

MICROSCOPIC DERIVATION OF THE GINZBURG-LANDAU EQUATIONS IN THE THEORY OF SUPERCONDUCTIVITY

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It is shown that the phenomenological Ginzburg-Landau equations follow from the theory of superconductivity in the London temperature region in the neighborhood of T_C . In these equations there occurs, however, twice the electronic charge; this is related to the physical meaning of $\Psi(x)$ as the wave function for Cooper pairs. The constant κ turns out to be small. The problem of the surface energy for the boundary between the normal and superconducting phases in the neighborhood of T_C is discussed.

It is well known that the behavior of superconductors in a magnetic field in the neighborhood of the critical temperature is qualitatively well described by Ginzburg and Landau's phenomenological theory.¹ We shall show in the present paper that equations of the same type as those in Ginzburg and Landau's theory follow indeed from the theory of superconductivity.

We shall start from the equations for the thermodynamic Green functions^{3,4} which we obtained earlier.² These equations are in a magnetic field of the form

$$\begin{aligned} & \left\{ -\frac{\partial}{\partial \tau} + \frac{1}{2m} \left(\frac{\partial}{\partial \mathbf{r}} - ie\mathbf{A}(\mathbf{r}) \right)^2 + \mu \right\} G(x, x') \\ & + \Delta(\mathbf{r}) F^+(x, x') = \delta(x - x'), \\ & \left\{ \frac{\partial}{\partial \tau} + \frac{1}{2m} \left(\frac{\partial}{\partial \mathbf{r}} + ie\mathbf{A}(\mathbf{r}) \right)^2 + \mu \right\} F^+(x, x') \\ & - \Delta^*(\mathbf{r}) G(x, x') = 0; \end{aligned} \tag{1}$$

where

$$\Delta^*(\mathbf{r}) = gF^+(\tau, \mathbf{r}; \tau, \mathbf{r}). \tag{1'}$$

The last relation expresses $\Delta(\mathbf{r})$ in terms of the coupling constant and the value of the function $F^+(x, x')$ for equal arguments. If there is no field, $\Delta = \text{const}$. The quantity 2Δ is in that case the energy gap in the spectrum. $F^+(x, x')$ tends, in fact, logarithmically to infinity as $x = x'$; this corresponds to the well known logarithmic divergence in the equation determining the gap when one integrates in momentum space. In the papers by Bardeen, Cooper, and Schrieffer⁵ and Bogolyubov⁶ this divergence was removed by cutting-off the energy of the interacting electrons at distances of the order of the Debye frequency $\tilde{\omega}$ from the Fermi surface; we

shall do the same in the following. One verifies easily that such a cut-off corresponds in the coordinate representation to a "spread out" in Eq. (1') over a distance of the order $\hbar v/\tilde{\omega}$.

Let us go over to the Fourier components of the Green functions $G(x, x')$ and $F^+(x, x')$ with respect to the difference of the variables⁴ $u = \tau - \tau'$, for instance,

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; u) &= T \sum_n e^{-i\omega_n u} \mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}'), \\ \mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}') &= \frac{1}{2} \int_{-1/T}^{+1/T} e^{i\omega_n u} G(\mathbf{r}, \mathbf{r}'; u) du, \end{aligned}$$

where $\omega_n = \pi(2n + 1)T$ ($n = \dots -1, 0, 1, \dots$). Equations (1) go over into the following equations for the Fourier components $\mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}')$ and $\mathfrak{F}_\omega^+(\mathbf{r}, \mathbf{r}')$:

$$\begin{aligned} & \left\{ i\omega_n + \frac{1}{2m} \left(\frac{\partial}{\partial \mathbf{r}} - ie\mathbf{A}(\mathbf{r}) \right)^2 + \mu \right\} \mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}') \\ & + \Delta(\mathbf{r}) \mathfrak{F}_\omega^+(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \\ & \left\{ -i\omega_n + \frac{1}{2m} \left(\frac{\partial}{\partial \mathbf{r}} + ie\mathbf{A}(\mathbf{r}) \right)^2 + \mu \right\} \mathfrak{F}_\omega^+(\mathbf{r}, \mathbf{r}') \\ & - \Delta^*(\mathbf{r}) \mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}') = 0, \end{aligned} \tag{2}$$

and condition (1') can be written in the form

$$\Delta^*(\mathbf{r}) = T \sum_n \mathfrak{F}_\omega^+(\mathbf{r}, \mathbf{r}). \tag{2'}$$

We introduce, finally, $\mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}')$, the Fourier component of the Green function for an electron in the normal metal in a magnetic field. The equation satisfied by $\mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}')$ can be written in two ways:

$$\left\{ i\omega_n + \frac{1}{2m} \left(\frac{\partial}{\partial \mathbf{r}} - ie\mathbf{A}(\mathbf{r}) \right)^2 + \mu \right\} \mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{3}$$

or

$$\left\{ i\omega_n + \frac{1}{2m} \left(\frac{\partial}{\partial \mathbf{r}'} + ie\mathbf{A}(\mathbf{r}') \right)^2 + \mu \right\} \tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}').$$

It is convenient to use the function $\tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{r}')$ to write Eqs. (2) in integral form, using the second of Eqs. (3):

$$\begin{aligned} \mathcal{G}_\omega(\mathbf{r}, \mathbf{r}') &= \tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{r}') - \int \tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{s}) \Delta(\mathbf{s}) \tilde{\mathcal{F}}_\omega^+(\mathbf{s}, \mathbf{r}) d^3\mathbf{s}, \\ \tilde{\mathcal{F}}_\omega^+(\mathbf{r}, \mathbf{r}') &= \int \mathcal{G}_\omega(\mathbf{s}, \mathbf{r}') \Delta^*(\mathbf{s}) \tilde{\mathcal{G}}_{-\omega}(\mathbf{s}, \mathbf{r}) d^3\mathbf{s}. \end{aligned} \quad (4)$$

Before we proceed, we find out what the function $\tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{r}')$ is equal to. If there is no magnetic field, one sees from (3) that

$$\tilde{\mathcal{G}}_\omega^0(\mathbf{r} - \mathbf{r}') = -\frac{m}{2\pi R} \exp \left\{ \left[i \operatorname{sign} \omega p_0 - \frac{|\omega_n|}{v} \right] R \right\}. \quad (5)$$

Here

$$\operatorname{sign} \omega = \omega / |\omega|, \quad R = |\mathbf{r} - \mathbf{r}'|, \quad \mu = p_0^2 / 2m \gg |\omega|.$$

$\tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{r}')$ in a magnetic field differs from (5) by a phase factor. Indeed,* because p_0 is a large quantity we can use the quasi-classical approximation to determine $\tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{r}')$, i.e., write it in the following form:

$$\tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{r}') = e^{i\varphi(\mathbf{r}, \mathbf{r}')} \tilde{\mathcal{G}}_\omega^0(\mathbf{r} - \mathbf{r}'), \quad \varphi(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} = 0. \quad (6)$$

Substituting (6) into (3) we find for the addition to the action of $\varphi(\mathbf{r}, \mathbf{r}')$

$$(\mathbf{n}, \nabla_{\mathbf{r}} \varphi(\mathbf{r}, \mathbf{r}')) = \frac{e}{c} (\mathbf{n}, \mathbf{A}(\mathbf{r})), \quad \mathbf{n} = (\mathbf{r} - \mathbf{r}') / |\mathbf{r} - \mathbf{r}'|. \quad (7)$$

Near the transition temperature $\Delta(\mathbf{r})$ (and at the same time $\tilde{\mathcal{F}}_\omega^+(\mathbf{r}, \mathbf{r}')$) is small. We shall therefore expand Eq. (4) in powers of Δ and Δ^* and express $\tilde{\mathcal{F}}_\omega^+(\mathbf{r}, \mathbf{r}')$ up to terms of the fourth order, and $\mathcal{G}_\omega(\mathbf{r}, \mathbf{r}')$ up to terms of second order in Δ , inclusive. The substitution of the expression obtained for $\tilde{\mathcal{F}}_\omega^+(\mathbf{r}, \mathbf{r}')$ into (2') gives one equation connecting $\Delta(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$:

$$\begin{aligned} \Delta^*(\mathbf{r}) &= gT \sum_n \int \tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{r}') \tilde{\mathcal{G}}_{-\omega}(\mathbf{r}, \mathbf{r}') \Delta^*(\mathbf{r}') d^3\mathbf{r}' \\ &- gT \sum_n \int \int \int \tilde{\mathcal{G}}_\omega(\mathbf{s}, \mathbf{r}) \tilde{\mathcal{G}}_{-\omega}(\mathbf{s}, \mathbf{l}) \tilde{\mathcal{G}}_\omega(\mathbf{m}, \mathbf{l}) \tilde{\mathcal{G}}_{-\omega}(\mathbf{m}, \mathbf{r}) \\ &\times \Delta(\mathbf{s}) \Delta^*(\mathbf{l}) \Delta^*(\mathbf{m}) d^3\mathbf{s} d^3\mathbf{l} d^3\mathbf{m}. \end{aligned} \quad (8)$$

The important distances in Eq. (8) are of the order $\xi = \hbar v / T_c$, since it can be seen from (5) and (6) that the Green function $\tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{r}')$ decreases exponentially for $R \gg \xi_0$. At the same time, the changes in the gap $\Delta(\mathbf{r})$ and the field $\mathbf{A}(\mathbf{r})$ take place at distances of the order of the penetration depth which is much larger than ξ_0 near the critical temperature. For the same reason the phase $\varphi(\mathbf{r}, \mathbf{r}')$ in (6) is small near T_c and equal to

$$\varphi(\mathbf{r}, \mathbf{r}') \approx \frac{e}{c} (\mathbf{A}(\mathbf{r}'), \mathbf{r} - \mathbf{r}'). \quad (9)$$

*This was pointed out by L. D. Landau.

Using these facts we can perform the integration in Eq. (8).

The first term on the right hand side is of the form

$$g \int K(\mathbf{r}, \mathbf{r}') \Delta^*(\mathbf{r}') d^3\mathbf{r}',$$

where the kernel

$$K(\mathbf{r}, \mathbf{r}') = K_0(\mathbf{r} - \mathbf{r}') \exp \left\{ \frac{2ie}{c} (\mathbf{A}(\mathbf{r}'), \mathbf{r} - \mathbf{r}') \right\}$$

has a singularity for $R = |\mathbf{r} - \mathbf{r}'| = 0$:

$$K_0(R) = m^2 T / (2\pi R)^2 \sinh(2\pi T R / v).$$

This singularity is connected, as was pointed out already in the foregoing, with the cut-off of the interaction at the Debye frequencies $\tilde{\omega}$.

Introducing this cut-off we get

$$\begin{aligned} \int K_0(R) d^3R &= \frac{mp_0}{2\pi^2} \int_0^{\tilde{\omega}} \frac{\tanh(\xi / 2T)}{\xi} d\xi \\ &= \frac{mp_0}{2\pi^2} \ln \left(\frac{2\gamma}{\pi} \frac{\tilde{\omega}}{T} \right) = \frac{mp_0}{2\pi^2} \left(\frac{1}{g} + \ln \frac{T_c}{T} \right), \end{aligned} \quad (10)$$

where the transition temperature T_c is connected to the gap in the energy spectrum at absolute zero in the well-known way²:

$$\frac{\Delta_0 \gamma}{\pi} = T_c \quad \left(\frac{1}{g} = \frac{mp_0}{2\pi^2} \ln \frac{2\tilde{\omega}}{\Delta_0} \right).$$

Expanding the exponents in the Green functions in terms of $\varphi(\mathbf{r}, \mathbf{r}')$ using the fact that $\Delta(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ vary slowly near T_c , and eliminating $\tilde{\omega}$ and g by using (10) we get the following equation

$$\begin{aligned} \left\{ \frac{1}{2m} \left(\frac{\partial}{\partial \mathbf{r}} + 2ie\mathbf{A}(\mathbf{r}) \right)^2 \right. \\ \left. + \frac{1}{\lambda} \left[\frac{T_c - T}{T_c} - \frac{7\zeta(3)}{8(\pi T_c)^2} |\Delta(\mathbf{r})|^2 \right] \right\} \Delta^*(\mathbf{r}) = 0, \end{aligned} \quad (11)$$

where $\lambda = 7\zeta(3) \epsilon_F / 12(\pi T_c)^2$ ($\zeta(x)$ is here Riemann's zeta function).

To get a second equation connecting Δ and \mathbf{A} we shall now calculate what the current density $\mathbf{j}(\mathbf{r})$ is equal to. To do this we use the relation expressing $\mathbf{j}(\mathbf{r})$ in terms of a Green function:

$$\mathbf{j}(\mathbf{r}) = \left\{ \frac{ie}{m} (\nabla_{\mathbf{r}'} - \nabla_{\mathbf{r}}) G(x, x') - \frac{2e^2}{mc} \mathbf{A}(\mathbf{r}) G(x, x') \right\}_{t'=t+0; \mathbf{r}=\mathbf{r}'}$$

(the additional factor of 2 is due to a summation over spin). We note that if we substitute everywhere the Green function for the normal metal in the form (6) and then sum over frequencies we get no contribution to the expression for the current, as should be the case. The total current is thus equal to

$$\mathbf{j}(\mathbf{r}) = \frac{ie}{m} (\nabla_{\mathbf{r}'} - \nabla_{\mathbf{r}}) \delta G(x, x')|_{x=x'}, \quad (12)$$

where

$$\delta G(x, x')|_{x=x'} = -T \sum_n \int \int \tilde{\mathcal{G}}_\omega(\mathbf{r}, \mathbf{s}) \tilde{\mathcal{G}}_\omega(\mathbf{l}, \mathbf{r}) \tilde{\mathcal{G}}_{-\omega}(\mathbf{l}, \mathbf{s}) \Delta^*(\mathbf{l}) \Delta(\mathbf{s}) d^3\mathbf{s} d^3\mathbf{l}. \quad (13)$$

Restricting ourselves in the expression for the current to terms linear in \mathbf{A} and assuming $\mathbf{A}(\mathbf{r})$ to vary slowly with \mathbf{r} in the London temperature range near T_c we get

$$\mathbf{j}(\mathbf{r}) = \left\{ \frac{ie}{m} \left(\Delta \frac{\partial \Delta^*}{\partial \mathbf{r}} - \Delta^* \frac{\partial \Delta}{\partial \mathbf{r}} \right) - \frac{4e^2 |\Delta|^2}{mc} \mathbf{A} \right\} \frac{7\zeta(3)N}{16(\pi T)^2} \quad (14)$$

We shall introduce a "wave function" $\Psi(\mathbf{r})$, proportional to $\Delta(\mathbf{r})$:

$$\Psi(\mathbf{r}) = \Delta(\mathbf{r}) \sqrt{7\zeta(3)N/4\pi T_c}. \quad (15)$$

The set of Eqs. (11) and (14) takes then a form completely analogous to the equations of the phenomenological Ginzburg-Landau theory:

$$\left\{ \frac{1}{2m} \left(\frac{\partial}{\partial \mathbf{r}} - ie^* \mathbf{A}(\mathbf{r}) \right)^2 + \frac{1}{\lambda} \left[\frac{T_c - T}{T_c} - \frac{2}{N} |\Psi(\mathbf{r})|^2 \right] \right\} \Psi(\mathbf{r}) = 0, \quad (16)$$

$$\mathbf{j}(\mathbf{r}) = -\frac{ie^*}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial \mathbf{r}} - \Psi \frac{\partial \Psi^*}{\partial \mathbf{r}} \right) - \frac{e^{*2}}{mc} \mathbf{A} |\Psi|^2,$$

where $e^* = 2e$, N is the number density of the electrons in the normal metal and λ was defined after Eq. (11). There is a difference, however, in that (16) contains the electronic charge e twice, clearly owing to the physical meaning of $\Psi(\mathbf{r})$ as the wave function of a Cooper pair.

These equations arise thus in a natural way in the theory of superconductivity in the London region* near T_c . The phenomenological constant defined in the same way as in the old theory, but with $e^* = 2e$, can now be evaluated and turns out to be equal to

$$\kappa = 3 T_c (\pi/v)^{3/2} (c/ep_0) \sqrt{2/7\zeta(3)}. \quad (17)$$

The region of applicability of Eqs. (16) is small for sharply expressed Pippard metals and occurs very near T_c ; at large distances from T_c the local relation (14) ceases to be valid.

For metals of the London type the region of applicability of (16) is determined solely by the smallness of the ratio $(T - T_c)/T_c$.

The possibility to apply (16) to describe the properties of thin films in a magnetic field with the microscopic value (17) of the constant κ is limited by the fact that usually films are polycrystalline specimens with grain sizes of the order of the film thickness. The presence of boundaries between different crystals will act like the presence of foreign impurities. One must therefore possibly describe

*In reference 5 the assumption was stated that some quantity related to the gap should play the role of the expansion parameter Ψ in the theory of reference 1.

real films in the microscopic theory from the same point of view as superconducting alloys.

We note now that to evaluate the difference in the free energy of the metal in the normal state and in the superconducting state in a magnetic field we can use the following formula:

$$F_{SH} - F_n = -(1/\lambda N) \int |\Psi(\mathbf{r})|^4 d^3\mathbf{r}. \quad (18)$$

Indeed, we shall use the thermodynamic relation

$$\delta \Omega / \delta g(\mathbf{r}) = - \langle H_{int}(\mathbf{r}) \rangle / g(\mathbf{r}),$$

where according to (5)

$$H_{int}(\mathbf{r}) = 1/2 g(\mathbf{r}) (\hat{\Psi}^+(\mathbf{r}) (\hat{\Psi}^+(\mathbf{r}) \hat{\Psi}(\mathbf{r})) \hat{\Psi}(\mathbf{r})),$$

Ω is the thermodynamic potential [we introduce here for the sake of convenience a variable "interaction constant" $g(\mathbf{r})$]. Taking averages we get

$$\Omega_s - \Omega_n = - \int d^3\mathbf{r} \int_0^g \frac{\delta g(\mathbf{r})}{g^2(\mathbf{r})} |\Delta(\mathbf{r})|^2. \quad (19)$$

Equation (8) determines $1/g(\mathbf{r})$ as a functional of $\Delta(\mathbf{r})$ [for the sake of simplicity we shall consider the real solution for $\Delta(\mathbf{r})$ as is usually done in one-dimensional problems]. Using (8) to integrate (19), and using the fact that small additions to all thermodynamic potentials in the corresponding variables are equal, we get Eq. (18).

The constant κ of (17) is connected with the magnitude of the critical field H_{cm} of a bulk specimen and the penetration depth δ_0 by the relation (which contains the charge e^*):

$$\kappa = \frac{\sqrt{2}e^*}{\hbar c} H_{cm} \delta_0^2. \quad (20)$$

For metals of the London type or such intermediate metals as tin the region of applicability of Eqs. (16) is fairly large and in that case we should consistently use the experimental data* for H_{cm} and δ_0^2 to compare the theory with experiments. For Pippard metals δ_0 is the penetration depth only in a very narrow range of temperatures near T_c . It is thus convenient in this case to turn to the theoretical formulae for a definition of κ . It can easily be verified that (17) can be written in the form

$$\kappa \approx 0.96 \delta_L / \xi_0, \quad (21)$$

where $\delta_L^{-1} = (4\pi Ne^2/mc^2)^{1/2}$ is the London penetration depth and $\xi_0 = 0.18 \hbar v/kT_c$ is the non-localization parameter introduced in Bardeen, Cooper, and Schrieffer's paper. Using the data given in reference 5 we get from (21) for tin $\kappa \approx 0.14$, and for aluminum $\kappa \approx 0.01$.

We note an interesting consequence of (21). The

*A detailed study of experimental data is given in a paper by Ginzburg.⁷

condition that a superconductor be a London one requires $\kappa \approx \delta_L / \xi_0 \gg 1$. At the same time if $\kappa \gg 1/\sqrt{2}$ a metal displays in a strong field the same behavior as for alloys. A metal which in weak fields at $T = 0$ must be assigned to the London class will thus behave in strong fields near T_c as an "alloy." At the same time the case of small κ corresponds to a Pippard metal.

Let us now stop a moment at the problem of the surface energy at the boundary between the normal and the superconducting phase. For strongly expressed Pippard superconductors we can, because κ is small, use the limiting solution¹

$$\sigma_{ns}(8\pi/H_{cm}^2) = 1.89 \delta_0 / \kappa, \quad (22)$$

where

$$\delta_0 = \delta_L(T=0) / \sqrt{2(1-T/T_c)}.$$

We note that for these metals the applicability of Eq. (22) in an appreciable temperature interval near T_c is just connected with the fact that κ is small, since, as was shown in reference 1, in that case the quantity σ_{ns} does not depend on the distribution of the field in the transition region.

For tin the accuracy of this equation is insufficient and one must use the results of numerical calculations. Estimating σ_{ns} from Ginzburg's calculations⁸ we get for $\kappa \approx 0.14$

$$\sigma_{ns}(8\pi/H_n^2) \approx (2 \div 3) \cdot 10^{-5} / \sqrt{1-T/T_c}.$$

According to Sharvin's data⁹

$$\sigma_{ns}(8\pi/H_c^2) = 2.5 \cdot 10^{-5} / \sqrt{1-T/T_c},$$

and according to Faber's data¹⁰

$$\sigma_{ns}(8\pi/H_c^2) = 1.88 \cdot 10^{-5} / \sqrt{1-T/T_c}.$$

These results do, apparently, not contradict the theory (See reference 7).

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