)-\Delta^*(1)\psi(1)\psi(1),\end{aligned}$$

where g is the coupling constant ($g<0$ for an attractive interaction) and Δ is the (constant) self-consistent pair potential or energy gap which is to be evaluated in a self-consistent manner by using the above form of the Hamiltonian to generate the equations of motion for the equilibrium G and F and then solving for Δ from the solution for F: $\Delta(1)=-igF(1,1)=\text{const}$. The equations of motion can be written as integral equations and Δ is then found in the form

$$\Delta(1)=ig\int d^3r_2\int_{-\infty}^{+\infty}dt_2G_0(2,1)G(2,1)\Delta(2), \qquad (2.4)$$

where G_0 denotes the normal-state Green's function ($g=0$).

In the nonequilibrium case, the pair potential varies with time but the Green's functions defined in Eqs. (2.2) and (2.3) satisfy formally the same equations of motion as in the equilibrium situation. However, because the boundary conditions are different, the corresponding integral equations are different. In fact, the integral equations are manifestly causal. That is, the gap function at time t_1, for example, is determined only by values of the gap function at earlier times. In this way, one can write down causal integral equations for G and F in the nonequilibrium case. From the latter, one obtains the integral equation for the gap function which corresponds to Eq. (2.4).

$$\begin{aligned}\Delta(1)=ig\int d^3r_2\int_{-\infty}^{t_1}&dt_2[G_0^<(2,1)G^<(2,1)\\&-G_0^>(2,1)G^>(2,1)]\Delta(2), \qquad (2.5)\end{aligned}$$

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[10] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

[11] Reference 3, Sec. 34.3.

where

$$G^{>}(2,1)=-i\langle\langle\psi(2)\psi^{\dagger}(1)\rangle\rangle,\quad G^{<}(2,1)=i\langle\langle\psi^{\dagger}(1)\psi(2)\rangle\rangle.$$

The two terms of Eq. (2.5) describe separately the electron and hole contributions to $\Delta(1)$. If Δ is taken as constant in time, Eqs. (2.4) and (2.5) are equivalent.

The boundary conditions of the nonequilibrium case are nicely kept track of in a scheme devised by Kadanoff and Baym.[12] Following them, we go over to new Green's functions defined in the imaginary time domain in the usual manner of the Matsubara technique by replacing t by $-i\tau$.[13] In the present case, however, τ is defined between τ_0 and $\tau_0+\beta$. The new Green's functions are given by

$$\begin{aligned}\mathcal{G}(1,2)=-\mathrm{Tr}e^{-\beta(H-\mu N)}T[\mathcal{U}(\tau_0+\beta,\,\tau_1)\psi(1)\mathcal{U}(\tau_1,\tau_2)\\ \times\psi^{\dagger}(2)\mathcal{U}(\tau_2,\tau_0)]/\mathrm{Tr}e^{-\beta(H-\mu N)},\end{aligned}\quad(2.6)$$

$$\begin{aligned}\mathcal{F}(1,2)=\mathrm{Tr}e^{-\beta(H-\mu N)}T[\mathcal{U}(\tau_0+\beta,\,\tau_1)\psi(1)\mathcal{U}(\tau_1,\tau_2)\\ \times\psi(2)\mathcal{U}(\tau_2,\tau_0)]/\mathrm{Tr}e^{-\beta(H-\mu N)},\end{aligned}\quad(2.7)$$

where the time-ordering operator T orders decreasing values of $\tau-\tau_0$ from left to right, the time development operator $\mathcal{U}$ is given by

$$\mathcal{U}(\tau,\tau')=T\exp\left[-\int_{\tau'}^{\tau}H'(\tau_1)d\tau_1\right],$$

$$(\tau_0+\beta>\tau_1,\ \tau_2>\tau_0)\quad(2.8)$$

and the τ dependence of operators $(H',\psi,\psi^{\dagger})$ in the new interaction representation is given by

$$O(\tau)=e^{(H-\mu N)\tau}Oe^{-(H-\mu N)\tau}.\quad(2.9)$$

As in the equilibrium case, analytic continuation of the new Green's functions gives the actual Green's functions. In the present case, the rule is to let all $\tau\rightarrow it$ and $\tau_0\rightarrow -i\infty$. For example, $\mathcal{G}(\tau)$ continued in this manner is just the causal $G(t)$ defined in Eq. (2.2). In performing the continuation [in Eq. (2.6), say], it is necessary to write

$$\begin{aligned}\mathcal{U}(\tau_0+\beta,\,\tau_1)=\mathcal{U}(\tau_0+\beta,\,\tau_0)\mathcal{U}(\tau_0,\tau_1)\rightarrow\\ \mathcal{U}(-i\infty+\beta,\,-i\infty)U(-\infty,\,t_1),\end{aligned}$$

where the last factor is the ordinary time-development operator of Eq. (2.1) obtained from $\mathcal{U}(\tau_1\rightarrow it_1,\,\tau_2\rightarrow it_2)=U(t_1,t_1)$. The other factor, $\mathcal{U}(-i\infty+\beta,\,-i\infty)$, is from its definition equal to unity if one takes into account an "adiabatic switching" parameter $\eta\rightarrow 0^{+}$ by means of which we insure $H'(t=-\infty)=0$. That is, we include a factor $\exp\eta|t|$ in the definition of $H'(t)$.

Now, $\mathcal{G}(1,2)$ satisfies periodicity properties similar to those of the thermal Green's functions in the usual (equilibrium) Matsubara technique.[13] In the present case,[12] we have

$$\mathcal{G}(\tau_0+\beta,\,\tau')=-\mathcal{G}(\tau_0,\tau').$$

It is then possible to expand $\mathcal{G}$ in a Fourier series whose coefficients, as in the usual technique, are just the corresponding Green's functions $\mathcal{G}(\omega_n)$ having discrete frequencies $i\omega_n=\pi i(2n+1)/\beta$. If one calculates quantities like $\mathcal{G}(\omega_n)$, then analytic continuation of $z=i\omega_n$ to the real axis in the usual manner gives $G(\omega)$, the Fourier transform of the original $G(t)$ given in Eq. (2.2).

It is easily verified, that the functions $\mathcal{G}$, $\mathcal{F}$ satisfy the usual equations of motion (Gor'kov equations[5]) with time-dependent external fields, if they are present, included. Thus, in matrix form, the equations of motion are

$$\begin{pmatrix}L_1^{-} & \Delta(1)\\ -\Delta^{\dagger}(1) & L_1^{+}\end{pmatrix}\begin{pmatrix}\mathcal{G}(1,2) & \mathcal{F}(1,2)\\ \mathcal{F}^{\dagger}(1,2) & -\mathcal{G}(2,1)\end{pmatrix}=\delta(1,2)\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\quad(2.10)$$

where $L_1^{\pm}=\pm\partial/\partial\tau_1+(\nabla\pm ie\mathbf{A}/c)^2/2m+\mu$, μ is the chemical potential and we restrict ourselves here to the case where there is only a transverse vector potential acting. The general case will be discussed in Sec. V. The energy gap $\Delta(1)$ may be obtained from the anomalous Green's function $\mathcal{F}$ by the relation

$$\Delta(1)=-g\mathcal{F}(1,1^{+}).\quad(2.11)$$

It should be pointed out that the energy gap function of Eqs. (2.10) and (2.11) is not in fact the actual gap function. The latter is given by the expression

$$-ge^{-2i\mu t_1}\mathcal{F}(1,1^{+}).$$

This can be verified by comparison of the analytic continuation of $\mathcal{F}$ [Eq. (2.7)] and the actual F of Eq. (2.3).

We solve the equations of motion by iteration on the slow variation of the energy-gap function in the following manner (we exclude here the external field to which we shall return in Sec. V): Imagine a superconductor with a constant gap parameter (not necessarily the equilibrium one) Δ_l. We call this the local gap. The corresponding local Green's functions $\mathcal{G}_l$, $\mathcal{F}_l$ solve the equations of motion, Eq. (2.10), with Δ replaced by Δ_l. It is easily verified that the solution of the equations of motion for a superconductor whose gap function varies in an arbitrary manner is given by the following integral equations

$$\begin{aligned}\mathcal{G}(1,2)=\mathcal{G}_l(1,2)-\int d3\;\mathcal{G}_l(1,3)\delta\Delta(3)\mathcal{F}^{\dagger}(3,2)\\ -\int d3\;\mathcal{F}_l(1,3)\delta\Delta^{\dagger}(3)\mathcal{G}(3,2),\end{aligned}\quad(2.12)$$

$$\begin{aligned}\mathcal{F}^{\dagger}(1,2)=\mathcal{F}_l^{\dagger}(1,2)+\int d3\;\mathcal{G}_l(3,1)\delta\Delta^{\dagger}(3)\mathcal{G}(3,2)\\ -\int d3\;\mathcal{F}_l^{\dagger}(1,3)\delta\Delta(3)\mathcal{F}^{\dagger}(3,2),\end{aligned}\quad(2.13)$$

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[12] Reference 10, Chap. 8.

[13] Reference 3, Chap. 3.

where $\delta\Delta(3)=\Delta(3)-\Delta_l$ is the deviation of the actual gap function at the space-time point 3 from the constant local value Δ_l.

We assume the varations $\delta\Delta$ to be small and iterate the integral equations. For example, the energy gap at point 1 requires knowledge of $\mathcal{F}$ (1,1) which is given, to second order in $\delta\Delta$, by the following expression:

$$\begin{aligned}\mathcal{F}^\dagger(1,1)=\mathcal{F}_l^\dagger(1,1)+\int d3\ \mathcal{G}_l(3,1)\delta\Delta^\dagger(3)\mathcal{G}_l(3,1)-\int d3\ \mathcal{F}_l^\dagger(1,3)\delta\Delta(3)\mathcal{F}_l^\dagger(3,1)\\ -\int\int d3d4[\mathcal{G}_l(3,1)\delta\Delta^\dagger(3)\mathcal{G}_l(3,4)\delta\Delta(4)\mathcal{F}_l^\dagger(4,1)+\mathcal{G}_l(3,1)\delta\Delta^\dagger(3)\mathcal{F}_l(3,4)\delta\Delta^\dagger(4)\mathcal{G}_l(4,1)\\ +\mathcal{F}_l^\dagger(1,3)\delta\Delta(3)\mathcal{G}_l(4,3)\delta\Delta^\dagger(4)\mathcal{G}_l(4,1)-\mathcal{F}_l^\dagger(1,3)\delta\Delta(3)\mathcal{F}_l^\dagger(3,4)\delta\Delta(4)\mathcal{F}_l^\dagger(4,1)]. \quad (2.14)\end{aligned}$$

In the causal perturbation theory which we are using, as remarked above, all interactions $H'(\tau)$ [including the pair potential or energy gap $\Delta(\tau)$] include an adiabatic switching parameter $\eta\rightarrow 0^+$ so we have to include, for example, the factor $\exp(-i\eta\tau_3)$ in $\delta\Delta(3)$. We recall also that the time integrations all run between τ_0 and $\tau_0+\beta$ and that $\tau_0\rightarrow -i\infty$ at the end.

The next step is to set $\Delta_l=\Delta(1)$. Then we may evaluate the right-hand side of Eq. (2.14), for example, in terms of $\Delta(1)$ by either Taylor series expansion of $\Delta(3)$ about $\Delta_l=\Delta(1)$ (Sec. III) or by Fourier analysis (Sec. IV). As we shall see, the procedures will be valid only if the variations in Δ are sufficiently slow.

III. TAYLOR SERIES METHOD

The original derivation, valid near T_c, of the GL equation by Gor'kov[2] rests on the fact that the energy gap is slowly varying in space compared to the Green's function. We may extend his method by taking advantage of the fact that the Green's functions $\mathcal{G}_l$ and $\mathcal{F}_l$ which appear in the kernels of the integral equations for $\mathcal{G}$ and $\mathcal{F}$ [for an example, see Eq. (2.14)] fall off rapidly compared to what we assume are the allowed variations in Δ. The spatial variation of $\mathcal{G}$ and $\mathcal{F}$ is exponential fall off with a characteristic length given in order of magnitude at all temperatures below the critical temperature T_c by the coherence length $\xi_0\approx v_F/kT_c$ (v_F=Fermi velocity) while the variations in Δ and electromagnetic fields occur over distances of the order of the penetration depth λ. In what follows, we assume $\lambda\gg\xi_0$ so that we may expand the spatial variation of Δ in Taylor series since it will change only slightly over ξ_0, the distance of importance in the integrands.

In the Taylor series technique, the time variation of Δ is treated in the same manner as the space variation: We assume that the variation of Δ is slow compared to the times of importance in the integrands. These times are again determined by the behavior of $\mathcal{G}_l$ and $\mathcal{F}_l$ which fall off exponentially in times of the order of $\hbar/kT_c$ as long as Δ_l is not different in order of magnitude from the equilibrium gap.

We now have a well-defined method for deriving a differential equation satisfied by the energy gap. In the integrands of the integral equation for the gap [Eq. (2.14)], we expand $\Delta(3)$ in a space-time Taylor series about the local value $\Delta_l=\Delta(1)$:

$$\begin{aligned}\delta\Delta(3)=\Delta(3)-\Delta(1)=\partial_i\Delta(1)x_{31}{}^i+\tfrac{1}{2}\partial_i\partial_j\Delta(1)x_{31}{}^ix_{31}{}^j\\ +[\partial\Delta(1)/\partial\tau_1]\tau_{31}+\tfrac{1}{2}[\partial^2\Delta(1)/\partial\tau_1{}^2]\tau_{31}{}^2, \quad (3.1)\end{aligned}$$

where ∂_i means $\partial/\partial x_1{}^i$ and repeated indices are summed from 1 to 3. We insert this expression into the integral equation for the gap and we keep only terms involving two derivatives. We obtain in this way the time-dependent GL equation

$$\Delta^\dagger(1)=-g\mathcal{F}_l^\dagger(1,1)+\mathcal{L}(\Delta,\Delta^\dagger),$$

where $\mathcal{L}(\Delta,\Delta^\dagger)$ is a nonlinear operator on $\Delta(1)$, $\Delta^\dagger(1)$ which contains space and time derivatives with coefficients determined by the integrals of the integral equation, Eq. (2.14), after the series substitution of Eq. (3.1) for $\Delta(3)$. There are no cross terms in involving space and time derivatives since we kept only two derivatives and terms with one space derivative vanish by space inversion symmetry.

Before deriving the time-dependent GL equation at an arbitrary temperature, we discuss the situation when $T\approx T_c$. In this case, the method is very similar to the original Gor'kov derivation[2] of the time-independent GL equation. Near T_c, Δ itself is small everywhere and we modify the integral equation for Δ by taking $\Delta_l=0$. Thus $\mathcal{F}_l=0$ and $\mathcal{G}_l$ is simply $\mathcal{G}_n$, the normal-state Green's function. Then the term in Eq. (2.14) for $\Delta^\dagger(1)$ which gives rise to derivatives in the GL equation is simply

$$\Delta^\dagger(1)=-g\int d3\ \mathcal{G}_n(3,1)\Delta^\dagger(3)\mathcal{G}_n(3,1)\exp(-i\eta\tau_3), \quad (3.2)$$

where $\eta\rightarrow 0^+$ is the adiabatic switching parameter. We now expand Δ (3) in Taylor series about the point 1 according to Eq. (3.1). The space parts give rise to the usual terms of the time-independent GL equation. We content ourselves here with the discussion of the time-derivative terms. We may note that our procedure is only valid when q_0, the characteristic frequency of the time variation of Δ is greater than Δ itself. Otherwise, it is not valid to drop Δ everywhere on the right-hand side of Eq. (2.14).

The time-derivative terms arise from the following part of Eq. (3.2):

$$-g\int d^3r_3\int_{\tau_0}^{\tau_0+\beta} d\tau_3\mathcal{G}_n{}^2(3,1)[\Delta^{\dagger\prime}\tau_{31}+\tfrac{1}{2}\Delta^{\dagger\prime\prime}\tau_{31}{}^2] \times\exp(-i\eta\tau_3)\,, \quad (3.3)$$

where $\Delta^{\dagger\prime}$ denotes $\partial\Delta^\dagger(1)/\partial\tau_1$. In performing the τ_3 integral we find that the convergence factor containing η causes contributions $\exp(-i\eta\tau_0)$ to vanish when we let $\tau_0\rightarrow -i\infty$. The result of the τ_3 integration is simply

$$-g\textstyle\sum_{\mathbf{p}}\tanh(\beta\xi/2)[\Delta^{\dagger\prime}(2\xi+i\eta)^{-2}+\Delta^{\dagger\prime\prime}(2\xi+i\eta)^{-3}]\,,$$

where we have first transformed the Green's function to momentum space and $\xi=p^2/2m-\mu$. Making the substitution $\sum_p\rightarrow N_0\int d\xi$, where N_0 is the density of states at the Fermi surface in the normal metal, we find the time-derivative terms to be

$$-gN_0(K_2\Delta^{\dagger\prime}+K_3\Delta^{\dagger\prime\prime})\,,$$

where

$$K_n=\int d\xi\,\tanh(\beta\xi/2)(2\zeta+i\eta)^{-n}.$$

We assume particle-hole symmetry and evaluate the K_n by residues. The result is

$$K_n=2(\beta/2\pi i)^{n-1}(1-2^{-n})\zeta(n)\,, \quad (3.4)$$

where ζ is the Riemann zeta function. After the substitution $\tau\rightarrow it$, we may add the time-derivative terms to the space derivatives of the usual GL equation. The result is

$$\{\nabla^2/4m-(1/c)\partial/\partial t+(3/8\epsilon_F)\partial^2/\partial t^2+(1/6)[1-T/T_c -7\zeta(3)|\Delta|^2/8\pi^2(kT_c)^2]\}\Delta^\dagger=0\,, \quad (3.5)$$

where ϵ_F = Fermi energy, $b=7\zeta(3)\epsilon_F/6\pi^2(kT_c)^2$, $c=(8kT_c/\pi)b$. The first time-derivative term is larger than the second by a factor $[2\pi^3/7\zeta(3)](kT_c/q_0)\gg1$ so that we may neglect the latter. We therefore have a differential equation of the diffusion type to describe the space-time variation of the order parameter near T_c when $q_0>\Delta$. The equation describes how the self-consistent superconducting interaction (pair potential) drives the order parameter towards its equilibrium value.

Actually, Eq. (3.5) as written is not for the actual gap parameter as discussed in the previous section below Eq. (2.11). The time derivatives in the equation must be altered to include the time-dependent phase involving the chemical potential. We defer this question to the end of this section.

We now return to the case of arbitrary temperature: Δ is not small. We must use the full integral equation of Eq. (2.14). We treat first the space derivatives by inserting the space part of the Taylor series [Eq. (3.1)] into the integral equation. It is convenient to make the Fourier expansion in space and time for the Green's functions which appear on the right-hand side of the resulting expression for $\mathcal{F}^\dagger(1,1)$. Thus, for example,

$$\mathcal{F}_l(1,3)=\beta^{-1}\textstyle\sum_\omega\exp(-i\omega\tau_{13})\sum_{\mathbf{p}}\mathcal{F}_l(\omega,\mathbf{p})\exp(i\mathbf{p}\cdot\mathbf{r}_{13})\,,$$

where ω labels the discrete Matsubara frequency[13] $\pi(2n+1)/\beta$ and $\tau_{13}=\tau_1-\tau_3$, $\mathbf{r}_{13}=\mathbf{r}_1-\mathbf{r}_3$. Then the factors $\mathbf{r}_{31}{}^i$ which appears on the right-hand side from the expansion of $\delta\Delta(3)$ can be replaced by the derivatives with respect to the ith component of $\mathbf{p}$ which in turn are transferred to the appropriate $\mathcal{F}_l{}^\dagger(\omega,\mathbf{p})$, $\mathcal{F}_l(\omega,\mathbf{p})$ or $\mathcal{G}_l(\omega,\mathbf{p})$ by partial integration in p space. The result of these steps is

$$\begin{aligned}\Delta^\dagger(1)=-g\mathcal{F}^\dagger(1,1)=-g\beta^{-1}\textstyle\sum_{\mathbf{p},\omega}\{\mathcal{F}^\dagger&+(\partial\mathcal{G}^-/\partial p_i)\\ &\times(\partial\mathcal{G}/\partial p_j)[\tfrac{1}{2}\partial_i\partial_j\Delta^\dagger(1)]-(\partial\mathcal{F}^\dagger/\partial p_i)(\partial\mathcal{F}^\dagger/\partial p_j)\\ &\times[\tfrac{1}{2}\partial_i\partial_j\Delta(1)]-(\partial\mathcal{G}^-/\partial p_i)\mathcal{G}(\partial\mathcal{F}/\partial p_j)\\ &\times[2\partial_i\Delta^\dagger(1)\partial_j\Delta(1)]-(\partial\mathcal{G}^-/\partial p_i)\mathcal{F}(\partial\mathcal{G}/\partial p_j)\\ &\times[\partial_i\Delta^\dagger(1)\partial_j\Delta^\dagger(1)]+(\partial\mathcal{F}^\dagger/\partial p_i)\mathcal{F}^\dagger(\partial\mathcal{F}^\dagger/\partial p_j)\\ &\times[\partial_i\Delta(1)\partial_j\Delta(1)]\}\,, \quad (3.6)\end{aligned}$$

where, on the right-hand side, we have dropped the subscripts and arguments of all the Green's functions. The notation $\mathcal{G}^-$ means $\mathcal{G}_l(-\omega,-\mathbf{p})$. No linear derivative appears because of space-inversion symmetry.

To evaluate the coefficients of the space derivatives of Δ on the right-hand side of Eq. (3.6), we use the fact that $\mathcal{G}_l$ and $\mathcal{F}_l$ solve the Gor'kov equations[5] with the local gap $\Delta_l=\Delta(1)$. Thus,

$$\mathcal{G}_l=-(i\omega+\xi)/(\omega^2+E^2)\,,\quad \mathcal{F}_l=\Delta(1)/(\omega^2+E^2)\,, \quad (3.7)$$

where $E^2=\xi^2+|\Delta(1)|^2$. It it here that we make the assumption[14] regarding the behavior of the thermal excitations to which we referred in the Introduction. The distribution of thermally excited quasiparticles as determined from $\mathcal{G}_l$, for example, is given by the Fermi distribution for energy E (which contains the local gap) and temperature T. That is, we assume the gap in the spectrum to be determined by the local value of the varying pair potential and the normal fluid to be in equilibrium at temperature T with this spectrum. Thus, the interaction of the normal fluid with the phonon heat bath is taken to be faster than the rate at which the pair potential itself varies.

The rest of the calculation is straightforward. We introduce Eq. (3.7) into Eq. (3.6). Derivatives with respect to p_i give rise to terms proportional to p_i. The integrands are peaked near $p=p_F$, the Fermi momentum, so we may replace $p_ip_j\partial_i\partial_j$ by $\frac{1}{3}p_F{}^2\partial_i\partial_i$ and $\sum_p$ by $N_0\int d\xi$. The final result is

$$\begin{aligned}(1+\tfrac{1}{2}gN_0I_1)\Delta^\dagger(1)&\\ =-(g\pi N_0\epsilon_F/6m)\{&J_3\nabla^2\Delta^\dagger(1)-\tfrac{1}{2}J_5(\Delta\nabla^2\Delta^\dagger+\Delta^\dagger\nabla^2\Delta)\\ &\times\Delta^\dagger(1)-\tfrac{1}{2}J_5(2\Delta^\dagger\boldsymbol{\nabla}\Delta+3\Delta\boldsymbol{\nabla}\Delta^\dagger)\cdot\boldsymbol{\nabla}\Delta^\dagger(1)\\ &+(5/8)J_7(\Delta^\dagger\boldsymbol{\nabla}\Delta^\dagger+\Delta\boldsymbol{\nabla}\Delta^\dagger)^2\Delta^\dagger(1)\}\,, \quad (3.8)\end{aligned}$$

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[14] One of us (EA) wishes to acknowledge an informative discussion with L. P. Kadanoff on this point.

where

$$I_1=\int d\xi\,\tanh(\beta E/2)E^{-1} \tag{3.9}$$

$$J_n=\beta^{-1}\sum_\omega[\omega^2+|\Delta(1)|^2]^{-n/2}. \tag{3.10}$$

I_1 is formally divergent but may be evaluated by using the usual cutoff of the ξ integral or the fact that $I_1=-2/gN_0$ when Δ is the equilibrium value of the gap at the temperature T. Note that the coefficients of the derivatives depend on $\Delta(1)$ itself. The result, Eq. (3.8), has been found previously by Werthamer.[6]

We treat the time-derivative terms by a method parallel to that used above near T_c. We consider the case $q_0\ll\Delta$ as is consistent with the Taylor series method. We insert the time part of the Taylor series [Eq. (3.1)] into the integral equation of Eq. (2.14). In the terms on the right-hand side, we use the Fourier coefficients

$$\begin{aligned}\mathcal{G}_l(\mathbf{p},\tau)=\tfrac{1}{2}\{&(1+\xi/E)e^{-E\tau}[n_E-\theta(\tau)]\\&-(1-\xi/E)e^{E\tau}[n_E-\theta(-\tau)]\},\\ \mathcal{F}_l^\dagger(\mathbf{p},\tau)=-[\Delta^\dagger&(1)/2E]\{e^{-E\tau}[n_E-\theta(\tau)]\\&+e^{E\tau}[n_E-\theta(-\tau)]\},\end{aligned} \tag{3.11}$$

where $n_E=(\exp\beta E+1)^{-1}$. We perform the time integrations as before, taking advantage of the convergence factor η. The result is the time-derivative terms of the time-dependent GL equation:

$$\begin{aligned}&(1+\tfrac{1}{2}gN_0I_1)\Delta^\dagger(\mathbf{r},t)\\&\quad=-(g\pi N_0\epsilon_F/6m)\{J_3\nabla^2\Delta^\dagger-\tfrac{1}{2}J_5(\Delta\nabla^2\Delta^\dagger+\Delta^\dagger\nabla^2\Delta)\Delta^\dagger\\&\qquad-\tfrac{1}{2}J_5(2\Delta^\dagger\boldsymbol{\nabla}\Delta+3\Delta\boldsymbol{\nabla}\Delta^\dagger)\cdot\boldsymbol{\nabla}\Delta^\dagger+(5J_7/8)\\&\qquad\times(\Delta^\dagger\boldsymbol{\nabla}\Delta+\Delta\boldsymbol{\nabla}\Delta^\dagger)^2\Delta^\dagger-(3/2\pi v_F^2)[I_3\Delta^{\dagger\prime\prime}\\&\qquad-\tfrac{1}{2}I_5(\Delta\Delta^{\dagger\prime\prime}+\Delta^\dagger\Delta^{\prime\prime})\Delta^\dagger-\tfrac{1}{2}I_5(2\Delta^\dagger\Delta^\prime+3\Delta\Delta^{\dagger\prime})\Delta^{\dagger\prime}\\&\qquad\qquad+(5I_7/8)(\Delta^\dagger\Delta^\prime+\Delta\Delta^{\dagger\prime})^2\Delta^\dagger]\},\end{aligned} \tag{3.12}$$

where

$$I_n=\int d\xi\,\tanh(\beta E/2)E^{-n} \tag{3.13}$$

and, as in Eq. (3.5), we have not corrected the partial time derivatives (denoted by primes) to include the time dependence arising from the chemical potential.

We may simplify the GL equation in the limiting case $T\rightarrow 0$. For $T=0$, we find

$$\begin{aligned}J_{2n+1}=I_{2n+1}/2\pi=[(n-1)!2^{n-1}]^2/[\pi(2n-1)!|\Delta|^{2n}],\\ 1+\tfrac{1}{2}gN_0I_1=\tfrac{1}{2}gN_0\ln|\Delta_0/\Delta|^2,\end{aligned} \tag{3.14}$$

where Δ_0 is the equilibrium gap at $T=0$. The relation between the GL order parameter $\Psi(\mathbf{r},t)$ and the energy-gap function $\Delta(\mathbf{r},t)$ is given, at $T=0$, by $\Psi=(N/2)^{1/2}\Delta/\Delta_0$ where N is the total electron density. Then the time-dependent GL equation at $T=0$ is simply

$$\begin{aligned}&N_0\ln|\Psi/\Psi_0|^2\\&\quad=(\Psi_0^4/6m\Delta_0^2|\Psi|^6)\{2\Psi^2[\Psi^\dagger\nabla^2\Psi^\dagger-(\boldsymbol{\nabla}\Psi^\dagger)^2]-(\Psi^\dagger)^2\\&\qquad\times[\Psi\nabla^2\Psi-(\boldsymbol{\nabla}\Psi)^2]-(3/v_F^2)(2\Psi^2[\Psi^\dagger\Psi^{\dagger\prime\prime}-(\Psi^{\dagger\prime})^2]\\&\qquad\qquad-(\Psi^\dagger)^2[\Psi\Psi^{\prime\prime}-(\Psi^\prime)^2])\},\end{aligned} \tag{3.15}$$

where $\Psi_0=(N/2)^{1/2}$ and v_F is the Fermi velocity. We have written the equation in a form suitable for the inclusion of external fields as discussed in Sec. V. The prescription for altering the derivatives in Eq. (3.15) to include fields is given later in Sec. VII, Eq. (7.1). In the absence of fields, Eq. (3.15) may be written in a more compact form which displays explicitly the longitudinal density oscillation for a neutral superconductor which we discuss again in Sec. VII:

$$\begin{aligned}N_0\ln(\Psi/\Psi_0)^2=(\Psi_0^4/6m\Delta_0^2|\Psi|^2)\\ \times[\nabla^2-(3/v_F^2)\partial^2/\partial t^2]\ln[(\Psi^\dagger)^2/\Psi].\end{aligned} \tag{3.16}$$

Unfortunately, the time-dependent GL equation we have derived in this section is valid only at absolute zero. The reason is that at finite temperatures, there is the possibility of local conversion of the thermally excited normal excitations to superfluid. Mathematically, the difficulty is due to the existence of a singularity in the product of Green's functions which form the kernel of the integral equation [Eq. (2.14)] for the gap function. Let q, q_0 be the characteristic wave number and frequency of the space-time variations of the order parameter. In the Taylor series method of this section, we calculate the time (space) variation by setting q (q_0) equal to zero and then taking the limit as q_0 (q) goes to zero. In the actual situation, we have either $q/q_0\xi\lessgtr 1$. Then if $q/q_0<1$, we are calculating the time derivatives correctly and the space derivatives incorrectly and the reverse in the other case. In the superconductor, the relevant ratio is vq/q_0 where v is the group velocity of the thermally excited quasiparticle. If the ratio is greater than one, local conversion, or diffusion, of normal fluid represented by excitations of wavenumber q may occur since the Čerenkov condition $\Delta E=\mathbf{v}\cdot\mathbf{q}=q_0$ can be satisfied. At absolute zero, there are no thermal excitations and for $q_0<\Delta_0$ there can be no conversion from pair dissociation either. In this case, the ratio vq/q_0 is irrelevant and the $T=0$ GL equation we have derived in this section is correct (in the neutral case). If the Čerenkov condition is satisfied, then the results derived in this section for the space derivatives are valid at all temperatures, while the time-derivative terms are incorrect. In fact, as we shall show in the next section where we analyze the frequency and wave-number–dependent response, a differential equation describing the time variation cannot be written in the Čerenkov region except near T_c where we again find a diffusion equation identical to the one derived above for the case $q_0>\Delta$, $T\approx T_c$ [Eq. (3.5)]. The remarks we have just made apply to the space derivatives at finite temperatures in the case $vq/q_0<1$. In the special case $q_0>\Delta$, $T\approx T_c$, however, the ratio vq/q_0 is again irrelevant and the diffusion-type equation of Eq. (3.5) is valid.

We turn now to the question of the time-dependent phase of the order parameter. As remarked in connection with Eq. (3.5), we have only derived time-dependent equations for the gap function as defined in Eq. (2.11). It does not include the phase factor involving the chemical potential. We may reintroduce the latter simply by the replacements

$$\Psi' \to (\partial/\partial t+2i\mu)\Psi\,,\quad \Psi^{\dagger\prime} \to (\partial/\partial t-2i\mu)\Psi^\dagger\,. \qquad (3.17)$$

However, this reveals another difficulty with the Taylor series method. As remarked above, in the calculation of the time-derivative terms, the spatial variation is taken to be zero. However, when there is a spatial term involving, for example, $\nabla^2\Psi$ in the GL equation $T=0$, then we expect the kinetic energy of the moving pairs to be reflected in the chemical potential which should be replaced by $\mu-\nabla^2/8m$. In this case, the time-derivative operators become $[\partial/\partial t+2i(\mu-\nabla^2/8m)]\Psi$. The new chemical potential which we have written here is that for an isolated specimen. In the case that there is a local-pair kinetic energy so that the chemical potential is μ far away from the point in question then the over-all constancy of the chemical potential is maintained by a local density change in the case of a neutral superconductor. In the charged case, the density is almost constant and a small electrostatic potential is built up. The addition of $-\nabla^2/8m$ to the chemical potential is essential for the Galilean invariance of the $T=0$ GL equation. With the extra term present, $\Psi(\mathbf{r}-\mathbf{q}t/m,\, t)\exp[i(\mathbf{q}\cdot\mathbf{r}-q^2t/4m)]$ is a solution when $\Psi(\mathbf{r},t)$ is. This fact is connected with the satisfying result that $\Psi(\mathbf{r},t)\exp(i\mathbf{q}\cdot\mathbf{r})$ satisfies the GL equation at $T=0$ if $\Psi(\mathbf{r},t)$ does. All the terms with q vanish identically. This is consistent with the original Gor'kov equations[5] at $T=0$ which have the same property and reflects the fact that for the current-carrying case with q small, the whole Fermi surface shifts slightly but the superconducting correlations are unchanged (rigidity of the wave function in the London sense, cf. Sec. V). The modification of the time derivatives due to the kinetic energy of the moving pairs which we have been discussing here appears naturally in the correct calculation of the behavior of the order parameter which we present in the next section.

IV. FREQUENCY AND WAVE-NUMBER RESPONSE TO GAP VARIATIONS

In this section, we analyze in detail the conditions under which a differential GL equation exists. The method is simply to retain finite values of q, q_0 in the kernels of the integral equation for the gap parameter, Eq. (2.14) and to investigate whether expansions in powers of q, q_0 are valid. For simplicity, we limit the discussion to the linear terms [first two terms on the right-hand side of Eq. (2.14)] of the integral equation. It is convenient to write the equations for $\Delta^\dagger(1)$ and $\Delta(1)$ together in matrix form:

$$\Lambda(1)=-gF_l(1,1)-g\int d3K(3,1)\delta\Lambda(3)\,, \qquad (4.1)$$

where

$$\Lambda=\begin{pmatrix}\Delta^\dagger\\ \Delta\end{pmatrix},\quad F_l=\begin{pmatrix}\mathfrak{F}_l^\dagger\\ \mathfrak{F}_l\end{pmatrix},\quad K=\begin{pmatrix}\mathfrak{G}_l^2 & -\mathfrak{F}_l^{\dagger 2}\\ -\mathfrak{F}_l^2 & \mathfrak{G}_l^2\end{pmatrix}.$$

We take for $\Lambda(3)$ the variation $\Lambda(\mathbf{q},q_0)\exp i(\mathbf{q}\cdot\mathbf{r}_3-\Omega\tau_3)$ where $i\Omega$ is a complex frequency which we afterward continue to the real axis $i\Omega\to q_0+i\eta$ in such a way as to recover the adiabatic switching parameter η thereby insuring causality. The first term on the right-hand of Eq. (4.1) is proportional to the integral I_1 as in the previous section [see Eqs. (3.6)–(3.9)]. With these substitutions, the equation for $\Lambda(1)$ becomes

$$(1+\tfrac{1}{2}gN_0I_1)\Lambda(1)=-g\Lambda(\mathbf{q},q_0)\exp i(\mathbf{q}\cdot\mathbf{r}_1-q_0t_1)$$
$$\times[L(\mathbf{q},q_0)-L(0,0)]\,, \qquad (4.2)$$

where

$$L(\mathbf{q},q_0)=\left[\int d3K(3,1)\exp i(\mathbf{q}\cdot\mathbf{r}_{31}-\Omega\tau_{31})\right]_{\Omega\to q_0+i\eta}. \qquad (4.3)$$

The matrix components of L are calculated as in the previous section. There, the Green's functions in momentum space have been given in Eq. (3.11) and a typical τ integral performed in Eq. (3.3). The result is

$$L_{11}=L_{22}=(N_0/8q)\int_{-q}^{+q}dx\int d\xi[(1-n_+-n_-)$$
$$\times(1+\xi_+\xi_-/E_+E_-)\mathfrak{D}_+-(n_+-n_-)$$
$$\times(1-\xi_+\xi_-/E_+E_-)\mathfrak{D}_-]\,, \qquad (4.4)$$

$$L_{12}/[\Delta^\dagger(1)]^2$$
$$=L_{21}/[\Delta(1)]^2=-(N_0/8q)\int_{-q}^{+q}dx\int d\xi$$
$$\times[(1-n_+-n_-)\mathfrak{D}_+-(n_+-n_-)\mathfrak{D}_-]/E_+E_-\,,$$

where

$$\mathfrak{D}_\pm=[(E_+\pm E_-+q_0+i\eta)^{-1}$$
$$+(E_+\pm E_--q_0-i\eta)^{-1}]\,. \qquad (4.5)$$

In the above, $n_\pm=(\exp\beta E_\pm+1)^{-1}$ and the subscripts $\pm$ indicate that the momentum argument is $\mathbf{p}\pm\mathbf{q}/2$. Further, $x=\mathbf{p}\cdot\mathbf{q}/p$. We have dropped terms in the ξ integrals which vanish due to particle-hole symmetry. We shall refer to the second term (containing n_+-n_-) of each component of L as the "irregular part" arising from thermally excited quasiparticles. The first terms are called regular parts.

It is in Eqs. (4.4) and (4.5) that the kinetic-energy correction to the chemical potential which we mentioned at the end of Sec. III makes itself evident. That is, $E_\pm^2=\xi_\pm^2+|\Delta(1)|^2$, where $\xi_\pm=p^2/2m\pm px/2m-(\mu-q^2/8m)$ and μ is the chemical potential. To handle the term with q^2, imagine that the local value of the chemical potential happens to be $\mu_l=\mu+q^2/8m$. Then $q^2/8m$ drops out of the energy, but the local gap parameter oscillates with μ_l. That is, μ_l replaces μ in (3.17). We may then proceed with μ_l and after expanding in powers of q, q_0, we restore the actual case by the replacement $\mu_l \rightarrow \mu - \nabla^2/8m$. All we have done is to isolate that part of the local "mechano-chemical" potential which is due to the kinetic energy of superfluid motion in order to handle the space derivatives of Ψ in a proper manner.

We now investigate the conditions under which it is possible to expand the kernel $L(\mathbf{q},q_0)$ in powers of q, q_0. If the expansion exists, then the coefficient of $\mathbf{q}^n$ is the coefficient of $(-i\nabla)^n$ in the GL equation and the coefficient of $q_0{}^n$ is the coefficient of $(i\partial/\partial t)^n$.

Case A. $T \approx T_c$, $q_0 > \Delta$

This case corresponds to the first calculation of Sec. III which resulted in Eq. (3.5). In the present method, we drop Δ everywhere in the kernel and find, from Eq. (4.4),

$$L_{11} = L_{22} = (N_0/2q)\int dx \int d\xi \tanh(\beta\xi/2)$$
$$\times[(2\xi + v_F x + q_0 + i\eta)^{-1} + (2\xi + v_F x - q_0 - i\eta)^{-1}],$$
$$L_{12} = L_{21} = 0.$$

After subtracting $L(0,0)$ we can see that the expansion of the kernel in q, q_0 is regular in the ratio $v_F q/q_0$. We recover the Taylor series result of the previous section. Thus:

$$L(\mathbf{q},q_0) - L(0,0) = N_0[-K_2 q_0 + K_3 q_0{}^2 + K_3 v_F{}^2 q^2/3]$$

where the K_n integrals are defined in Eq. (3.4). Transforming back to coordinate space we find

$$(1+\tfrac{1}{2}gN_0I_1)\Delta^\dagger = -gN_0 b[\nabla^2/4m + (3)8\epsilon_F)$$
$$\times(\partial/\partial t - 2i\mu)^2 - (1/c)(\partial/\partial t - 2i\mu)]\Delta^\dagger, \quad (4.6)$$

which, if we expand I_1 near T_c, becomes the diffusion equation given in Eq. (3.5) where the constants b, c are defined.

Case B. $T \approx T_c$, $v_F q > q_0$

This is the Čerenkov region near T_c. We shall find, as remarked at the end of Sec. III, that the diffusion equation again obtains. We limit ourselves to the expansion of the kernel in powers of q_0 since in the Čerenkov region, as discussed earlier, the spatial variation is described correctly by the Taylor series method of the previous section. In each matrix component of L, Eqs. (4.4, 5), the second term (containing $n_+ - n_-$) describes the effect of thermally excited quasiparticles. The energy denominators $\mathfrak{D}_-$ of these "irregular" terms, $E_+ - E_- \pm q_0$, go to zero when q and q_0 do thereby causing irregularities in the expansion of the kernel. However, since the leading term of $n_+ - n_-$ is itself proportional to q, in the case that $vq > q_0$ we may hope to expand these irregular denominators in the first power of q_0/vq and retrieve a first time-derivative GL equation. It turns out to be possible (because of the temperature dependence of the group velocity v of the low-lying excitations) only when $T \approx T_c$. In all other cases at finite temperatures, these irregular terms are impossible to expand and a time-dependent GL equation cannot be derived. At absolute zero, of course, the irregular terms are zero.

We illustrate these points by examining the imaginary part of L. The regular terms have no imaginary part if $q_0 < \Delta$ as may be seen from the structure of the denominators in $\mathfrak{D}_+$ [Eq. (4.5)]. The case $q_0 > \Delta$ has already been treated so we only have to consider the irregular part of L. The terms in question are

$$\mathrm{Im}L_{11}{}^{\mathrm{irr}} = -(\pi N_0/4q)\int dx \int d\xi (n_+ - n_-)$$
$$\times(1 - \xi_+\xi_-/E_+E_-)\delta(E_+ - E_- - q_0). \quad (4.7)$$

For L_{12}, the term in square brackets is replaced by $[\Delta^\dagger(1)]^2/E_+E_-$.

We note immediately that for small q and the limit $(dE/dp)q/q_0 = vq/q_0 \rightarrow 0$ the δ function in Eq. (4.7) can never be satisfied and there is no contribution. We therefore consider the Čerenkov region. The terms we are discussing will be seen to give rise to the first time derivative of the diffusion equation when $\Delta(T)/v_F q$ is small, that is for $T \approx T_c$.

The δ function, considered as a function of x, can only be satisfied for $\xi > -\frac{1}{2}(v_F q - q_0 S) = \xi_1$ where $S^2 = 1 + 4|\Delta|^2/(v_F{}^2 q^2 - q_0{}^2)$. We have assumed that $v_F q > [2q_0\Delta(T)]^{1/2}$, thereby restricting ourselves to the neighborhood of T_c. We perform the x integral and find

$$\mathrm{Im}L_{11}{}^{\mathrm{irr}} = (\pi N_0/2v_F q)\int_{\xi_1}^{\infty} d\xi\{(\xi/E) - (E+q_0)$$
$$\times[(E+q_0)^2 - |\Delta|^2]^{-1/2}\}[n(E+q_0) - n(E)].$$

For L_{12}, replace the curly bracket by $-[\Delta^\dagger(1)]^2 \times E^{-1}[(E+q_0)^2 - |\Delta|^2]^{-1/2}$. An analysis of the integrand shows that for the case $v_F q \gg \Delta \gg q_0$ ($T \approx T_c$) we may drop Δ and q_0 in the first square bracket which becomes $-2\theta(-\xi)$ and take $\xi_1 = \frac{1}{2}v_F q$. For $\beta\Delta \ll 1$, the second square bracket may be expanded to the first order in q_0. In this way, we get the results

$$\mathrm{Im}L_{11}{}^{\mathrm{irr}} = (\pi N_0/8)(q_0/kT) = iN_0K_2q_0,$$
$$\mathrm{Im}L_{12}{}^{\mathrm{irr}} = \mathrm{Im}L_{21}{}^{\mathrm{irr}} = O(\Delta^2) = 0.$$

We may expand L_{11} in powers of q in a straightforward manner. In the present case, $v_F q \gg \Delta \gg q_0$, $\beta\Delta \ll 1$, and the result is the same as in the preceding case A of this section. We then find, as before,

$$L(\mathbf{q},q_0) - L(0,0) = N_0[-K_2 q_0 + K_3 v_F{}^2 q^2/3]$$

and the time-dependent diffusion-type GL equation is valid near T_c in the Čerenkov region as well as when $q_0 > \Delta$.

Before leaving the case $T \approx T_c$, we should convince ourselves that the real part of the kernel L_{11} makes no contribution to the time dependence. An analysis of the real part shows that it is at most of order $q_0^2/v_F q\Delta$ and we may safely neglect it as being of higher order than the imaginary term of first order in q_0 which we are keeping.

The conclusions of this section are as follows:

Case A. When $q_0 \gg \Delta$, the result of the Taylor series method in the case $\Delta \rightarrow 0$ as given at the beginning of Sec. III is valid.

Case B. When $q_0 < v_F q$ (Čerenkov region), the spatial derivatives may be obtained from the regular part of the kernel L by expansion in powers of q, or equivalently by the Taylor series method. However, a time-dependent GL equation only exists for $T \approx T_c$ or $T=0$ (see below). In the former case, the irregular part of the kernel which arises from thermally excited quasiparticles contributes a first time derivative and the equation is of diffusion type and is the same as in case A. For general temperatures, it is impossible to expand the irregular part.

Case C. When $\Delta > q_0 > v_F q$, the time derivatives are obtained from the regular part of the kernel and are the same as the result of the Taylor series method. However, above absolute zero, the irregular term cannot be expanded [it behaves like $(v_F q/q_0)^2$], there is no differential equation, even near T_c. For $T \approx 0$, see below.

Case D. When $T \approx 0$ ($kT \ll \Delta$), there are no thermal excitations and the irregular part of the kernel is zero. Then everything is given by the expansion of the regular part and the results of the Taylor series method at $T=0$ are recovered.

V. CHARGE, CURRENT, AND EXTERNAL FIELDS

We now turn to the expressions for the charge and current densities which are to be associated with the space-time variations of the order parameter.

For clarity, we first consider the case of a neutral superconductor. We can obtain the density and current responses from the integral equation for the Green's function $\mathcal{G}$ given by Eq. (2.12). For slow variations of the gap, we can replace $\mathcal{G}^\dagger$ and $\mathcal{G}$ by their zeroth-order local values $\mathfrak{F}_l^\dagger$ and $\mathcal{G}_l$ as before. We then have, for the deviation of $\mathcal{G}$ from its local value when the gap is constant, $\Delta = \Delta_l$ (we limit ourselves to terms linear in $\delta\Delta$):

$$\delta\mathcal{G}(1,2) = -\int d3[\mathfrak{F}_l(1,3)\mathcal{G}_l(3,2)\delta\Delta^\dagger(3) + \mathcal{G}_l(1,3)\mathfrak{F}_l^\dagger(3,2)\delta\Delta(3)].$$

From $\delta\mathcal{G}$, we may obtain the charge and current responses[15]

$$\delta\rho(1) = \rho(1) - \rho_l = 2\delta\mathcal{G}(1,1^+), \tag{5.1}$$

$$\mathbf{j}(1) = (i/2m)[(\nabla_2 - \nabla_1)2\delta\mathcal{G}(1,2)]_{2\rightarrow 1^+}. \tag{5.2}$$

The subsequent calculations are quite similar to Secs. III and IV. From the Taylor series method, valid at $T=0$, we find

$$\delta\rho = (iN_0/4)I_3(\Delta^\dagger\Delta' - \Delta\Delta^{\dagger\prime}), \tag{5.3}$$

$$\mathbf{j} = -(i\pi N_0 v_F^2/6)J_3(\Delta^\dagger\nabla\Delta - \Delta\nabla\Delta^\dagger), \tag{5.4}$$

where I_n and J_n have been defined in Eqs. (3.13) and (3.10). Note that at $T=0$, Eq. (3.14) applies for I_n and J_n.

The continuity equation at $T=0$ is satisfied by these expressions as may be verified by using the GL equation at $T=0$ given in Eq. (3.15) which relates the space and time derivatives of Δ. It is to be noted that the density involves a first time derivative since the GL equation contains Δ''. If the spatially varying chemical potential is introduced into the time derivatives of Eqs. (3.15) and (5.3) as discussed at the end of Sec. III, then the continuity equation still obtains provided terms of order ∇^4 are neglected in the GL equation, Eq. (3.15).

When $T \neq 0$, we restrict ourselves to the Čerenkov region. Then, as before, the spatial derivatives have been treated correctly and the expression we have given for $\mathbf{j}$ remains valid [Eq. (5.4)]. For the density, we use the method of Sec. IV and we have to consider the irregular terms in the density kernel which arise from thermal excitations. These are proportional to

$$(q_0/q)\int dx \int d\xi(n_+ - n_-) \times [E_+E_-(E_+ - E_- - q_0 - i\eta)]^{-1}. \tag{5.5}$$

The notation is that of Eq. (4.4). Equation (4.7) is the corresponding irregular term of the gap kernel. The leading term of the real part of the expression (5.5) is just

$$2q_0\int d\xi E^{-2}\partial n/\partial E = q_0(2\pi J_3 - I_3).$$

If we combine this with the contribution of the regular term found from the Taylor series in Eq. (5.3), the factor I_3 in the latter equation becomes $2\pi J_3$ and we may write

$$\delta\rho = (i\pi N_0 J_3/2)(\Delta^\dagger\Delta' - \Delta\Delta^{\dagger\prime}), \tag{5.6}$$

$$\mathbf{j} = -(i\pi N_0 v_F^2/6)J_3(\Delta^\dagger\nabla\Delta - \Delta\nabla\Delta^\dagger). \tag{5.7}$$

There are two remarks to be made. First of all, we are neglecting the imaginary part of the expression (5.5) for the irregular part of the density kernel. This

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[15] Reference 3, Sec. 37.1; L. P. Kadanoff and P. Martin, Phys. Rev. 124, 670 (1961).

neglected part corresponds to a dissipative contribution to $\delta\rho$ but it cannot be expressed in differential form and, unlike the situation for the analogous real part of the gap kernel L_{11}^{irr} [cf. Eq. (4.4)], we have not succeeded in demonstrating that it is smaller than the term we keep. We may note, however, that this dissipative term is proportional to q_0^2 as may easily be seen from the expression (5.5). Secondly, with the approximations used (first order in q, q_0) and the neglect of the dissipative term, the final expressions, Eqs. (5.6) and (5.7), for $\delta\rho$ and j do not satisfy the continuity equation according to the time-dependent GL equation in the Čerenkov region near T_c given by Eq. (4.6). Of course, the superfluid density $\rho_s \propto |\Delta|^2 J_3$ is not conserved under Čerenkov conditions as discussed at the end of Sec. III. However, the original equations are consistent with continuity. Indeed, if we write, as in Sec. IV [Eq. (4.1)] and in this section,

$$\Lambda(1) = -gF_l(1,1) - g\int d3\, K_\Lambda(3,1)\delta\Lambda(3)\,,$$

$$\rho(1) = \rho_l + \int d3\, K_\rho(3,1)\delta\Lambda(3)\,,$$

$$j(1) = (i/2m)\left[(\nabla_2 - \nabla_1)\int d3\, K_j(1,3,2)\delta\Lambda(3)\right]_{2\to1}\,,$$

then we can prove $q_0\rho(q,q_0) = \mathbf{q}\cdot\mathbf{j}(q,q_0)$.

We turn now to the case of a charged system in the presence of external fields. As we have earlier remarked, we restrict ourselves to the local limit. Then we may take electromagnetic fields to be everywhere slowly varying in space and time. That is, they will be essentially constant in a region ξ_0 (coherence length) and over times of the order of $1/kT_c$. Then we may follow the procedure used by Gor'kov in the static case.[2,3] If $A_\mu = (\mathbf{A}/c, -\phi)$, $\nabla\cdot\mathbf{A} = 0$, and $x_\mu = (\mathbf{r},t)$, it may be shown that

$$\begin{aligned} G(x,x') &= \exp[ieA_\mu(x)(x-x')_\mu]G^0(x,x')\,,\\ F(x,x') &= \exp[ieA_\mu(x)(x+x')_\mu]F^0(x,x')\,, \end{aligned} \tag{5.8}$$

where G^0, F^0 satisfy the Gor'kov equations without A_μ. This form for the Green's functions evidently implies that we should replace $\partial\Delta/\partial x_\mu$ by $(\partial/\partial x_\mu - 2ieA_\mu)\Delta$ wherever it appears in all of our previous expressions.

In addition, we have to modify the charge expression: The prescription of Eq. (5.8) does not account for the static local density shift due to the scalar potential ϕ (Thomas-Fermi term), $\delta\rho = -2N_0e^2\phi$. Furthermore, the chemical potential appearing in the phase of the order parameter is now a local one μ_l which reflects the local density change ($\mu_l = \mu + \delta\rho/2N_0e$). Then for the charge and current, we have

$$\delta\rho = (i\pi N_0 e J_3/2)[\Delta^\dagger(\partial/\partial t + 2i\tilde{\mu})\Delta - \mathrm{c.c.}] - 2N_0e^2\phi\,, \tag{5.9}$$

$$\mathbf{j} = (-i\pi N_0 v_F^2 e J_3/6)[\Delta^\dagger\nabla'\Delta - \mathrm{c.c.}]\,, \tag{5.10}$$

where[16]

$$\tilde{\mu} = \mu_l + e\phi - \nabla'^2/8m\,, \tag{5.11}$$

$$\nabla' = \nabla - 2ie\mathbf{A}/c\,. \tag{5.12}$$

These same results may be derived by a perturbation procedure and similar expressions have previously been written down by others.[7,9,17] From Eq. (5.11) we see that if there is a local spatial variation of Δ, then it may be balanced by a scalar potential ϕ to make the mechano-electrochemical potential constant throughout an isolated specimen. Similar observations have been made before by several people.[18] In the presence of the long-range Coulomb interaction, we impose the condition $\delta\rho = 0$, otherwise the motion of the order parameter couples to the plasmon mode. This puts a restriction on the motion of the order parameter through Eq. (5.9). We shall refer to this again in Sec. VII.

If we follow the prescription above for the GL equation, Eq. (3.15), at absolute zero we find that the vector potential disappears completely (recall, we have the London gauge $\nabla\cdot\mathbf{A} = 0$). This does not occur for the impure case to be discussed in the next section. The result is expected and reflects the London rigidity of the superfluid wave function against a magnetic field. Under these circumstances, the expression for the current reduces simply to the London equation $\mathbf{j} = -e^2\mathbf{A}N/mc$. The application of the prescriptions of this section to the time-dependent GL equation at $T = 0$ is made in Sec. VII.

VI. MODIFICATIONS FOR DILUTE ALLOYS

In this section we outline the procedure necessary to discuss the case of dilute superconducting alloys and we apply it to the linear terms of the GL equation. The general procedure for dealing with the case of a dirty superconductor is well known[19]: It is convenient to work always in the imaginary frequency domain rather than in the time domain of the Matsubara technique. In the pure case, the corresponding $\mathfrak{F}(\omega,p)$ and $\mathcal{G}(\omega,p)$ are given in Eq. (3.7). In the impure case, the technique for averaging over the positions of randomly placed impurities is as follows: One replaces ω and Δ by $\tilde{\omega} = \eta\omega$ and $\tilde{\Delta} = \eta\Delta$ where $\eta = 1 + 1/2\tau\mathcal{E}$. Here $1/2\tau$ is the decay rate from impurity scattering in the normal state and $\mathcal{E} = [\omega^2 + |\Delta|^2]^{1/2}$. In addition, one must include the vertex corrections due to the impurity scattering. Our method is similar to that used by Maki and Tsuneto.[20] Finally, we observe that

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[16] In Eq. (5.11) we have included the kinetic-energy correction to the chemical potential which we discussed at the end of Sec. III.

[17] P. W. Anderson, N. R. Werthamer, and J. M. Luttinger, Phys. Rev. **138**, A1157 (1965). Our charge expression for $q = 0$ (no kinetic-energy term) is equivalent to that of this reference if in the latter one takes full Thomas-Fermi screening. That is, one assumes the total electrochemical potential to be constant all over.

[18] See, for example, Ref. 17 and M. Stephen, Phys. Rev. **139**, A197 (1965).

[19] Reference 3, Sec. 39.

[20] K. Maki and T. Tsuneto, Progr. Theoret. Phys. (Kyoto) **28**, 163 (1962).

just as in the theory of conductivity,[19] the variations in the energy gap couple with variations in density via the impurity scattering. In the pure case we may write our starting equations [Eqs. (2.12) and (2.13)] in matrix form

$$G=G_l-G_l\delta\Lambda G\,, \tag{6.1}$$

where

$$G=\begin{pmatrix}\mathcal{G} & \mathfrak{F}\\ \mathfrak{F}^\dagger & -\mathcal{G}^-\end{pmatrix},\quad \delta\Lambda=\begin{pmatrix}0 & \delta\Delta\\ \delta\Delta^\dagger & 0\end{pmatrix}$$

where the Green's function $\mathcal{G}^-$ is defined by $\mathcal{G}^-(1,2)=\mathcal{G}(2,1)$. In the presence of impurity scattering, we have to modify these expressions as described above. G goes over to the Green's function for the alloy and the vertex $\delta\Lambda$ has to be corrected for impurity scattering and coupling to the density. Call the corrected vertex $\delta\tilde{\Lambda}$. Then Eq. (6.1) remains the same but with $\delta\Lambda$ replaced by $\delta\tilde{\Lambda}$ and Green's functions for the alloy are used in the matrix G. The corrected vertex is given by the matrix

$$\delta\tilde{\Lambda}=\begin{pmatrix}\pi & \lambda\\ \lambda^\dagger & \pi^\dagger\end{pmatrix},$$

where λ is the corrected gap vertex and π is the density vertex. These quantities satisfy an integral equation similar to that of Maki and Tsuneto[20] which we may write as follows

$$\delta\tilde{\Lambda}=\delta\chi+n|v|^2K\delta\tilde{\Lambda}\,,$$

where $|v|^2$ represents symbolically two scatterings from the same impurity and n is the number of impurities. We have rearranged the notation so that $\delta\tilde{\Lambda}$, $\delta\chi$ are four-rowed column vectors and K is a 4×4 matrix:

$$\delta\chi=\begin{bmatrix}\delta\Delta\\ \delta\Delta^\dagger\\ 0\\ 0\end{bmatrix}\qquad \delta\tilde{\Lambda}=\begin{bmatrix}\lambda\\ \lambda^\dagger\\ \pi\\ \pi^\dagger\end{bmatrix},$$

$$K=\begin{bmatrix}\mathcal{G}_l^-\mathcal{G} & -\mathfrak{F}_l\mathfrak{F} & -\mathcal{G}_l\mathfrak{F} & \mathfrak{F}_l\mathcal{G}^-\\ -\mathfrak{F}_l^\dagger\mathfrak{F}^\dagger & \mathcal{G}_l^-\mathcal{G} & -\mathfrak{F}_l^\dagger\mathcal{G} & \mathcal{G}_l^-\mathcal{G}^\dagger\\ \mathcal{G}_l\mathfrak{F}^\dagger & \mathfrak{F}_l^\dagger & \mathcal{G}_l\mathcal{G} & \mathfrak{F}_l\mathfrak{F}^\dagger\\ -\mathfrak{F}_l^\dagger\mathcal{G}^- & -\mathcal{G}_l^-\mathcal{G} & \mathfrak{F}_l^\dagger\mathfrak{F} & \mathcal{G}_l^-\mathcal{G}^-\end{bmatrix}. \tag{6.2}$$

Note that $\delta\chi$ gives the uncorrected vertex part and corresponds to $\delta\Lambda$ in the pure case. There is no bare density change; π and π^+ represent the density change generated from $\delta\Delta$ and $\delta\Delta^\dagger$ in the presence of impurity scattering.

We now have coupled integral equations for G and $\delta\tilde{\Lambda}$. We solve them by iteration. As remarked above, we are going to limit ourselves to linear terms in $\delta\chi$. It is a straightforward matter to write the equations to the second order in $\delta\chi$. In fact, the static case has already been treated by Tewordt.[21] Here, we replace G by G_l everywhere in the kernels of the integral equations. It is then easy to solve the integral equation for $\delta\tilde{\Lambda}$, a quantity labeled by incoming 4-momentum $p_+=p+q/2$, outgoing 4-momentum $p_-=p-q/2$ and 4 momentum transfer q:

$$\delta\tilde{\Lambda}(p,q)=\chi(q)+n\textstyle\sum_{p'}|v_{\mathbf{p},\mathbf{p}'}|^2K^l(p_+',p_-')\delta\tilde{\Lambda}(p',q)\,, \tag{6.3}$$

where K^l is given by Eq. (6.2) with $\mathcal{G}_l$ and $\mathfrak{F}_l$ everywhere. Since we are dealing with elastic impurity scattering, the frequency part of the 4-momentum p' in Eq. (6.3) is the same as that of p. We neglect the small dependence of $\delta\tilde{\Lambda}$ on $\mathbf{p}$[19] and perform the integral over $\mathbf{p}'$. We then find

$$\delta\tilde{\Lambda}=(1-L)^{-1}\delta\chi\,,$$

where

$$L=n\textstyle\sum_{\mathbf{p}'}|v_{\mathbf{p}'\mathbf{p}'}|^2K^l(p',q)$$
$$\approx(8\pi^2\tau)^{-1}\int d\xi'd\Omega'K^l(p_+',p_-')\,. \tag{6.4}$$

In Eq. (6.4), $\delta\Omega'$ is the element of solid angle for the vector $\mathbf{p}'$. The calculations of the matrix components of L is a straightforward matter and is carried out in Appendix A where the result is displayed. By matrix manipulation we can find $\delta\tilde{\Lambda}=(1-L)^{-1}\delta\chi$. The result is

$$\mathcal{E}_+\mathcal{E}_-(1-2I)\delta\tilde{\Lambda}$$
$$=\begin{bmatrix}[\mathcal{E}_+\mathcal{E}_--(\mathcal{E}_+\mathcal{E}_--\omega_+\omega_-)I]\delta\Delta-\Delta^2I\delta\Delta^\dagger\\ -(\Delta^\dagger)^2I\delta\Delta+[\mathcal{E}_+\mathcal{E}_--(\mathcal{E}_+\mathcal{E}_--\omega_+\omega_-)I]\delta\Delta^\dagger\\ -i[\Delta^\dagger\omega_+\delta\Delta+\Delta\omega_-\delta\Delta^\dagger]I\\ -i[\Delta^\dagger\omega_-\delta\Delta+\omega_+\Delta\delta\Delta^\dagger]I\end{bmatrix},$$

where $\omega_\pm=\omega\pm\frac{1}{2}\Omega$, $\mathcal{E}_\pm=[\omega_\pm^2+|\Delta|^2]^{1/2}$. Here Ω is the Matsubara frequency $2\pi n/\beta$ associated with the frequency component of the 4-momentum q. In the end, $i\Omega\rightarrow q_0+i\eta$ as in Sec. IV [cf. Eq. (4.3)]. The integral I is defined by (see Appendix A)

$$I=(1/4\tau q)\int_{-q}^{+q}dx(\mathcal{E}_++\mathcal{E}_-+1/\tau+iv_Fx)^{-1}.$$

We use the result for $\delta\tilde{\Lambda}$ in the 2,1 and 1,2 components of the matrix equation for G [Eq. (6.1)] to get the linear term of the equation for the energy gap which is analogous to Eqs. (4.1)–(4.3) of the pure case:

$$\Delta^\dagger(1)=-(g/\beta)\{\sum_{\mathbf{p},\omega}\mathfrak{F}_l^{a\dagger}(\mathbf{p},\omega)$$
$$-\sum_{\alpha=1}^{4}\sum_{\mathbf{p},\omega}[K_{2,\alpha}{}^l(p_+,p_-)-K_{2,\alpha}{}^l(p,p)]$$
$$\times\delta\tilde{\Lambda}_\alpha(\mathbf{q},\Omega)|_{i\Omega\rightarrow q_0+i\eta}\exp i(\mathbf{q}\cdot\mathbf{r}_1-q_0t_1)\}\,, \tag{6.5}$$

where the a on $\mathfrak{F}_l^{a\dagger}$ inducates that we use the Green's function in the alloy.

We observe that the first term on the right-hand side of Eq. (6.5) is similar to the ordinary gap in the alloy. It is well known that nonmagnetic impurity scattering

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[21] L. Tewordt, Phys. Rev. 137, A1745 (1965).

has no effect; therefore, its value is once again $-\frac{1}{2}gN_0I_1 \times\Delta^\dagger(1)$ [cf. Eq. (3.8)]. What remains is the evaluation of the integrals

$$(N_0|2\beta q)\sum_\omega \int_{-q}^{+q} dx \int d\xi[K_{2,\alpha}{}^l(p_+,p_-) \\ -K_{2,\alpha}{}^l(p,p)]\delta\tilde{\Lambda}_\alpha(\mathbf{q},\Omega)\,,$$

where $x=\mathbf{p}\cdot\mathbf{q}/p$. We perform the ξ integral first. This has already been done in the evaluation of the matrix L in Appendix A. The result is

$$(1+\tfrac{1}{2}gN_0I_1)\Delta^\dagger(1) \\ =-(g\pi N_0/2\beta q)\sum_\omega[4v_Fq\tau I/(1-2I)-(v_Fq/\mathcal{E})\delta_{q,0}\delta_{\Omega,0}] \\ \times[(1+\omega_+\omega_-/\mathcal{E}_+\mathcal{E}_-)\delta\Delta^\dagger-(\Delta^{\dagger 2}/\mathcal{E}_+\mathcal{E}_-)\delta\Delta]\,, \quad (6.6)$$

where, on the right-hand side, after performing the frequency sum and continuing $i\Omega\rightarrow q_0+i\eta$, we interpret $\mathbf{q}$, q_0 as $-i\boldsymbol{\nabla}$ and $i\partial/\partial t$ just as in Sec. IV. We remark that the effect of impurity scattering appears only in the quantity

$$g_\tau(q,\ \mathcal{E}_++\mathcal{E}_-)=4v_Fq\tau I/(1-2I) \qquad (6.7)$$

and that the pure case is obtained immediately with g_∞.

We now investigate the terms on the right-hand side of Eq. (6.6) which can appear in the GL equation. The various limits now involve τ and are quite complicated. We do not give a complete discussion here. We begin with the space-derivative terms, proportional to q^2. For these, when $v_Fq>q_0$, we may set $\Omega=0$. Then we have the following simplifications

$$\mathcal{E}_\pm=\mathcal{E}\,,\quad \omega_\pm=\omega\,, \\ I=(1/2v_Fq\tau)\tan^{-1}[v_Fq\tau/(2\mathcal{E}\tau+1)]\,.$$

To obtain the term in $(v_Fq)^2$, we expand the q-dependent quantity $g_\tau(q,2\mathcal{E})$ of Eq. (6.7):

$$g_\tau(q,2\mathcal{E})\approx(v_Fq/\mathcal{E})[1-(v_F{}^2q^2/12\mathcal{E})(\mathcal{E}+1/2\tau)^{-1}]\,.$$

The linear term in q is cancelled by the second term in the square bracket of Eq. (6.6). We drop it and find for the term proportional to q^2

$$-(g\pi N_0\epsilon_F/6m)[\tilde{J}_3\nabla^2\Delta^\dagger \\ -\tfrac{1}{2}\tilde{J}_5(|\Delta|^2\nabla^2\Delta^\dagger+\Delta^{\dagger 2}\nabla^2\Delta)]\,, \quad (6.8)$$

where

$$\tilde{J}_n=(1/\beta)\sum_\omega \mathcal{E}^{1-n}(\mathcal{E}+1/2\tau)^{-1}\,.$$

Comparison with Eq. (3.8) shows that the space derivative terms which are linear in the gap variation have precisely the same form as in the pure case but with the coefficients J_n replaced by $\tilde{J}_n$. The contribution of the second-order terms in $\delta\Delta$ have a similar structure and may be extracted from Ref. 21.

To discuss the time-derivative terms it is necessary to evaluate the sum on frequencies and perform the continuation $i\Omega\nrightarrow q_0+i\eta$. This is a delicate matter with which we deal in Appendix B. In the pure case, we recover the results of Sec. IV. We may anticipate the results for the dirty case at $T=0$ by the following argument. In the pure case, we found that the second time-derivative terms are found at $T=0$ by setting $q=0$ first since the irregular terms arising from thermal excitations are not present. If we do this for the alloy, we expect that the impurity scattering does not alter the time-derivative terms since the scattering is elastic This conjecture is easily verified. The relevant quantity depending on q, τ is, from Eqs. (6.6) and (6.7),

$$(1/2q)g_\tau(q,\ \mathcal{E}_++\mathcal{E}_-)\underset{q\rightarrow 0}{\longrightarrow} v_F/(\mathcal{E}_++\mathcal{E}_-)\,,$$

which is independent of τ as is the rest of the right-hand side of Eq. (6.6). Therefore, for the second time-derivative terms at $T=0$ we have the same expression as in the pure case. Actually, this result holds even if $q\nrightarrow 0$ if the scattering is strong enough. The discussion is in Appendix B. The same conclusion (pure result) obtains for the diffusion, or first time derivative, term when $q_0>\Delta$ near T_c.

Finally, we look for the first time derivative near T_c. We must investigate the imaginary part of the right-hand side of Eq. (6.6) which is linear in q_0. We assume the real part is small as we were able to prove in the pure case in Sec. IV. The details of the analysis of the imaginary part are presented in Appendix B. The result is that in the extremely dirty limit, the same diffusion term is obtained near T_c as in the pure case but the Čerenkov condition is relaxed since the momentum is not sharp in the alloy.

We conclude that the effect of alloying on the linear GL terms proportional to $\delta\Delta$, $\delta\Delta^\dagger$ appears only in the space derivatives as given in Eq. (6.8). The time derivative terms given in Secs. III and IV for the pure case are unaffected.

VII. REMARKS AND CONCLUSIONS

A. Comparison with Previous Work

The most prominent feature of superconductivity as well as superfluidity in liquid helium is that quantum-mechanical effects are exhibited on a macroscopic scale, From the analysis of flux quantization,[22] for example, we know that the order parameter Δ plays the role of a macroscopic wave function. It is therefore reasonable to expect the time-dependent generalization of the GL equation to have the same form as the Schrödinger equation, similar to the Pitaevskii equation[23] for the condensate wave function in the Bose system. In fact, Ginzburg proposed just such an equation back in 1951.[24] Our analysis has lead us to a more complicated result even at $T=0$ [see Eq. (3.16)] where one would expect a purely wave-like behavior for Δ. That the derivative

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[22] J. Bardeen, Phys. Rev. Letters **7**, 162 (1961).

[23] E. P. Gross, Nuovo Cimento **20**, 454 (1961); L. P. Pitaevskii, Zh. Eksperim. i Teor. Fiz. **40**, 646 (1961) [English transl.: Soviet Phys.— JETP **13**, 451 (1961)].

[24] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **21**, 979 (1951).

$\partial^2/\partial t^2$ appears together with $\frac{1}{3}v_F^2\partial^2/\partial x^2$ in Eq. (3.16) is of course due to the fact that superconductivity involves electrons near the Fermi surface and is not surprising if we remember that the system possesses a phonon-like collective mode with the dispersion relation $q_0^2=\frac{1}{3}v_F^2q^2$ (see below). Nevertheless, the essential features of a quantum-mechanical wave are retained in the expression for the phase of Δ, that is for the chemical potential with which Δ oscillates in time. This is clear from Eqs. (5.9) and (5.11), for example. Consequently, as we shall see below, the London acceleration equation results, not from the time-dependent GL equation, but from the charge equation. In considering this problem, one must bear in mind that the chemical potential and hence the charge density are not directly related to the magnitude of Δ but rather to its phase.

A more recent discussion of the time variation of the GL order parameter has been made by Stephen and Suhl[9] in a brief note. They discussed the problem near T_c from a point of view similar to that of the present work. They omitted all dissipative terms and therefore failed to obtain the diffusion equation.

The spatial part of the GL equation, generalized to all temperatures, in the local limit has previously been worked out by several people.[6–8,21] In particular, Tsuzuki[7] and Werthamer[8] give the result in a form which is equivalent to ours.

Finally, we would like to mention the recent work of Stephen[16] who has discussed transport equations for superconductors by the Green's function technique. In his paper, local equilibrium is assumed to have been established. It is the development of this local equilibrium by interelectronic interactions which is described by the diffusion equation of our work.

B. Collective Modes

The time-dependent GL equation near $T=0$ which is of the wave type [Eqs. (3.14)–(3.15)] leads to the propagation of collective modes in the following manner: We first linearize the equation about equilibrium. Note that $I_1\approx(-2/gN_0)-2\pi\Delta_eJ_3{}^e\,\mathrm{Re}\chi$ where χ is the deviation of the gap from its (real) equilibrium value Δ_e and $J_3{}^e$ is given by Eq. (3.10) with $\Delta=\Delta_e$. The result of the linearization is

$$\Delta_e^2J_3{}^e\,\mathrm{Re}\chi=(v_F^2/12)(J_3{}^e\nabla^2\chi^\dagger-\Delta_e^2J_5{}^e\nabla^2\,\mathrm{Re}\chi)\\ -(1/8\pi)(I_3{}^e\chi^{\dagger\prime\prime}-\Delta_e^2I_5{}^e\,\mathrm{Re}\chi''),$$

where $I_n{}^e$ is given by Eq. (3.13) with $\Delta=\Delta_e$. We equate separately the real and imaginary parts and assume the variation $\exp(iq\cdot r-iq_0t)$. We find the dispersion relations

$$(\mathrm{Im}\Delta)\quad q_0^2=(2\pi J_3{}^e/3I_3{}^e)v_F^2q^2,$$

$$(\mathrm{Re}\Delta)\quad q_0^2=[8\pi/(I_3{}^e-\Delta_e^2I_5{}^e)]\\ \times[(J_3{}^e-\Delta_e^2J_5{}^e)v_F^2q^2/12+\Delta_e^2J_3{}^e].$$

The first dispersion relation, for oscillations of the imaginary part of Δ, corresponds to the Anderson mode[25] of the neutral superconductor. At $T=0$, we have $2\pi J_3=I_3$ and the mode propagates with the velocity $v_F/\sqrt{3}$ as may be seen immediately from Eq. (3.16). That this mode couples to the density is easily seen from Eq. (5.6). Of course, in the charged case, when the long-range Coulomb interaction is present, this longitudinal density fluctuation occurs at the plasma frequency. This comes about because the motion of Δ is restricted through Eq. (5.9), Poisson's equation and the requirement $\delta\rho=0$. For a detailed discussion from the Green's function point of view, see Ambegaokar and Kadanoff.[26]

We note from Eq. (5.6) that the oscillations of the real part of Δ which are described by the second dispersion relation give no density fluctuations. Unfortunately, the second dispersion relation is inconsistent with our approximations. At $T=0$, the threshold is $q_0=8\pi J_3/(I_3-\Delta_e^2I_5)$ and is greater than Δ_e itself, i.e., the condition for slow variation is not satisfied. At higher temperatures, we cannot produce a differential equation in the regime $\Delta>q_0>v_Fq$.

C. Nucleation

We have used the time-dependent GL equation near T_c to investigate the question of nucleation of superconducting regions due to interelectronic interactions. In reduced units, the important terms of Eq. (3.5) or Eq. (4.6) are the diffusion equation

$$\partial\Psi/\partial t=\nabla^2\Psi+(1-|\Psi|^2)\Psi,$$

where $\Psi=1$ in equilibrium, the unit of length is $v_F/\Delta_e\sqrt{6}$, the unit of time is $\pi^3kT_c/8\Delta_e^2$ and Δ_e is, as before, the equilibrium value of the gap (we have $\hbar=1$, as usual). An interesting example is that of the growth of the order parameter Ψ starting from an initial distribution representing a superconducting bubble of width 1 and height $\ll 1$. The growth of Ψ offers no surprises. The bubble spreads faster than it grows. Before $t=2$ it has spread to a width ≈ 10 while the height at the center has doubled. Of course, if the curvature of the initial Ψ is great enough, it will initially decrease in the maximum region as diffusion takes place to regions of small Ψ.

D. London Acceleration Equation

An important problem related to the time variation of the order parameter is that of determining under what conditions one can derive London's acceleration equation for the superfluid.[27] We have throughout made the assumption that the thermal excitations are at rest; we therefore limit the present discussion to $T=0$.

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[25] P. W. Anderson, Phys. Rev. **112**, 1900 (1958).

[26] V. Ambegaokar and L. P. Kadanoff, Nuovo Cimento **22**, 914 (1961).

[27] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. 1, p. 54.

We begin by writing the time-dependent GL equation of Eq. (3.15) and we include the external fields according to the prescriptions of Sec. V [cf. in particular, Eqs. (5.8)-(5.12)]. Then the only change in Eq. (3.15) is to replace the space and time derivatives of ψ by

$$\begin{aligned} \nabla'\Psi &= (\nabla - 2ie\mathbf{A}/c)\Psi\,, \\ D\Psi &= [\partial/\partial t + 2i(\mu_l + e\phi - \nabla'^2/8m)]\Psi\,. \end{aligned} \tag{7.1}$$

As we remarked near the end of Sec. V, the terms involving A in the spatial derivative part cancel when the London gauge is used. However, we may proceed in a general gauge. It is convenient to separate the real and imaginary parts of Ψ by writing

$$\Psi = Re^{iS}\,,$$

where $R(\mathbf{r},t)$ and $S(\mathbf{r},t)$ are real. The GL equation for Ψ reduces to

$$\begin{aligned} (4m\Delta_0^2R^2/R_0^4)\ln(R/R_0) &= \tfrac{1}{3}\{[\nabla^2R/R - (\nabla R/R)^2] \\ &\quad - (3/v_F^2)[R''/R - (R'/R)^2]\}\,, \end{aligned} \tag{7.2}$$

$$\nabla^2 S - (3/v_F^2)S'' = 2e[(1/c)\nabla\cdot\mathbf{A} + (3/v_F^2)\phi']\,. \tag{7.3}$$

In writing these equations, we have, as before, restricted ourselves to second derivatives and dropped cross terms in space and time derivatives. We have as well not written terms of higher order than first in the fields when a derivative is also involved (to do better is straightforward but tedious). Equation (7.3) has been written before by Ambegaokar and Kadanoff.[26] It is shown there how Eq. (7.3) arises in a gauge-invariant perturbation treatment of the external fields.

We can also give the charge and current expressions in terms of R and S by making the appropriate transformations of Eqs. (5.9) and (5.10). The results are

$$\mathbf{j} = Ne\mathbf{v}\,, \tag{7.4}$$

$$\begin{aligned} \rho = -eN_0[S' + 2(\mu_l + e\phi) - \nabla^2R/4mR + mv^2] \\ -2N_0e^2\phi\,, \end{aligned} \tag{7.5}$$

where $\mathbf{v} = (\nabla S - 2e\mathbf{A}/c)/2m$ is the superfluid velocity.

We now show that the London acceleration equation follows from Eq. (7.5) if we can neglect the spatial variation of R. We note that the external field does not appear in Eq. (7.2) for R. We may then take $R = R_0$, the equilibrium value, and from the gradient of Eq. (7.5) we derive

$$\begin{aligned} \partial\mathbf{v}/\partial t + \mathbf{v}\cdot\nabla\mathbf{v} &= (e/m)(\mathbf{E} + \mathbf{v}\times\mathbf{H}/c) \\ &\quad - (1/m)\nabla[\mu_l + (\rho/2eN_0 + e\phi)]\,, \end{aligned} \tag{7.6}$$

which is just the acceleration equation.

We wish to make several comments on these results: First, we remark that the derivation of the London equation depended on the neglect of the ∇^2R term in Eq. (7.5) which is justified if the external fields do not appear in Eq. (7.2) for R. At $T = 0$, they only can enter in the time-derivative part of the GL equation. As indicated below Eqs. (7.2) and (7.3), we have not succeeded in formulating precise criteria for dropping the field-dependent terms. However, in case all the time-derivative terms are small then everything follows. The criterion for this is

$$q_0/\Delta_0 \ll 1/\kappa \approx \xi_0/\lambda \approx v_Fq/\Delta_0\sqrt{3}\,, \tag{7.7}$$

where λ is the penetration depth and κ is the Abrikosov parameter. Under this condition then, $|\Psi| = R$ changes quasistatically. Also, from Eq. (7.3), we find that the superfluid behaves as an incompressible ideal fluid:

$$\nabla^2 S - 2e\nabla\cdot\mathbf{A}/c = \nabla\cdot\mathbf{v} = 0\,.$$

Thus, we conclude that at $T = 0$ and in the local limit, London's theory is valid if condition (7.7) is satisfied. As remarked earlier, it is interesting to note that the hydrodynamical equation arises not from the GL equation itself but rather from the charge equation.

At finite temperature, Eqs. (7.4) and (7.5) are still valid provided we assume that the normal fluid is at rest and that the other approximations of Sec. V which led to Eqs. (5.9) and (5.10) for the charge and current are valid. We can still drop the time-derivative terms in the GL equation when the criterion (7.7) is satisfied. However, the equation for R which corresponds to Eq. (7.2) now contains the phase S and the vector potential $\mathbf{A}$ explicitly (recall that $\mathbf{A}$ only drops out of the spatial derivative part of the GL equation at $T = 0$). Therefore, another condition is required for neglecting the spatial derivative of R on the right-hand side of Eq. (7.5) to obtain the acceleration equation. We do not pursue this matter here because of our restrictive assumption concerning the motion of the normal component. In the impure case also the situation is much more complicated since the equation for R will contain $\mathbf{A}$, even at $T = 0$.

Note added in proof. Using a slightly different method, M. P. Kemoklidze and L. P. Pitaevskii, Zh. Eksperim. i Teor. Fiz. **50**, 243 (1966) [English transl.: Soviet Phys.—JETP **23**, 160 (1966)] have derived results similar to ours for the neutral pure superconductor at absolute zero.

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APPENDIX A

In this Appendix, we evaluate the integrals of Eq. (6.4) in order to determine the elements of the matrix L

which determines the vertex corrections in the impure case. The integrand is the matrix K^l defined in Eq. (6.2) with $\mathcal{G}_l$ and $\mathcal{F}_l$ everywhere. These Green's functions are

$$\mathcal{G}_l(\mathbf{p},\omega)=-(\xi+i\tilde{\omega})/(\xi^2+\mathcal{E}^2),\quad \mathcal{G}_l^-(\mathbf{p},\omega)=-(\xi-i\tilde{\omega})/(\xi^2+\mathcal{E}^2),\quad \mathcal{F}_l(\mathbf{p},\omega)=\tilde{\Delta}/(\xi^2+\mathcal{E}^2),\quad \mathcal{F}_l^\dagger(\mathbf{p},\omega)=\tilde{\Delta}^\dagger/(\xi^2+\mathcal{E}^2),$$

where $\xi=p^2/2m-\mu$, ω is the Matsubara frequency $(2n+1)\pi/\beta$, $\mathcal{E}^2=\tilde{\omega}^2+|\tilde{\Delta}|^2$ and $\Delta=\Delta_l=\Delta(1)$. Quantities with tildes are the original quantities multiplied by $\eta_\omega=1+1/2\tau\mathcal{E}$. Thus, $\tilde{\omega}=\eta_\omega\omega$.

As an example, we compute L_{12}.

$$L_{12}=(1/8\pi^2\tau)\int d\xi' d\Omega' K_{12}{}^l(p_+{}',p_-{}')=(1/8\pi^2\tau)\int d\xi' d\Omega' \mathcal{G}_l^-(\mathbf{p}_+{}',\omega_+)\mathcal{G}_l(\mathbf{p}_-{}',\omega_-)$$

$$=(1/4\pi\tau q)\int dx\int d\xi(\xi_+-i\tilde{\omega}_+)(\xi_-+i\tilde{\omega}_-)[(\xi_+{}^2+\mathcal{E}_+{}^2)(\xi_-{}^2+\mathcal{E}_-{}^2)]^{-1}.$$

In the above, $\xi_\pm=\xi\pm v_Fx$, $\omega_\pm=\omega\pm\frac{1}{2}\Omega$ where Ω is the Matsubara frequency $2n\pi/\beta$ associated with the frequency component of the 4-momentum q. It is convenient to perform the ξ integral first. The result is

$$L_{12}=(1+\omega_+\omega_-/\mathcal{E}_+\mathcal{E}_-)I,$$

where

$$I=(1/4\tau q)\int_{-q}^{+q} dx(\mathcal{E}_++\mathcal{E}_-+1/\tau+iv_Fx)^{-1}.$$

The other elements of L are evaluated in a similar manner. The complete matrix is given by

$$L=\frac{I}{\mathcal{E}_+\mathcal{E}_-}\begin{bmatrix}\mathcal{E}_+\mathcal{E}_-+\omega_+\omega_- & -(\Delta)^2 & i\omega_+\Delta & i\Delta\omega_- \\ -(\Delta^\dagger)^2 & \mathcal{E}_+\mathcal{E}_-+\omega_+\omega_- & i\Delta^\dagger\omega_- & i\omega_+\Delta^\dagger \\ -i\omega_+\Delta^\dagger & -i\Delta\omega_- & \mathcal{E}_+\mathcal{E}_--\omega_+\omega_- & \Delta\Delta^\dagger \\ -i\Delta^\dagger\omega_- & -i\omega_+\Delta & \Delta^\dagger\Delta & \mathcal{E}_+\mathcal{E}_--\omega_+\omega_-\end{bmatrix}.$$

APPENDIX B

We outline in this Appendix the analysis of Eq. (6.6). We rewrite the required frequency sum by shifting the origin of ω by $\frac{1}{2}\Omega$ and defining $U=i\mathcal{E}=[-\omega^2-|\Delta|^2]^{1/2}$. We then have, in an otherwise obvious notation, the frequency sum

$$-(gnN_0/2v_Fq\beta)\sum_\omega g_\tau(q,\,U+U_-)[(1-\omega\omega_-/UU_-)\delta\Delta^\dagger+(UU_-)^{-1}(\Delta^\dagger)^2\delta\Delta],\quad\text{(B1)}$$

where

$$g_\tau(q,Z)=4v_Fq\tau I/(1-2I)\quad\text{(B2)}$$

$$I=(i/4q\tau)\int_{-q}^{+q}dx(Z+i/\tau-v_Fx)^{-1}.\quad\text{(B3)}$$

We express the sum as an integral in the standard manner by considering $i\omega$ to be the complex variable z:

$$-(gN_0/8iv_Fq)\oint dz\tanh(\beta z/2)g_\tau(q,U+U_-)$$

$$\times[(1+zz_-/UU_-)\delta\Delta^\dagger+(UU_-)^{-1}(\Delta^\dagger)^2\delta\Delta],\quad\text{(B4)}$$

where $z_-=z-i\Omega$ and U is now given in terms of z by $U=[z^2-|\Delta|^2]^{1/2}$. The contour encircles the poles of $\tanh\beta z/2$ in the counterclockwise sense and no other singularities of the integrand are included.

In addition to the poles, the integrand has four branch points coming from the square roots U and U_-. They are located at $z=\pm\Delta$, $\pm\Delta+i\Omega$. We choose cuts extending from these points to $\pm\infty$. There are no other singularities arising from $g_\tau(q,Z)$. We deform the contour so that it encircles the cuts as shown in Fig. 1. It is not difficult to show that the integrals along 1 and 8 are equal. The same is true for the pairs (2,7), (3,6), and (4,5). Thus, the integral is just twice the contribution from the lower cuts. Now we perform the continua-

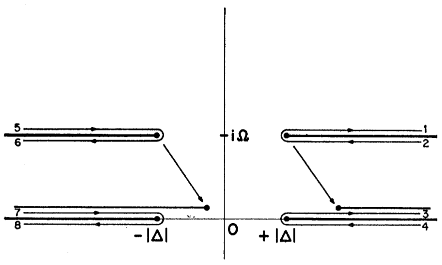

FIG. 1. Contours for the integration of Eq. (B4). The arrows indicated how the upper cuts approach the lower ones in the continuation $i\Omega\rightarrow q_0+i\eta$. The upper branch points go to $\pm|\Delta|+q_0+i\eta$. The numbers indicate portions of the integration that are referred to in the text.

tion $i\Omega \rightarrow q_0+i\eta$. The upper cuts approach the lower ones and take up the position shown in Fig. 1. The upper branch points (for U_-) are shifted and then U_- has different phases along the lower cuts (integrals 3, 4, 7, 8) than it had before continuation. In the pure case, this leads to the appearance of poles in the integrand of the integral I which appears in the definition of $g_\infty(q,Z)$ [cf. Eq. (B2)]. These poles insure energy and momentum conservation in the diffusion process, they only appear (for $q_0<\Delta$, $T\approx T_c$) when $v_Fq>q_0$, and they give rise to the first time-derivative terms. In the alloy, it is more complicated since the momentum is no longer a good quantum number. We remark, however, that no poles appear between the cuts but that the phases of U_- must be kept careful track of. The result of the analysis is

$$\begin{aligned}-(gN_0/4iv_Fq)\Big\{&-2i\int_\Delta^{\Delta+q_0} dy\,\tanh(\beta y/2)[\mathrm{Re}g_\tau(q,Z_1)(yy_-\delta\Delta^\dagger+\Delta^{\dagger 2}\delta\Delta)/ww_- - \mathrm{Im}g_\tau(q,Z_1)\delta\Delta^\dagger]\\&+\int_\Delta^\infty dy[\tanh(\beta y_+/2)-\tanh(\beta y/2)]g_\tau(q,Z_2)[(1-yy_+/ww_+)\delta\Delta^\dagger-\Delta^{\dagger 2}\delta\Delta/ww_+]\\&-\int_\Delta^\infty dy[\tanh(\beta y_+/2)g_\tau^*(q,Z_3)-\tanh(\beta y/2)g_\tau(q,Z_3)][(1+yy_+/ww_+)\delta\Delta^\dagger+\Delta^{\dagger 2}\delta\Delta/ww_+]\Big\}\,,\end{aligned}\qquad\text{(B5)}$$

where

$$w=[y^2-\Delta^2]^{1/2},\qquad w_-=[\Delta^2-(y-q_0)^2]^{1/2},$$
$$w_+=[(y+q_0)^2-\Delta^2]^{1/2},\quad y_\pm=y\pm q_0,$$

and

$$Z_1=w+iw_-,\quad Z_2=w_+-w,\quad Z_3=w_++w.$$

We may understand the role of the three integrals by passing to the pure limit and comparing with Sec. IV. All three integrals contribute to the second time-derivative terms; they combine in a simple manner when $q\rightarrow 0$. However, at $T=0$, where we expect this procedure to be valid, the second integral is zero and it is sufficient to consider only the first and third.

The diffusion term near T_c comes from the second and third integrals which contain $[\tanh\beta y_+/2-\tanh\beta y/2]$, the factor which describes thermal excitations.

For the space derivatives, we set $q_0\rightarrow 0$ at once and only the third integral survives in the pure case. This remains true in the alloy but we have already analyzed this case in the main text.

To analyze the second time-derivative terms we look at absolute zero. Then only the first and third integrals survive and are given by

$$\begin{aligned}-(gN_0/2v_Fq)\Big\{\int_\Delta^{\Delta+q_0} &dy[\mathrm{Im}g_\tau(q,Z_1)\delta\Delta^\dagger-\mathrm{Re}g_\tau(q,Z_1)\\&\times(yy_-\delta\Delta^\dagger+\Delta^{\dagger 2}\delta\Delta)/ww_-]+\int_\Delta^\infty dy\,\mathrm{Im}g_\tau(q,Z_3)\\&\times[(1+yy_+/ww_+)\delta\Delta^\dagger+\Delta^{\dagger 2}\delta\Delta/ww_+]\Big\}\,.\end{aligned}$$

To evaluate the functions g_τ we work in the very dirty limit $v_Fq\tau=ql\ll 1$. Then from Eq. (B2) we may write

$$\begin{aligned}g_\tau(q,Z)\approx(2iv_Fq/Z)&[1+\tfrac{1}{3}v_F^2q^2\tau^2(Z\tau+i)^{-2}]\\&\times[1-i(v_F^2q^2\tau/3Z)(Z\tau+i)^{-2}]^{-1}.\end{aligned}\qquad\text{(B6)}$$

In the first integral, $|Z_1|=|w+iw_-|\approx(q_0\Delta)^{1/2}\ll v_Fq\ll 1/\tau$. We furthermore assume that the impurity scattering is strong enough that $v_Fq\tau\ll(q_0\Delta)^{1/2}/v_Fq\ll 1$. Then $g_\tau(q,Z_1)$ is simply $2iv_F/q/Z_1$ which is the same result as for the pure case when $q\rightarrow 0$. The other integral contains $g_\tau(q,Z_3)$ where $(2q_0\Delta)^{1/2}\leq Z_3=w_++w\leq\infty$. Then in the same extremely dirty limit

$$\begin{aligned}\mathrm{Im}g_\tau(q,Z_3)\approx(2v_Fq/Z_3)&[1+\tfrac{1}{3}v_F^2q^2\tau^2\\&\times(Z_3^2\tau^2+1)^{-1}]\approx 2v_Fq/Z_3\,,\end{aligned}$$

which once again is the pure result when $q\rightarrow 0$. The conclusion is that if $(v_Fq)^2\tau(q_0\Delta)^{-1/2}\ll 1$ then the second time-derivative terms are the same as in the pure case no matter how q goes to zero.

We conclude this Appendix with a discussion of the diffusion term near T_c. We need only the imaginary part of the whole expression (B4). The first integral does not contribute. The contributions of the second and third integrals may be combined by a change of variable from y to $Z_2=(y_+^2-\Delta^2)^{1/2}-(y^2-\Delta^2)^{1/2}$ in the second integral and to $Z_3=(y_+^2-\Delta^2)^{1/2}+(y^2-\Delta^2)^{1/2}$ in the third. We work near T_c so we neglect second order in Δ where feasible. The result is

$$\begin{aligned}-(gN_0i/4v_Fq)\int_{q_0}^\infty dZ\{&\tanh[\beta(ZT+q_0)/4]\\&-\tanh[\beta(ZT-q_0)/4]\}\mathrm{Re}g_\tau(Z)\delta\Delta^\dagger/T\,,\\T^2=1+4|\Delta|^2/(Z^2-q_0^2)&.\end{aligned}$$

Because of the temperature-dependent statistical factor, the integrand is exponentially small if Z is as large as $1/\tau$. It behaves as $\exp(-\xi_0/l)\ll 1$ where ξ_0 is the coherence length. Then, from Eq. (B5) we have

$$\mathrm{Re}g_\tau(q,Z)\approx 2v_Fq(v_F^2q^2\tau/3)[Z^2+(v_F^2q^2\tau/3)^2]^{-1}.$$

Furthermore, we may expand $\tanh[\beta(ZT\pm q_0)/4]$ about

$q_0=0$, keep only the first-order terms and drop q_0 everywhere else. The result is

$$-(gN_0i\beta q_0/4)\int_0^\infty dZ\,\mathrm{sech}^2[\beta(Z^2+4|\Delta|^2)^{1/2}/4]$$
$$\times(\tfrac{1}{3}Z\tau v_F{}^2q^2)[(Z^2+4|\Delta|^2)^{1/2}(Z^2+\tfrac{1}{9}v_F{}^4q^4\tau^2)]^{-1}\delta\Delta^\dagger.$$

We consider the case $v_F{}^2q^2\tau/3\gg 2\Delta$. Then we may drop $|\Delta|^2$ everywhere and pass to the limit of strong scattering so that the τ-dependent term may be replaced by $\frac{1}{2}\pi\delta(Z)$. The final result is the same as in the pure case:

$$-(gN_0i\pi\beta q_0/8)\delta\Delta^\dagger.$$

The approximations we have used to obtain this result are summarized as follows:

$$ql\ll 1,$$
$$T\approx T_c,$$
$$l/\xi_0\approx kT_c\tau\ll 1,$$
$$\Delta\ll v_F{}^2q^2\tau\ll kT_c.$$

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Superconductivity of Thorium and Uranium*

J. E. Gordon
Physics Department, Amherst College, Amherst, Massachusetts

AND

H. Montgomery
Solid State Division, Atomic Energy Research Establishment, Harwell, Berkshire, England

AND

R. J. Noer
Physics Department, Amherst College, Amherst, Massachusetts

AND

G. R. Pickett†
Clarendon Laboratory, Oxford, England

AND

R. Tobón
Departamento de Fisica, Universidad del Valle, Cali, Colombia

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The low-temperature susceptibility and specific heat of thorium and uranium have been measured. It is found that thorium becomes a superconductor at $T_c=(1.374\pm0.001)$°K, and has a value of $C_{es}(T_c)/\gamma T_c=2.42$, in good agreement with BCS theory. (Here C_{es} is the superconducting electronic specific heat, and γ is the temperature coefficient of the normal electronic specific heat.) The γ and Θ_D for thorium were found to be (4.31 ± 0.05) mJ/mole deg^2 and (163.3 ± 0.7)°K, respectively. Both uranium samples appeared to undergo superconducting transitions when observed magnetically, yet both exhibited only normal-state behavior in their specific heat. Hence it seems likely that the apparent superconductivity of alpha uranium is not characteristic of the bulk metal. The γ and Θ_D of the purer uranium sample were found to be (10.03 ± 0.02) mJ/mole deg^2 and (207 ± 1)°K, respectively.

INTRODUCTION

THERE have been several investigations of superconductivity in the actinide metals thorium[1,2] and α uranium.[2–5] According to magnetic measurements, both metals become superconducting below 1.5°K, but whereas thorium shows a narrow transition at a temperature (~1.37°K) which varies little among samples, α uranium shows surprisingly broad transitions at temperatures which vary considerably from sample to sample, even in high-purity material. The transition temperature of thorium, like that of most superconductors, is depressed by the application of pressure,[6] whereas that of α uranium rises dramatically, 10 kbar being sufficient to raise it above 2°K.[7] Another sur-

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† Present address: Department of Technical Physics, Institute of Technology, Otanieme (Helsinki), Finland.

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