Quantum Fluctuations in Continuous Superconducting Films

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Motivated by recent experiments on ultrathin continuous superconducting films, we study the dependence of T_c *and* Δ *(for zero temperatures) on the film thickness* d. *Using field-theoretical methods, we express the Coulomb interaction in terms of a fluctuating potential, and the fluctuation correction to the free energy (in one-loop approximation) is determined. Based on the standard dirty-limit expressions for the response functions, we find* T_c *and* Δ *by a numerical investigation of the gap equation. Generally, we find that the decrease of* T_c *and* Δ *vs.* d^{-1} *is quite similar, but depends sensitively on both the large-wave-vector cut-off and the strength of the interaction. In particular, however, for a strong interaction (Coulomb interaction), the order parameter is more strongly suppressed than the critical temperature, which is due to long-wavelength fluctuations of the phase and the potential.*

1. INTRODUCTION

During the past decade, extensive experimental and theoretical efforts have been devoted to the study of low-dimensional (in particular, two-dimensional) metallic systems in the presence of disorder. (For some recent reviews, see Refs. 1-4.) Many studies have especially concentrated on the weak localization regime, i.e., $k_F l > 1$, where k_F is the Fermi wave vector and l the mean free path, in which a perturbative treatment, starting from the metallic side, can be applied.

In this context, the influence of disorder and Coulomb interactions on superconductivity in two (and one) dimensions is of considerable interest. In fact, it was shown experimentally[5-7] that the critical temperature and the zero-temperature order parameter are dramatically reduced upon decreasing the film thickness d of a homogeneous superconducting film toward a few Å. Quite remarkably, the decrease of T_c and $\Delta(T=0)$ is very similar.[7] A further reduction of T_c, as well as an increasing width of the superconducting transition, is found when the one-dimensional limit is approached.[8] Up to now, only few theoretical attempts toward an understanding of this behavior have been made.[9-15]

As an example, and in order to introduce the relevant parameters of the problem, let us briefly discuss some results for the decrease of the transition temperature of a thin superconducting film, $\delta T_c = T_c - T_{c0}$, where T_{c0} is the corresponding bulk value, in the regime $d \lessdot \xi_0$; here $\xi_0 \simeq 0.36 \cdot (v_F l / T_c)^{1/2}$ is the dirty limit coherence length extrapolated to zero temperatures (typically, $\xi_0 \sim 100$ Å). A simple dimensional analysis shows that, for $\delta T_c \ll T_{c0}$,

$$\ln(T_c/T_{c0}) \simeq \delta T_c/T_{c0} = -A\rho; \qquad \rho \equiv R_\square/R_0 \tag{1}$$

where $R_\square = (\sigma d)^{-1}$ is the sheet resistance, $R_0 = \hbar/(2e)^2 \simeq 6.45$ kΩ the unit of resistance, and A a "constant of order unity."* As is well known, classical fluctuations of the order parameter[16] give a result of the form of Eq. (1), with $A \simeq [7\zeta(3)/2\pi^3]\ln(\rho^{-1})$; however, the logarithmic dependence on ρ is practically quite unimportant, and the slope of δT_c vs. $R_\square$ calculated in this way turns out to be about a factor of ten too small compared with the data.[5-7] Including the leading contribution from the Coulomb interaction, the following asymptotic result has been obtained:[9-13]

$$A \simeq (24\pi)^{-1} \ln^3(\alpha y_m) \tag{2}$$

which holds for $\ln y_m \gg 1$, where y_m is related to a large-wave-vector cutoff q_m by $y_m = \hbar D q_m^2 / 2\pi k T_c$.† Equation (2) is in good agreement with experiment, provided one chooses $q_m \simeq l^{-1}$, and adjusts the parameter α. Though the dependence on the cutoff is "only" logarithmic, it should be noted that a typical value is $\ln(\alpha y_m) \simeq 7, \ldots, 8$, i.e., $A \simeq 5, \ldots, 7$, leading by a linear extrapolation of Eq. (1) to a destruction of superconductivity at $R_\square \sim 0.2 R_0$. Experimentally, however, the magnitude of the slope $\delta T_c / R_\square$ is found to decrease with increasing $R_\square$, such that T_c goes to zero at a somewhat higher value,[5,6] or such that T_c saturates when the limit of about one atomic layer is approached.[7] The former behavior was explained by Finkel'stein[13] on the basis of a renormalization group analysis.

However, we wish to emphasize that two important questions arise in connection with the results of Refs. 10–13 (in contrast to Refs. 9 and 14), which are related to the fact that two-dimensional systems are considered; actually, in these articles, the critical temperature relative to the critical temperature of the clean system is determined, i.e., $\delta T_c \equiv T_c(l) - T_c(\infty)$, in

*Note that $R_\square/R_0 = [\pi\hbar N(0) D d]^{-1} = 6\pi/k_F^2 l d$, where $N(0)$ is the density of states at the Fermi surface (for one spin), and D the diffusion coefficient.

†Ovchinnikov[9] found a minus sign in this expression, which we believe not to be correct (see Section5).

which case $q_m \simeq l^{-1}$ appears to be the natural cutoff. By appropriate identification of $R_\Box$, the results are applied to what is actually measured, namely the decrease of T_c as a function of the film thickness, d, relative to its bulk value, at the same mean free path. In the latter case, which we address in this paper (see also Ref. 9), in the inverse of the film thickness is the relevant cutoff, namely $q_m \sim d^{-1}$. As is evident already from Eq. (2), with this interpretation the slope ($\sim A$) actually becomes small for $d \simeq \xi_0$. Second, a quantitative analysis of the decrease of the critical temperature, as well as the decrease of the zero-temperature order parameter, has not been given.

The above remarks indicate the questions we intend to discuss in this paper. Our analysis will be based on the path integral formulation of the theory of superconductivity,[17-20] in which the electron–electron interaction is taken into account in terms of a fluctuating potential.[21-23] Thus, by expanding around the saddlepoint (which is equivalent to usual BCS theory), it is possible to calculate in a systematic way higher order corrections to the free energy functional. Since we consider the Gaussian (one-loop) approximation, these "fluctuation corrections" are given in terms of the various response functions, which can be easily calculated within standard dirty limit theory.[24-27] As it turns out, this approach is closely related to the one of Ref. 9. Here, in addition, a detailed numerical investigation of the gap equation, close to T_c as well as for zero temperatures, will be given. To be explicit, we emphasize that we are considering homogeneous superconducting films; in contrast, in granular films, other remarkable phenomena have been found recently.[28]

In the next section (Section 2), we describe the path integral formulation of the theory, which allows in a straightforward way the determination of the fluctuation corrections to the free energy functional, as well as (upon differentiation) the corresponding corrections to the gap equation. The decrease of the critical temperature, in particular its dependence on the electron–electron interaction strength, is discussed in Section 3. In Section 4, we present the results for the suppression of the zero-temperature order parameter, and we give some concluding remarks in Section 5. Finally, some technical details are presented in the Appendices. In particular, we discuss in some detail: the question of the cutoff; the derivation of the response functions; a number of analytic results close to the critical and zero temperature; and the connection between response and correlation functions.

2. THEORETICAL FORMULATION

The present theoretical formulation is based on the path integral representation of the microscopic theory and proceeds in close analogy to Refs.

17–20 (see also, for example, Ref. 21). Applying the standard Hubbard-Stratonovich procedure, we rewrite the (attractive) electron-phonon interaction as well as the Coulomb interaction by introducing a complex order parameter field $\Delta(x)$, $x \equiv (\mathbf{r}, \tau)$ and a real potential field $\phi(x)$, respectively. Then the partition function is given as follows:

$$Z_G = \mathrm{tr}_{\psi,\psi^+}\left\{\int \mathscr{D}\Delta\mathscr{D}\Delta^*\mathscr{D}\phi T_\tau \exp - \int_0^\beta d\tau\, \mathscr{H}_{\mathrm{eff}}(\tau)\right\} \tag{3}$$

where ($\hbar = k = 1$) $\beta = 1/T$ is the inverse temperature, T_τ is the time ordering operator, and the trace is over the electron operators. The effective Hamiltonian is given by

$$\mathscr{H}_{\mathrm{eff}} = \mathscr{H}^K_{\mathrm{eff}} + \mathscr{H}^\Delta_{\mathrm{eff}} + \mathscr{H}^C_{\mathrm{eff}} \tag{4}$$

where $\mathscr{H}^K_{\mathrm{eff}}$ contains the standard kinetic energy as well as the (random) impurity potential, and $\mathscr{H}^\Delta_{\mathrm{eff}}$ and $\mathscr{H}^C_{\mathrm{eff}}$ depend on the order parameter and the potential field, respectively. Explicitly, we have

$$\begin{aligned}\mathscr{H}^\Delta_{\mathrm{eff}} = &-i \int d^3r\, \Delta^*(x)\psi_\downarrow(\mathbf{r})\psi_\uparrow(\mathbf{r}) + h.c. \\ &+ N(0)\lambda^{-1}\int d^3r\, |\Delta(x)|^2\end{aligned} \tag{5}$$

where λ is the dimensionless electron-phonon coupling constant. Furthermore,

$$\mathscr{H}^C_{\mathrm{eff}} = i\int d^3r\, \rho(\mathbf{r})\phi(x) + \tfrac{1}{2}\int d^3r\, \phi(x)V^{-1}\phi(x) \tag{6}$$

where $\rho(\mathbf{r})$ is the charge density operator, and $V^{-1} = -\nabla^2/4\pi$ is the inverse of the Coulomb interaction. Note that ϕ has been introduced such that i appears in the first term of (6) in order to have a standard Gauss integration with respect to ϕ—otherwise, analytic continuation procedures must be employed, however, with the same final result. Furthermore, we will also consider a local interaction, in which case $V(\mathbf{r}-\mathbf{r}) \to v_0\delta(\mathbf{r}-\mathbf{r})$, and $V^{-1} \to v_0^{-1}$ in Eq. (6).

In the next step, we perform the trace with respect to the electron operators, with the result that the partition function is written as

$$Z_G = \int \mathscr{D}\Delta\mathscr{D}\Delta^*\mathscr{D}\phi \exp - S_{\mathrm{eff}}[\Delta, \Delta^*, \phi] \tag{7}$$

where the effective action is given by

$$S_{\mathrm{eff}} = \int_0^\beta d\tau \int d^3r \left[N(0)\frac{|\Delta|^2}{\lambda} + \tfrac{1}{2}\phi V^{-1}\phi\right] - \mathrm{tr}\ln \hat{G}^{-1} \tag{8}$$

Here, tr indicates the trace with respect to space and (imaginary) time and with respect to the 2×2 Nambu space. The inverse of the matrix Green's function $\hat{G}$ is given by

$$\hat{G}^{-1}=\hat{G}_0^{-1}+[i\hat{\Delta}-ie\phi\hat{1}]\delta(x-x') \tag{9}$$

where

$$\hat{G}_0^{-1}=\left\{-\partial_\tau\cdot\hat{\tau}_3-\left[-\frac{\nabla^2}{2m}+u_{\text{imp}}(\mathbf{r})\right]\hat{1}\right\}\delta(x-x') \tag{10}$$

and

$$\hat{\Delta}=\begin{bmatrix}0 & \Delta\\ \Delta^* & 0\end{bmatrix} \tag{11}$$

The present formulation has the considerable advantage that much of the essential physics is already captured by the saddle point of the effective action, and that higher order corrections ("fluctuation corrections") to the free energy functional can be calculated in a straightforward and systematic way. This is easily illustrated by applying standard field-theoretical methods: We consider a slight generalization of Eq. (7), and introduce external fields $\eta(x)$, $\eta^*(x)$ such that

$$Z[\eta,\eta^*]=\int\mathscr{D}^2\Delta\mathscr{D}\phi\, e^{-S_{\text{eff}}}\exp\int dx[\eta\Delta^*+\eta^*\Delta] \tag{12}$$

Clearly, we have relations like

$$\langle\Delta\rangle=\frac{\delta}{\delta\eta^*}W[\eta,\eta^*] \tag{13}$$

where $W=\ln Z$, etc. In the next step, we perform a Legendre transformation such that $\bar{\Delta}=\langle\Delta\rangle$, $\bar{\phi}=\langle\phi\rangle$ appear as the independent variables; the corresponding potential, which we denote by Γ, is defined through the relation

$$\Gamma(\bar{\Delta},\bar{\Delta}^*,\bar{\phi})=\int dx\,[\eta^*\bar{\Delta}+\eta\bar{\Delta}^*]-W \tag{14}$$

where η, η^* are functions of the new variables, in principle to be computed through Eq. (13) and similar relations. (Of course, we could easily include an external field generating ϕ-correlation functions. This has been omitted to simplify the notation.) In any case, we now have the relation

$$\eta=\frac{\delta\Gamma}{\delta\bar{\Delta}^*} \tag{15}$$

Finally, to determine the state of thermal equilibrium, we consider $\eta=\eta^*=0$; in this case, we may choose $\bar{\Delta}$ to be real and $\bar{\phi}=0$, having in mind, of course, the appropriate impurity average.

As an illustration, consider evaluating (12) by the saddle point approximation. Then we find Γ to be given by Γ_0, where

$$\Gamma_0 = S_{\text{eff}}[\Delta, \Delta^*, \phi = 0] = \int dx\, N(0) \frac{|\Delta|^2}{\lambda} - \operatorname{tr} \ln \hat{G}^{-1} \tag{16}$$

which for time-independent Δ is easily identified with the BCS free energy divided by T. For example, one finds the gap equation from

$$0 = \frac{\delta \Gamma_0}{\delta \Delta^*} = N(0) \frac{\Delta}{\lambda} - i\hat{G}_{21}(x, x) \tag{17}$$

by noting that ($\xi_p = p^2/2m - \mu$)

$$\hat{G}(x, x) = T \sum_{\omega} \int \frac{d^3p}{(2\pi)^3} [i\omega\hat{\tau}_3 - \xi_p + i\Delta\hat{\tau}_1]^{-1} \tag{18}$$

Performing the momentum integration, $d^3p/(2\pi)^3 \to N(0)\, d\xi$, one obtains

$$i\hat{G}_{21}(x, x) = N(0)\pi T \sum_{\omega}{}' \frac{\Delta}{(\omega^2 + \Delta^2)^{1/2}} \tag{19}$$

which leads to the standard result:

$$\frac{\Delta}{\lambda} = \pi T \sum_{\omega}{}' \frac{\Delta}{(\omega^2 + \Delta^2)^{1/2}} \tag{20}$$

Note that the frequency sum has to be restricted to $|\omega| < \omega_D$, where ω_D is the Debye frequency.

In the next step, we demonstrate how higher order corrections to the free energy can be calculated in a systematic way. In particular, the next-to-leading order corrections arise from a quadratic expansion of the effective action around the saddle point (one-loop approximation), and are completely determined by the various response functions of a superconductor, which can be calculated easily in the dirty limit (see Appendix B).

As an example, consider fluctuations of the magnitude of the order parameter. Thus we replace, in the effective action, Δ by $\Delta + \delta\Delta^L$, where $\delta\Delta^L$ is real, and expand S_{eff} in second order. This gives

$$S_{\text{eff}}^{(2)} = \int dx\, N(0) \frac{(\delta\Delta^L)^2}{\lambda} - \{\operatorname{tr} \ln(\hat{G}^{-1} + i\delta\Delta^L\hat{\tau}_1)\}^{(2)} \tag{21}$$

where the notation implies that the second-order term should be taken in the last part of this expression. As a formal device, write this term as

$$\int_0^1 d\varepsilon \frac{\partial}{\partial \varepsilon} \operatorname{tr} \ln(\hat{G}^{-1} + i\varepsilon \cdot \delta\Delta^L\hat{\tau}_1) = \int_0^1 d\varepsilon \operatorname{tr}(\hat{G}_\varepsilon \cdot i\delta\Delta^L\hat{\tau}_1) \tag{22}$$

Here, $\hat{G}_\varepsilon$ denotes the Green's function in the presence of the perturbation $(\varepsilon \cdot \delta\Delta^L)$, and has to be computed linearly in $\delta\Delta^L$. Thus, we may easily perform the ε-integral, giving

$$S_{\text{eff}}^{(2)} = \int dx\, N(0)\frac{(\delta\Delta^L)^2}{\lambda} - \tfrac{1}{2}\,\mathrm{tr}[\hat{G}_{\varepsilon=1}(x,x)i\delta\Delta^L(x)\hat{\tau}_1]^{(2)} \tag{23}$$

Furthermore, we introduce the quasiclassical Green's function, i.e., the Green's function integrated with respect to the magnitude of the momentum, and averaged over all directions, according to

$$\pi N(0)\hat{g}(\tau, \tau', \mathbf{r}) = i\hat{G}(\mathbf{r}, \mathbf{r}; \tau, \tau') \tag{24}$$

such that*

$$\begin{aligned} S_{\text{eff}}^{(2)} &= N(0)\int dx \left\{\frac{(\delta\Delta^L)^2}{\lambda} - \frac{\pi}{2}\mathrm{tr}_2[\hat{g}(\tau,\tau,\mathbf{r})\delta\Delta^L\hat{\tau}_1]^{(2)}\right\} \\ &= N(0)\int dx\, \delta\Delta^L(\lambda^{-1} - \chi_{\Delta\Delta}^L)\delta\Delta^L \end{aligned} \tag{25}$$

where the longitudinal response function $\chi_{\Delta\Delta}^L$ has been introduced (see Appendix B). The integration with respect to $\delta\Delta^L$ is straightforward, leading to the fluctuation correction to Γ which is given by

$$\Gamma_{\Delta\Delta} = \tfrac{1}{2}\,\mathrm{Sp}\ln(\lambda^{-1} - \chi_{\Delta\Delta}^L) \tag{26}$$

The evaluation of phase and potential fluctuations proceeds similarly, with the final result

$$\Gamma = \Gamma_0 + \Gamma_{\text{fl}}; \qquad \Gamma_{\text{fl}} = \Gamma_{\Delta\Delta} + \Gamma_{\Delta\phi} + \Gamma_{\phi\phi} \tag{27}$$

where (see Appendix B for the definitions)

$$\Gamma_{\phi\phi} = \tfrac{1}{2}\,\mathrm{Sp}\ln(V^{-1} - \chi_{\phi\phi}) \tag{28}$$

$$\Gamma_{\Delta\phi} = \tfrac{1}{2}\,\mathrm{Sp}\ln\{(\lambda^{-1} - \chi_{\Delta\Delta}^T) + 2e^2N(0)\chi_{\Delta\phi}(V^{-1} - \chi_{\phi\phi})^{-1}\chi_{\phi\Delta}\} \tag{29}$$

In these equations, Sp is to be identified with $\sum_{\omega,\mathbf{q}}$. Equations (26)–(29) are the central results of this paper, on which the subsequent analysis will be based. As mentioned above, to investigate thermal equilibrium states, it is sufficient to take $\bar{\Delta}$ to be real and spatially homogeneous, and $\bar{\phi} = 0$. Then the fluctuation corrections to the gap equation are obtained from (27) by (ordinary) differentiation with respect to the order parameter. The response functions, as determined within the dirty limit theory, are given in Appendix B. At this point, we remark that we are working exclusively within the BCS approximation, i.e., we neglect the energy dependence of the phonon self energy (we return to this question in the discussion).

*Note that tr_2 is the ordinary trace over 2×2 Nambu matrices.

From a diagrammatic point of view, the fluctuation corrections to the thermodynamic potential are best characterized as "string of bubbles" diagrams, which contain in each bubble all nonintersecting impurity lines. However, differentiation with respect to the order parameter is not so easily visualized, so we remark that the resulting contributions to the gap equation can also be derived as follows (using longitudinal fluctuations for illustration; see also Fig. 1). In the first step, we imagine that we calculate the second order corrections to Gorkov's $\mathscr{F}$-function, i.e., the off-diagonal part of the Green's function. Second, we average with respect to the fluctuating fields, e.g., $\delta\Delta^L$, thereby introducing the correlation functions, $\langle\delta\Delta^L\delta\Delta^L\rangle \sim (\lambda^{-1} - \chi^L_{\Delta\Delta})^{-1}$, i.e., a "string of bubbles," which is shown in Fig. 1 as a curly line. Finally, this contribution is inserted into the gap equation, represented by connecting the open ends by a phonon Green's function, which, in the present approximation, is reduced to a single dot.

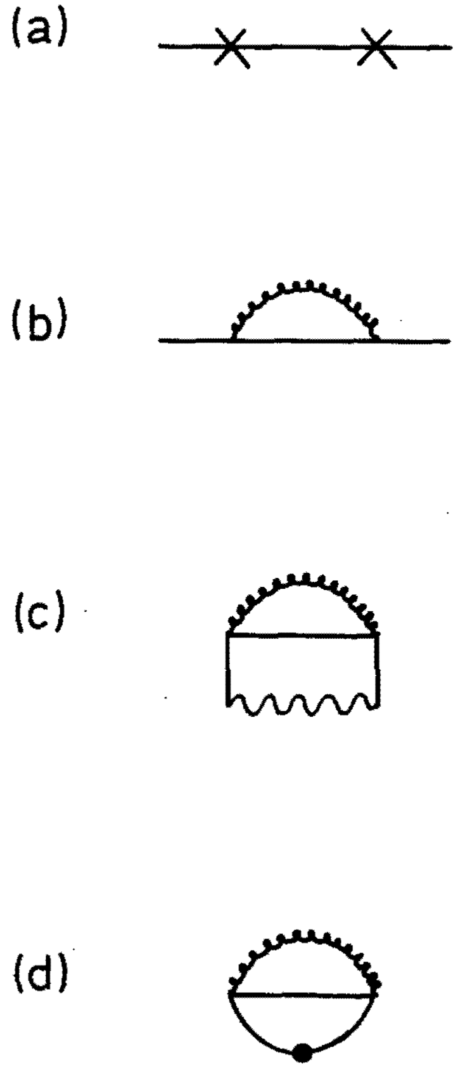

Fig. 1. Graphical representation of the fluctuation corrections to the self-energy. (a) correction to the Green's function in second order in the fluctuating fields; (b) averaging with respect to the fields; (c) contribution to the self-energy; the wavy line denotes the phonon propagator, which reduces to (d) a dot in the BCS approximation.

3. THE CRITICAL TEMPERATURE

3.1. Order Parameter Correlations above T_c

Before establishing the equation for the critical temperature of a thin film, we briefly discuss the order parameter response and correlations for $T > T_c$ ($\langle\Delta\rangle = 0$). In this case (see Appendix C), we have $\chi^T_{\Delta\Delta} = \chi^L_{\Delta\Delta}$, and we will omit the superscripts T, L for simplicity. The order parameter correlation function is related to the response function as follows (Appendix E):

$$N(0)\langle T_\tau(\delta\Delta\delta\Delta^*)\rangle_{q,\omega_0} = [\lambda^{-1} - \chi_{\Delta\Delta}(q, \omega_0)]^{-1} \tag{30}$$

where $\delta\Delta = \delta\Delta^L - i\delta\Delta^T$, and $\omega_0 = 2\pi Tm$ denotes the Matsubara (Bose) frequency. Defining T_0, the critical temperature of the bulk system without fluctuation corrections, by the relation $\lambda^{-1} = \ln(1.13\omega_D/T_0)$, we find the following result:

$$\lambda^{-1} - \chi_{\Delta\Delta} = \ln\frac{T}{T_0} + \psi\left(\frac{1}{2} + \frac{|\omega_o| + Dq^2}{4\pi T}\right) - \psi(\tfrac{1}{2}) \tag{31}$$

where ψ denotes Euler's psi function; note that this quantity, for $\omega_0 = q = 0$, equals zero for $T = T_0$, the usual BCS approximation. After analytic continuation, $\omega_0 \to -i\omega + 0$, and for $\delta T \equiv T - T_0$, ω, $Dq^2 \ll T_0$, we find the following expression which is well known from the (simple) time-dependent Ginzburg-Landau theory:

$$\lambda^{-1} - \chi_{\Delta\Delta} \to \frac{\delta T}{T_0} + \frac{\pi}{8T_0}[-i\omega + Dq^2] \tag{32}$$

At this point, it is instructive to briefly recall the formalism outlined in Section 2. In particular, we remark that the order parameter correlation function is given by [see (12) and (13)]

$$\langle T_\tau(\delta\Delta_x\, \delta\Delta^*_y)\rangle = \frac{\delta\langle\Delta_x\rangle}{\delta\eta_y} = \frac{\delta^2}{\delta\eta_y\, \delta\eta^*_x} W[\eta, \eta^*] \tag{33}$$

where arguments x, y, $x \equiv (\mathbf{r}, \tau)$, etc., have been included. On the other hand, from (15), we obtain

$$\gamma_2(x, y) \equiv \frac{\delta^2\Gamma}{\delta\Delta_x\, \delta\Delta^*_y} = \frac{\delta\eta_y}{\delta\Delta_x} = N(0)[\lambda^{-1}\delta(x-y) - \bar{\chi}_{\Delta\Delta}(x-y)] \tag{34}$$

This relation, in fact, defines the exact response functions; the above approximation follows by replacing Γ by Γ_0 [Eq. (16)]. Furthermore, it follows immediately that for homogeneous and time-independent Δ, we have the relation

$$[\partial\Gamma/\partial\Delta^2]_{\Delta=0} = \mathcal{V}\beta\gamma_2(q=0, \omega_0=0) \tag{35}$$

where $\mathcal{V} = \mathcal{A}d$ is the volume, and $\mathcal{A}$ the area.

3.2. Determination of T_c

To determine the critical temperature of a thin film, we consider the potential $\Gamma[\Delta, \Delta^*, \phi]$ for homogeneous and time-independent states; thus, we may choose $\Delta = \Delta^*$ and $\phi = 0$. Consequently, T_c is determined from

$$[\mathscr{V}\beta N(0)]^{-1}(\partial\Gamma/\partial\Delta^2)_{\Delta=0} = 0 \tag{36}$$

which is equivalent to $\gamma_2(q=0, \omega_0=0)=0$. From this relation, by introducing $\Gamma = \Gamma_0 + \Gamma_{\mathrm{fl}}$, we find

$$\ln(T_c/T_0) = -[\mathscr{V}\beta N(0)]^{-1}(\partial\Gamma_{\mathrm{fl}}/\partial\Delta^2) \tag{37}$$

where $\Delta = 0$ is understood after differentiation. This equation contains T_0, which is not desirable. Thus, we define the bulk value of the fluctuation correction Γ_{fl}^B and the difference $\tilde{\Gamma}_{\mathrm{fl}} = \Gamma_{\mathrm{fl}} - \Gamma_{\mathrm{fl}}^B$; more precisely, Γ_{fl}^B is given by Eqs. (26)-(29), where the summation over the perpendicular wave-vector component (say, q_z) is replaced by an integration in the usual way. Thus we find

$$\ln\frac{T_c}{T_{c0}} = -\frac{T_c}{N(0)d}\left(\frac{\partial}{\partial\Delta^2}\mathscr{A}^{-1}\tilde{\Gamma}_{\mathrm{fl}}\right)_{T=T_c} \tag{38}$$

where T_{c0} is the critical temperature of the bulk material, for the same parameters, in particular for the same mean free path, as the corresponding film. Furthermore, the difference $\tilde{\Gamma}_{\mathrm{fl}}$ is approximately evaluated by taking $q_z = 0$ and by restricting the parallel wave vectors such that $q_\parallel^2 < q_m^2$, where $q_m \simeq d^{-1}$, which is valid in the regime $d < \xi_0$ (see Appendix A). We emphasize again that we find it not to be correct to identify the cutoff with l^{-1}, the inverse of the mean free path (note that $l^{-1} > d^{-1}$). Clearly, it is convenient to introduce a dimensionless variable $y = Dq^2/2\pi T_c$; thus, the prefactor $[\pi N(0)dD]^{-1} = R_\square/R_0 \equiv \rho$ arises in a natural way.*

As an important point, we stress that in the present formulation, the fluctuation contribution $\tilde{\Gamma}_{\mathrm{fl}}$ contains the response functions as calculated without fluctuation corrections. Clearly, an extension of (38) into a self-consistent formulation is adequate, analogous to what was done by Schmid;[16] however, the most important correction concerns the $\omega_0 = q = 0$ part of the response, which has to be corrected such that [compare to (31)]

$$\lambda^{-1} - \chi_{\Delta\Delta} \to \ln\frac{T}{T_c} + \psi\left(\frac{1}{2} + \frac{|\omega_0| + Dq^2}{4\pi T}\right) - \psi(\tfrac{1}{2}) \tag{39}$$

to ensure that the singular behavior of, e.g., the order parameter fluctuations or the coherence length is at the correct critical temperature, namely T_c.

*Note that $y_m = Dq_m^2/2\pi T_c \simeq (4/\pi^2)(\xi_0/d)^2$.

However, the above prescription introduces the usual logarithmic divergence (for $D=2$) into the calculation of T_c, from the classical ($\omega_0=0$) order parameter fluctuations. Introducing a long-wavelength cutoff y_c, and for $\delta T_c = T_c - T_{c0} \ll T_{c0}$, this contribution is given by[16]

$$(\delta T_c/T_{c0})^{\text{class}} \simeq -[7\zeta(3)/2\pi^3]\rho \ln y_c^{-1} \tag{40}$$

where $\zeta(3)=1.202\ldots$. In fact, the long-wavelength cutoff can be justified by noting that, in addition to the shift of the critical temperature, there is also a smearing of the transition, with a width (relative to T_c) given by[9] $\tau_c \simeq \pi\rho/32$, as estimated from the fluctuation contribution to the conductivity. Thus, we are led to exclude small wave vectors, namely $q^2 < \tau_c/\xi_0^2$, which gives $y_c \simeq \rho/8\pi$. From a slightly different point of view, this procedure is also equivalent to calculating, e.g., the temperature dependence of the order parameter for temperatures outside the critical region (where the present theory is applicable), and determining T_c by extrapolation into the critical region (which is found to be much smaller than the shift of T_c).

3.3. Results

From Eq. (38), the fluctuation shift of the critical temperature is easily determined. Quite generally, we consider two cases, a short-range interaction (case I), which physically can be justified by considering the capacitative interaction with a metallic counterelectrode, as well as the long-range Coulomb interaction (case II). Note however, that for realistic parameter values, the Coulomb interaction is the dominant contribution. Explicitly, we define

$$\text{(I)}\quad V_{\text{I}}(q)=v_0; \qquad \text{(II)}\quad V_{\text{II}}(q)=2\pi d/q \tag{41}$$

Note that the 2D form of the Coulomb interaction has to be used (since $q<d^{-1}$). As a convenient dimensionless measure of the strength of the interaction, define the parameter $c_\eta = [2e^2N(0)V_\eta(q)]^{-1}$, $\eta = \text{I}, \text{II}$. Thus we find, for the above-mentioned example, $c_{\text{I}} \simeq \lambda_{TF}^2/dx_0$, where λ_{TF} is the screening length and x_0 is the distance to the counterelectrode. Below, c_{I} will be considered a parameter, in order to demonstrate the dependence on the strength of the interaction. Furthermore, we have the following relation:

$$\text{(II)}\quad c_{\text{II}} = 2\lambda_{TF}^2 q/d = (\pi\lambda_{TF}^2/d\xi_0)y^{1/2} \tag{42}$$

where $y = Dq^2/2\pi T_c$ as introduced above. Note that ξ_0, and thus the large-y cutoff $y_m \simeq 0.41(\xi_0/d)^2$, depends on the actual critical temperature. As typical parameters, applicable to the lead films of Ref. 7, we estimate $l \simeq 4$ Å, giving $\rho(d\simeq l)\simeq 0.5$ (i.e., for extremely thin films). In addition, $\xi_{00} \equiv \xi_0(T_{c0}) \simeq 100$ Å, leading to $y_m \simeq 10^3\rho^2 T_{c0}/T_c$, where the numerical factor is proportional to $(\xi_{00}l)^2 p_F^4$.

Quite generally, it is convenient to rewrite (38) into the following form:

$$\ln(T_{c0}/T_c) = \rho\tilde{A} \tag{43}$$

We briefly discuss the dependence of $\tilde{A}$ on the parameters. Case I: For fixed c_{I}, $\tilde{A}$ depends explicitly on ρ through the classical contribution as discussed above, and on ρ and T_c through $y_m \sim \rho^2/T_c$. As an illustration, the y_m dependence is shown in Fig. 2, where $A \equiv \tilde{A}(\rho = 0.1, y_m)$ is given. Evidently, A increases with increasing y_m, and with increasing strength of the interaction ($\sim c_{\mathrm{I}}^{-1}$). For the present range of parameters, the dependence of A on y_m is slightly weaker than the asymptotic result,[9-13] $A \sim \ln^3 y_m$. (The asymptotic behavior is easily confirmed with the results of Appendix C, by taking into account the contribution from potential fluctuations in the regime $2\pi T_c \ll |\omega_0| \ll Dq^2$). From a practical point of view, an approximation to A with a third-order polynomial in $\ln y_m$ is entirely sufficient. For case II, on the other hand, we note the very small prefactor on the right-hand side of Eq. (42); thus, the Coulomb interaction is practically identical* to $c_{\mathrm{I}} \simeq 10^{-2}$, which in turn is, on the scale of this plot, identical to $c_{\mathrm{I}} = 0$.

Of course, Eq. (43) is also easily solved for $T_c(\rho)$, with the results shown in Fig. 3. As an important feature, we note the weak dependence on ρ for† $\rho < 0.1$, which is due to the dependence of y_m on the thickness, followed by a close to linear decrease. We have confirmed that these results are independent of small changes of the numerical factors in $y_c \simeq \rho/8\pi$ and

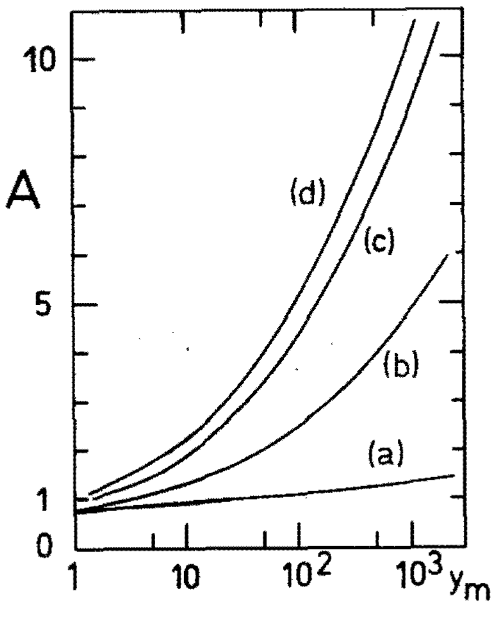

Fig. 2. The quantity A [see Eq. (43)] vs. y_m for (a) $c_{\mathrm{I}} = \infty$, (b) $c_{\mathrm{I}} = 1$, (c) $c_{\mathrm{I}} = 10^{-1}$, (d) $c_{\mathrm{I}} = 10^{-2}$; curve (d) is practically identical to the one for the Coulomb interaction.

*Note that the $q \to 0$ singularity (for the case of the Coulomb interaction), which seemed to lead to unphysical results in Ref. 14, is not present in the consistent treatment of phase and potential fluctuations [as given by Eqs. (28) and (29)].

†Of course, the sharp wave-vector cutoff may become unreliable for too small ρ, say, $\rho \lesssim 0.03$.

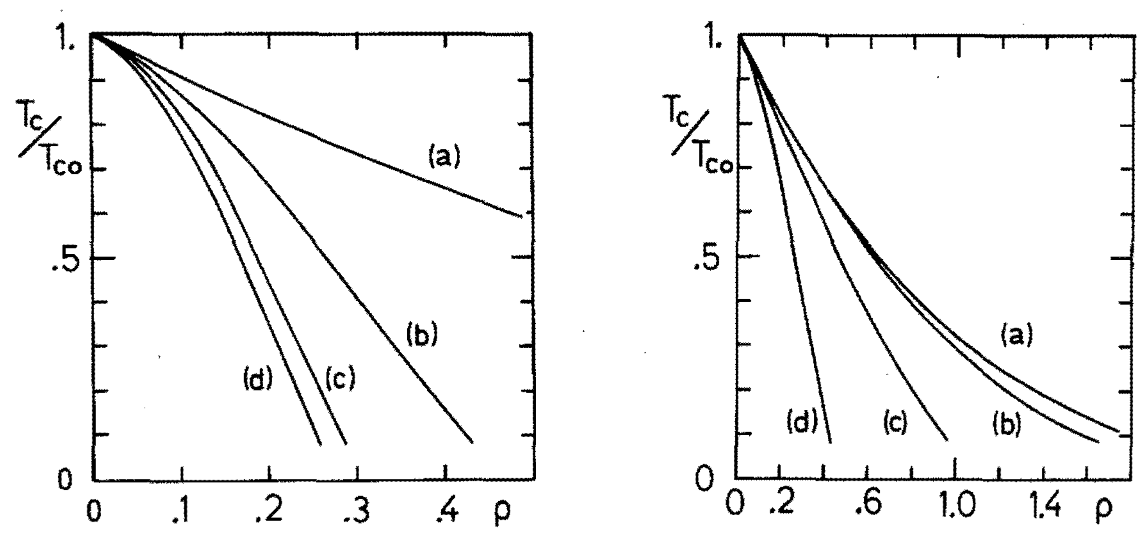

Fig. 3. (A) The critical temperature T_c relative to the bulk value T_{c0} vs. $\rho = R_\square/R_0$ for the same parameters as in Fig. 2. (B) T_c/T_{c0} vs. ρ for (a) $c_I=\infty$, (b) $c_I=10^2$, (c) $c_I=10$, (d) $c_I=1$. Note the difference in scale compared to (A).

in $c_{II} \simeq 4\times 10^{-3}(yT_c/T_{c0})^{1/2}$. On the other hand, writing $y_m = \gamma\times 10^3\rho^2 T_{c0}/T_c$, we find for strong interactions ($c_I = 10^{-2}$, Coulomb) a kind of scaling relation:

$$T_c(\rho, \gamma) \simeq T_c(\gamma^{0.2}\rho, 1) \tag{44}$$

which we have confirmed in the range $0.25 < \gamma < 2$. Note that in Figs. 2 and 3, we have chosen $\gamma = 1$.

4. THE ORDER PARAMETER ($T = 0$)

Clearly, it is straightforward to apply the present formalism at zero temperature to calculate the suppression of the order parameter Δ of a thin film. The frequency summation is replaced by an integration in the usual way, and the equation analogous to (38) is found to be given by

$$\ln\left(\frac{\Delta}{\Delta_0}\right) = -[N(0)d]^{-1}\left(\frac{\partial}{\partial\Delta^2}\, T\mathscr{A}^{-1}\tilde{\Gamma}_{\mathrm{fl}}\right)_{T\to 0} \tag{45}$$

Here, Δ_0 is the order parameter of the corresponding bulk system, and $\tilde{\Gamma}_{\mathrm{fl}}$ denotes again the fluctuation correction to the potential relative to its bulk value. Similar to the discussion in connection with Eq. (39), the present scheme has to be extended (at least partly) into a self-consistent one, which for $T = 0$ is equivalent to

$$\chi^{T,L}_{\Delta\Delta} \to \chi^{T,L}_{\Delta\Delta} - \delta\mathscr{C} \tag{46}$$

after differentiation with respect to Δ in (45), where the constant $\delta\mathscr{C}$ has to be chosen such that $\chi^{T}_{\Delta\Delta}(\omega_0 = q = 0) - \lambda^{-1} - \delta\mathscr{C} = 0$. Taking (46) into account, we have

$$\chi^{T,L}_{\Delta\Delta} - \lambda^{-1} \to J^{T,L} \quad . \tag{47}$$

where $J^{T,L}$ is defined in Appendix D. This procedure is also motivated by considering the spectrum of phase fluctuations (see below).

As a technical remark, we introduce dimensionless variables $x = \omega_0/2\Delta$, $y = Dq^2/2\Delta$; then the y cutoff is given by $y^*_m = Dq^2_m/2\Delta$, such that $y^*_m(\Delta_0) = 1.78 y_m(T_{c0})$, where the BCS relation $\Delta_0 = 1.76 T_{c0}$ was inserted. We thus have, for the same parameters as above, $y^*_m \simeq (1.78 \times 10^3)\rho^2 \Delta_0/\Delta$ and $c_{\mathrm{II}} \simeq 3 \times 10^{-3} \rho(\Delta \cdot y/\Delta_0)^{1/2}$. Of course, at zero temperatures, a long-wavelength cutoff is not necessary.

4.1. The Phase Mode

As an illustration, we consider briefly the collective mode connected to fluctuations of the phase and the potential, in the limit of small frequencies and long wavelengths. Defining the quantity (see Appendix E)

$$\mathscr{K} = (\lambda^{-1} - \chi^{T}_{\Delta\Delta})(V^{-1} - \chi_{\phi\phi})/2e^2 N(0) + \chi_{\Delta\phi}\chi_{\phi\Delta} \tag{48}$$

we find for $x, y \ll 1$

$$\mathscr{K} \simeq (\pi y/2 + x^2)\{1 + [2e^2 N(0) V]^{-1}\} - x^2 \tag{49}$$

After analytic continuation, i.e., defining $\mathscr{K}^R = \mathscr{K}(\omega_0 \to -i\omega + 0)$, the collective mode is determined by $\mathscr{K}^R = 0$, with the following result:

$$\omega^2 = \pi \Delta D q^2 (1 + c_\eta)/c_\eta \tag{50}$$

with $\eta = \mathrm{I}, \mathrm{II}$ for the short-range and the Coulomb interaction, respectively [see (41) and (42)]. Note that, from $\pi\Delta D = \pi\Delta\tau v_F^2/3$, the standard fourth sound velocity is identified, namely $c_4^2 = \pi\Delta D = (n_s/n)v_F^2/3$, where n_s denotes the (dirty limit) superfluid density. Clearly, for the short-range interaction (case I), c_{I}^{-1} corresponds to the Landau parameter F_0 of Fermi liquid theory. Finally, for the Coulomb interaction (case II) we have $c_{\mathrm{II}} = 2\lambda^2_{TF} q/d$ such that $\omega \sim q^{1/2}$, the usual result for two dimensions. (The case of a very thin wire is discussed in Ref. 29.) Clearly, for three dimensions (or $q \gg d^{-1}$), the frequency of the mode is shifted to the plasma frequency.

4.2. Results

In analogy to (43), we rewrite (45) into the following form:

$$\ln(\Delta_0/\Delta) = \rho B \tag{51}$$

Considering first case I, it is clear that B is a function of the cutoff y_m^* only. The results of a numerical evaluation, which is more lengthy than the previous one, since the response functions have to be calculated numerically, are given in Fig. 4. For easy comparison with Fig. 2, we put $y_m^* = 1.78y_m$. The general behavior in both figures is quite similar, though there are differences in detail, which are related to the stronger influence of long-wavelength phase and potential fluctuations at zero temperatures. In particular, from the results of Section 4.1, it becomes apparent that $B \sim -\ln c_{\mathrm{I}}$ in the limit $c_{\mathrm{I}} \to 0$. Consequently, B is larger than A for small y_m^* if c_{I} is small (strong interaction). Furthermore, we find that, for the relevant range of y_m, an excellent fit can be given for B with a second-order polynomial in $\ln y_m^*$, reflecting the fact that the increase is weaker as compared to that of A for large y_m. Finally, note that for $c_{\mathrm{I}} = \infty$ [curve (a)], B is about a factor two smaller than the corresponding A, though A does somewhat depend on the special choice in Fig. 2 (namely $\rho = 0.1$ in the classical contribution). The numerical error in Fig. 4 may be up to a few percent.

For case II (Coulomb interaction), we write c_{II} in the following form:

$$c_{\mathrm{II}} = 3 \times 10^{-3} \gamma^* y^{1/2} \tag{52}$$

where $\gamma^* = \rho(\Delta/\Delta_0)^{1/2}$. Thus, considering $B = B(y_m^*, \gamma^*)$, it is clear from the above discussion that $B \sim -\ln \gamma^*$ for $\gamma^* \to 0$. It turns out, however, that for most values of ρ and Δ to be considered, a typical value is $\gamma^* \sim 0.1$; $B(y_m^*, 0.1)$ is also shown in Fig. 4 (dashed line).

The features discussed are clearly reflected in the final result, shown in Fig. 5, namely Δ/Δ_0 vs. ρ. Similar to $T_c(\rho)$, the dependence on ρ for small ρ is weaker than linear, followed by a linear decrease, and then a

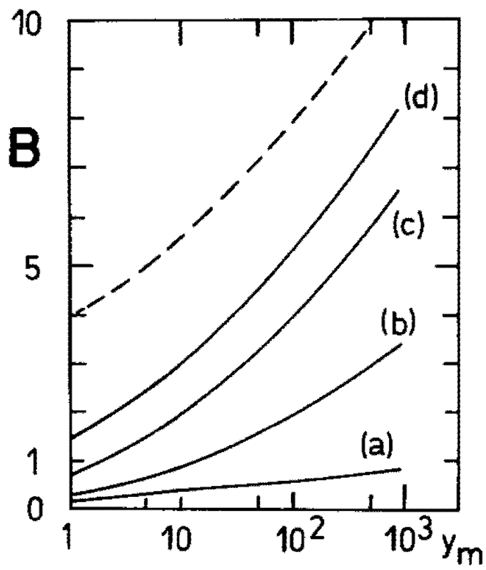

Fig. 4. The quantity B [see Eq. (51)] vs. y_m ($y_m^* = 1.78y_m$) for the same parameters as in Fig. 2, and for the Coulomb interaction (dashed line; see text).

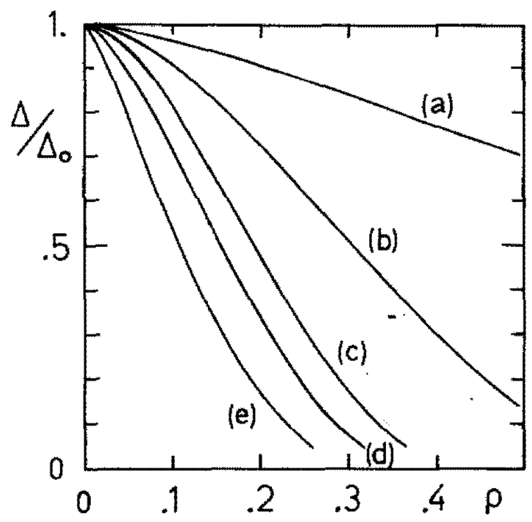

Fig. 5. The zero-temperature order parameter Δ relative to the bulk value Δ_0 vs. ρ for the same parameters as in Fig. 2 (a–d), and for the Coulomb interaction (e).

regime of decreasing magnitude of the slope. While the small-ρ behavior reflects again the thickness dependence of the cutoff, the behavior for $\Delta \leq 0.3\Delta_0$ is related to the weaker dependence on y_m^* for large y_m^* compared to the calculation of T_c, where the linear decrease persisted. Note also that there is a clear difference between $c_I = 10^{-2}$ and the Coulomb interaction, which reflects the increasing importance of long-wavelength fluctuations, as discussed above. Comparing Δ/Δ_0 with T_c/T_{c0}, we find that for the Coulomb interaction, Δ/Δ_0 is more strongly suppressed with decreasing film thickness (increasing ρ) than T_c/T_{c0}, by about a factor two for $\rho \sim 0.2$.

5. DISCUSSION AND CONCLUSION

In this paper, we have used the path integral formulation of the microscopic theory of superconductors to derive the fluctuation corrections (one-loop approximation) to the free energy functional. Based on the standard dirty limit expressions for the response functions, we thus have been able to determine the leading corrections to the gap equation. In particular, we applied these results to calculate the decrease of the critical temperature, and the (zero temperature) order parameter, of a very thin film ($d < \xi_0$). We emphasize again that we have determined T_c (and Δ) of a film relative to its bulk value T_{c0} (and Δ_0), and *not* the dependence of the critical temperature (and the order parameter) on the mean free path (for example). The latter question is, in general, the more difficult one (see, e.g., Ref. 30).

As a consequence of calculating difference quantities as described, the large-wave-vector cutoff is given by the inverse film thickness, leading to a weaker than linear decrease of T_c and Δ vs. $R_\square \sim d^{-1}$ for $R_\square \ll R_0 = h/4e^2$.

Quite generally, we find the decrease of T_c and Δ to be roughly of the same order, and superconductivity is found to be strongly suppressed (for fixed d) by increasing the strength of the (repulsive) interaction. For the physically relevant case of the Coulomb interaction, we find that long-wavelength phase fluctuations play an important role at zero temperature, such that Δ/Δ_0 is smaller by up to a factor two than T_c/T_{c0} for the same thickness. The results have been summarized in Figs. 3 and 5.

In applying the present theory in the regime $T_c \ll T_{c0}$, $\Delta \ll \Delta_0$, it turned out to be important that, for the relevant range of parameters, the dependence of $\tilde{A}$ [see (43)] and B [see (45)] on the cutoff is actually weaker than the asymptotic behavior, Eq. (2). In particular, the flattening off of Δ is directly related to the fact that B is proportional to $\ln^2(y_m^*)$ only. Note that a similar behavior was found by Finkel'stein[13] in his calculation of T_c by including higher order corrections via a renormalization group calculation. It is not clear how these corrections can be included in our formulation.

Returning to another question alluded to in the introduction, we note that Ovchinnikov[9] actually found an *increase* in the critical temperature due to potential fluctuations; in magnitude, however, his expression is equal to the one given by Eq. (2). This result, which we believe is not the correct one, becomes understandable when working consistently with the path integral formalism as described in Section 2. In fact, there is a subtle difference between the auxiliary field ϕ introduced to decouple the electron-electron interaction and the electric potential $\tilde{\phi} = i\phi$ ($\tilde{\phi}$ is also introduced in Appendix B). Working consistently with the auxiliary field, and taking into account the results for the correlation functions given in Appendix E, we have explicitly (for $\Delta \to 0$) worked out the correction to the gap equation by calculating the second-order correction to the off-diagonal Green's function. The result, which is identical to the one following from Eq. (38), differs by a minus sign from the one in Ref. 9 [Eq. (7)] in the terms proportional to the ϕ-Δ and the ϕ-ϕ correlator.

While different theoretical questions could be settled, comparison with experiment[5-7] is less satisfactory in detail. In particular, the experiments seem to indicate a very sharp initial drop of T_c vs. $R_\Box$, which we cannot confirm; however, it may be problematic to identify the measured T_c^{Bulk} with T_{c0}. Furthermore, the experiment[7] also shows that T_c approaches a constant for $R_\Box \sim 0.5 R_0$; for this value, however, the limit of one atomic layer is approached, for which the present theory certainly is problematic. In addition, while Δ/T_c is roughly constant experimentally,[7] we find that Δ is suppressed more strongly than T_c; it is just a speculation that strong coupling corrections may be of importance for the lead films investigated.[7]

Finally, we emphasize again that in the present formulation of the theory, we restricted ourselves to the BCS limit, i.e., we did not take into account the energy dependence of the self-energy, thereby ignoring, e.g., the linewidth in the density of states. This is partly motivated by the experimental result[7] that the density of states remains sharp although T_c and Δ are strongly suppressed, but also by an investigation of a phenomenological model based on the idea of pair-breaking due to fluctuations of the supercurrent.[31] This model, which gives corrections to the gap equation similar to those due to paramagnetic impurities, but extending over a frequency range of the order of the gap, leads to the conclusion (at $T=0$) that the reduction of the order parameter is much larger than the smearing of the density of states (see, however, Ref. 32). This result also becomes clear by comparison with the effect of paramagnetic impurities (local in frequency), where the decrease of the order parameter and the "smearing" are of the same order. However, from this model, we have not been able to determine the decrease of Δ quantitatively. On the other hand, it should be noted that pair-breaking due to current fluctuations apparently gives a good explanation for experimental results concerning the linewidth of thick films.[31] This, we believe, is also an interesting aspect, which we leave for future investigation.

APPENDIX A. THE LARGE-WAVE-VECTOR CUTOFF

An important concept in evaluating the sum over wave vectors in restricted geometries is the calculation of difference quantities. To be specific, consider a film of thickness d, and let the parallel dimensions be sufficiently large to allow for the usual replacement of the sum by an integral. Thus, one encounters expressions like

$$K(d)=\frac{1}{d}\sum_{q_z}\int\frac{d^2q}{(2\pi)^2}\,h(q^2+q_z^2) \tag{A1}$$

where $q^2=q_x^2+q_y^2$ and $q_z=2\pi n/d$, $n=0,\pm 1,\ldots$. The interesting quantity is the difference $\Delta K=K(d)-K(\infty)$, i.e., the value of K relative to the bulk value. Applying a standard formula, we note that

$$\kappa(d)\equiv\frac{1}{d}\sum_{q_z}h(q^2+q_z^2)=\int_C\frac{dz}{4\pi i}\coth\left(\frac{dz}{2}\right)h(q^2-z^2) \tag{A2}$$

where C is a contour enclosing the poles of $\coth(dz/2)$. Considering a simple example, namely $h=(q^2+q_z^2)^{-1}$, we immediately find $\Delta\kappa=\kappa(d)-\kappa(\infty)$ to be given by

$$\Delta\kappa=\frac{1}{2q}\left[\coth\left(\frac{qd}{2}\right)-1\right] \tag{A3}$$

i.e., $\Delta\kappa \simeq (dq^2)^{-1}$ for $qd \ll 1$, equal to the $q_z = 0$ contribution of (A2), while $\Delta\kappa$ is exponentially small for $qd \gg 1$, $\Delta\kappa \simeq q^{-1}\exp(-qd)$. This leads to the prescription

$$\Delta K \simeq \frac{1}{d}\int_{q^2<q_m^2} \frac{d^2q}{(2\pi)^2} h(q^2) \tag{A4}$$

where the cutoff is given by $q_m \simeq d^{-1}$. Of course, we have in mind situations where $d \ll \xi_0$, where $\xi_0 \simeq (v_F l/T_c)^{1/2}$ is the coherence length. An inspection of the results of the main text, in fact, shows that the above example, for $q\xi_0 \gg 1$, is quite representative, though we actually encounter expressions of the form $h \sim \ln^2(q^2+q_z^2)/(q^2+q_z^2)$. Nevertheless, it is easily seen by an appropriate deformation of the contour that the difference $\Delta\kappa$ is again exponentially small for $q > d^{-1}$, justifying the assertion made above.

APPENDIX B. LINEAR RESPONSE OF A DIRTY SUPERCONDUCTOR

A detailed investigation of the linear response of a superconductor, starting directly from Gorkov's equations, has been given by Schön[25] in his study of the propagating collective mode. Here we briefly summarize (and slightly extend) his results, and indicate their derivation in the dirty limit.

In the dirty limit, $T_c\tau \ll 1$, it is most convenient to consider the equation of motion for the quasiclassical Green's function

$$\hat{g}(\omega, \omega'; \mathbf{r}) = \frac{i}{\pi N(0)}\int \frac{d^3p}{(2\pi)^3}\hat{G}(\omega, \omega'; \mathbf{p}, \mathbf{r}) \tag{B1}$$

which has the following form:[24-27]

$$\{[\omega\hat{\tau}_3 + i\hat{U} + \hat{\Delta}, \hat{g}]\}_{\omega\omega'} = D\{[\nabla, \hat{g}[\nabla, \hat{g}]]\}_{\omega\omega'} \tag{B2}$$

Here, $D = v_F^2\tau/3$ is the diffusion constant, $\hat{U} = e\tilde{\phi}\hat{1}$, $\tilde{\phi}$ is the electric potential, ω and ω' are Matsubara frequencies, and we use the shorthand notation

$$\{AB\}_{\omega\omega'} = T\sum_{\omega''} A(\omega, \omega'')B(\omega'', \omega') \tag{B3}$$

Note that the quasiclassical Green's function is normalized according to

$$\{\hat{g}\hat{g}\}_{\omega\omega'} = (1/T)\delta_{\omega\omega'}\hat{1} \tag{B4}$$

and that

$$\hat{\Delta} = \begin{bmatrix} 0 & \Delta \\ \Delta^* & 0 \end{bmatrix} \tag{B5}$$

In a state of equilibrium, taken to be spatially homogeneous, we may choose Δ to be real, and the solution of (B2) is given by

$$\hat{g}^{(e)} = \alpha\hat{\tau}_3 + \beta\hat{\tau}_1, \qquad \alpha^2 + \beta^2 = 1 \tag{B6}$$

where $\alpha = \omega/W$, $\beta = \Delta/W$, $W = (\omega^2 + \Delta^2)^{1/2}$.

We consider now the linear change of the Green's function due to a perturbation of wave vector $\mathbf{q}$ and frequency ω_0. Then $\hat{g} = \hat{g}^{(e)} + \delta\hat{g}$, where $\delta\hat{g} = \delta\hat{g}(\omega, \omega' = \omega - \omega_0)$, and we write

$$\delta\hat{g} = a^T\hat{1} + b^T\hat{\tau}_2 + a^L\hat{\tau}_3 + b^L\hat{\tau}_1 \tag{B7}$$

In addition,

$$\Delta \to \Delta + \delta\Delta^L - i\delta\Delta^T \tag{B8}$$

such that $\delta\Delta^{L,T}$ are real, and connected with magnitude and phase variations of the order parameter. Since the L and the T parts are decoupled, it is straightforward to calculate the various components of $\delta\hat{g}$. For example, there are relations like

$$\frac{a^T}{b^T} = \frac{i\Delta\omega_0}{WW' + \omega\omega' + \Delta^2} \tag{B9}$$

where $W' = (\omega'^2 + \Delta^2)^{1/2}$. Finally, we introduce response functions according to the following relations:

$$\pi T \sum_\omega b^L = \chi^L_{\Delta\Delta}\delta\Delta^L \tag{B10}$$

$$\pi T \sum_\omega b^T = \chi^T_{\Delta\Delta}\delta\Delta^T + \chi_{\Delta\phi} e\tilde{\phi} \tag{B11}$$

$$i\pi T \sum_\omega a^T = \chi_{\Delta\phi}\,\delta\Delta^T - \left[\frac{\chi_{\phi\phi}}{2e^2N(0)} + 1\right] e\tilde{\phi} \tag{B12}$$

Note that the linear change of the charge density is related to a^T by

$$\delta\rho = -2\pi i e N(0) T \sum_\omega a^T - 2e^2N(0)\tilde{\phi} \tag{B13}$$

justifying the square bracket expression in (B12). We obtain the following results:

$$\chi^{T(L)}_{\Delta\Delta} = \pi T \sum_\omega{}' \frac{WW' + \omega\omega' \underset{(-)}{+} \Delta^2}{WW'(W + W' + Dq^2)} \tag{B14}$$

$$\chi_{\Delta\phi} = -\chi_{\phi\Delta} = \pi T \sum_\omega \frac{\Delta\omega_0}{WW'(W + W' + Dq^2)} \tag{B15}$$

$$-\frac{\chi_{\phi\phi}}{2e^2N(0)} = 1 - \pi T \sum_\omega \frac{\Delta^2\omega_0^2}{WW'(W + W' + Dq^2)(WW' + \omega\omega' + \Delta^2)} \tag{B16}$$

Here, $\sum_\omega'$ indicates that the sum has to be restricted to $|\omega_1| < \omega_D$, where ω_D is the Debye frequency. In addition, it follows directly that

$$\chi_{\Delta\phi} = \frac{\omega_0}{2\Delta}(\chi_{\Delta\Delta}^T - \chi_{\Delta\Delta}^L) \tag{B17}$$

and after a slightly longer calculation

$$-\frac{\chi_{\phi\phi'}}{2e^2N(0)} = 1 + \tfrac{1}{2}(\chi_{\Delta\Delta}^T - \chi_{\Delta\Delta}^L) - \pi T \sum_\omega \frac{WW' - \omega\omega'}{WW'(W + W' + Dq^2)} \tag{B18}$$

Comparing these results with the more general ones from Gorkov's equations,[25] we find the above results to be valid in the regime $\omega_0\tau < 1$, $q < l^{-1}$, where $l = v_F\tau$ is the mean free path.

APPENDIX C. RESPONSE FUNCTIONS, $T \simeq T_c$

Here we give some specific results close to the critical temperature. Considering first the order parameter response functions, we define

$$\chi_{\Delta\Delta}^{L,T} = \ln\frac{1.13\omega_D}{T} + I^{L,T} \tag{C1}$$

such that

$$I^{T(L)} = \pi T \sum_\omega \left[\frac{WW' + \omega\omega' \genfrac{}{}{0pt}{}{+}{(-)} \Delta^2}{WW'(W + W' + Dq^2)} - \frac{1}{W}\right] \tag{C2}$$

and introduce $m = |\omega_0|/2\pi T$, $y = Dq^2/2\pi T$. Then we find, for $\Delta = 0$,

$$I^L = I^T = \psi(\tfrac{1}{2}) - \psi\left(\frac{1 + m + y}{2}\right) \tag{C3}$$

where ψ is Euler's psi function. In addition, we also encounter the correction to $I^L + I^T$ in order Δ^2, which is calculated to be given by

$$2\pi^2T^2\frac{\partial}{\partial\Delta^2}(I^L + I^T)|_{\Delta=0} = \frac{y}{y^2 - m^2}\left[\psi'\left(\frac{1 + m + y}{2}\right) - \psi'(\tfrac{1}{2} + m)\right] \tag{C4}$$

where ψ' is the derivative of the psi function.

The coupling between order parameter and potential is already linear in Δ. Thus the following expression is sufficient ($m \neq 0$):

$$\chi_{\Delta\phi} = \frac{\Delta \cdot \operatorname{sgn}\omega_0}{\pi T(m^2 - y^2)}\left\{m\left[\psi\left(\frac{1 + m + y}{2}\right) - \psi(\tfrac{1}{2})\right] - y[\psi(\tfrac{1}{2} + m) - \psi(\tfrac{1}{2})]\right\} \tag{C5}$$

Finally, $\chi_{\phi\phi}$ is easily calculated in the normal state, with the standard result

$$\chi_{\phi\phi}|_{\Delta=0} = -2e^2 N(0) \frac{Dq^2}{|\omega_0| + Dq^2} \tag{C6}$$

Furthermore, the contribution $\sim\Delta^2$ is given as follows ($m \neq 0$):

$$\begin{aligned}
-\frac{2\pi^2 T^2}{2e^2 N(0)} \frac{\partial}{\partial\Delta^2} \chi_{\phi\phi}|_{\Delta=0} = &+\frac{y}{2(m^2-y^2)} \psi'(\tfrac{1}{2}+m) \\
&+\frac{1}{2(m+y)^2}\left[\psi\left(\frac{1+m+y}{2}\right) + \psi(\tfrac{1}{2}+m) - 2\psi(\tfrac{1}{2})\right] \\
&+\frac{1}{2(m-y)^2}\left[\psi\left(\frac{1+m+y}{2}\right) - \psi(\tfrac{1}{2}+m)\right] \\
&+\frac{1}{m(m+y)}[\psi(\tfrac{1}{2}+m) - \psi(\tfrac{1}{2})] \\
&+\frac{1}{m^2-y^2}\left[\psi\left(\frac{1+m+y}{2}\right) - \psi(\tfrac{1}{2}+m)\right]
\end{aligned} \tag{C7}$$

APPENDIX D. RESPONSE FUNCTIONS, $T \simeq 0$

In the regime of low temperatures, $T \to 0$, the frequency summation in (B14)-(B16) must be replaced by an integration and, in general, the various functions cannot be calculated analytically. Defining, in this case, the dimensionless variables $x = |\omega_0|/2\Delta$ and $y = Dq^2/2\Delta$, some results are easily derived for small x, y and for $x=0$ and $y=0$, respectively. Again, we consider first the order parameter response functions, and define

$$\chi_{\Delta\Delta}^{L,T} = \ln\frac{2\omega_D}{\Delta} + J^{L,T} \tag{D1}$$

such that

$$J^{T(L)} = \frac{1}{2}\int_{-\infty}^{\infty} d\omega \left[\frac{WW' + \omega\omega' {}^{+}_{(-)}\Delta^2}{WW'(W+W'+Dq^2)} - \frac{1}{W}\right] \tag{D2}$$

Then we find the following results:

$$J^T(x=0, y) = -y \begin{cases} \dfrac{1}{(1-y^2)^{1/2}}\left(\dfrac{\pi}{2} - \arcsin y\right) & \text{for} \quad y \leq 1 \\[2ex] \dfrac{1}{(y^2-1)^{1/2}} \ln[y + (y^2-1)^{1/2}] & \text{for} \quad y \geq 1 \end{cases} \tag{D3}$$

Furthermore, $J^L(0, y)$ is related to J^T as follows:

$$J^L(0, y) = \frac{y^2-1}{y^2} J^T(0, y) - \frac{\pi}{2y} \tag{D4}$$

On the other hand, for $y=0$,

$$J^T(x,0) = -\frac{x}{(1+x^2)^{1/2}} \ln[x+(1+x^2)^{1/2}] \tag{D5}$$

and

$$J^L(x,0) = \frac{1+x^2}{x^2} J^T(x,0) \tag{D6}$$

From these results, it is straightforward to verify that, for small x, y,

$$\begin{aligned} J^T(x,y) &\simeq -\frac{\pi}{2} y - x^2 + \cdots \\ J^L(x,y) &\simeq -1 - \frac{\pi}{4} y - \tfrac{1}{3} x^2 + \cdots \end{aligned} \tag{D7}$$

Note that there is no mixed term $\sim xy$ in J^T, which reflects the absence of dissipation in the phase mode at zero temperatures. On the other hand, for $x, y \gg 1$,

$$\begin{aligned} J^T(0,y) &\simeq -\ln 2y - \frac{1}{2y^2}[\ln 2y - \tfrac{1}{2}] + \cdots \\ J^T(x,0) &\simeq -\ln 2x + \frac{1}{2x^2}[\ln 2x - \tfrac{1}{2}] + \cdots \end{aligned} \tag{D8}$$

while for the longitudinal response

$$\begin{aligned} J^L(0,y) &\simeq -\ln 2y - \frac{\pi}{2y} + \frac{1}{2y^2}(\ln 2y + \tfrac{1}{2}) + \cdots \\ J^L(x,0) &\simeq -\ln 2x - \frac{1}{2x^2}(\ln 2x + \tfrac{1}{2}) + \cdots \end{aligned} \tag{D9}$$

Of course, the leading contributions in the limit of large x, y are in agreement with the corresponding limit of (C3), since the gap is unimportant in this regime.

Finally, from the relation (B17), which is valid for all temperatures, corresponding expressions for $\chi_{\Delta\phi}$ follow. In addition, we note that, for $y=0$,

$$\chi_{\phi\phi}(x,0) = 2e^2 N(0) J^T(x,0)/x^2 \tag{D10}$$

giving, for $x \ll 1$,

$$\chi_{\phi\phi}(x,0) \simeq -2e^2 N(0)[1 - 2x^2/3 + \cdots] \tag{D11}$$

Furthermore, we find the following relation, which is valid for all x, and $y \to 0$:

$$J^T + (\chi_{\Delta\phi})^2 \left[\left(-\frac{\chi_{\phi\phi}}{2e^2 N(0)} \right)^{-1} \right] \simeq -yH(x) \tag{D12}$$

$$H(x) = (1+x^2)^{1/2} E(r) \tag{D13}$$

Here $E(r)$ is the complete elliptic integral, and $r = x/(1+x^2)^{1/2}$. Note that $H(0) = \pi/2$, while $H(x \gg 1) \simeq x$.

APPENDIX E. CORRELATION FUNCTIONS

The correlation functions are related to the response functions in the usual way. For a concise summary of the results, define

$$\mathcal{K} = (\lambda^{-1} - \chi^T_{\Delta\Delta})(V^{-1} - \chi_{\phi\phi})/2e^2N(0) + \chi_{\Delta\phi}\chi_{\phi\Delta} \tag{E1}$$

where it is understood, here and in the following, that all functions depend on wave vector $\mathbf{q}$ and frequency ω_0. Then we have the following results:

$$2N(0)\langle T_\tau(\delta\Delta^L \delta\Delta^L)\rangle = (\lambda^{-1} - \chi^L_{\Delta\Delta})^{-1} \tag{E2}$$

Clearly, the magnitude (longitudinal) fluctuation does not couple to the phase (transverse), $\delta\Delta^T$, and potential, $\delta\phi$, fluctuations. Furthermore, we obtain

$$2N(0)\langle T_\tau(\delta\Delta^T \delta\Delta^T)\rangle = (V^{-1} - \chi_{\phi\phi})/[2e^2N(0)\mathcal{K}] \tag{E3}$$

$$2N(0)\langle T_\tau(\delta\Delta^T e\delta\phi)\rangle = i\chi_{\Delta\phi}/\mathcal{K} \tag{E4}$$

$$2e^2N(0)\langle T_\tau(\delta\phi\delta\phi)\rangle = (\lambda^{-1} - \chi^T_{\Delta\Delta})/\mathcal{K} \tag{E5}$$

Of course, for temperatures above the critical temperature, (E5) reduces to the standard expression, namely

$$\langle T_\tau(\delta\phi\delta\phi)\rangle = (V^{-1} - \chi_{\phi\phi})^{-1} \tag{E6}$$

where

$$\chi_{\phi\phi} = -2e^2N(0)Dq^2/(|\omega_0| + Dq^2) \tag{E7}$$

These results follow directly from the second-order contribution to the effective action, which, for longitudinal fluctuations, is given in Eq. (25); note that we put $\Delta = \bar{\Delta} + \delta\Delta^L - i\delta\Delta^T$, and $\phi = \bar{\phi} + \delta\phi$, in general. Then we find, for the contribution relating to phase and potential fluctuations, the following expression:

$$S^{(2)}_{\text{eff}} = N(0)\int dx\, dx' \begin{pmatrix} \delta\Delta^T \\ e\delta\phi \end{pmatrix}_x W(x, x') \begin{pmatrix} \delta\Delta^T \\ e\delta\phi \end{pmatrix}_{x'} \tag{E8}$$

where

$$W_{11} = \lambda^{-1} - \chi^T_{\Delta\Delta} \tag{E9}$$

$$W_{22} = (V^{-1} - \chi_{\phi\phi})/2e^2N(0) \tag{E10}$$

$$W_{12} = -i\chi_{\Delta\phi} \tag{E11}$$

$$W_{21} = -i\chi_{\phi\Delta} \tag{E12}$$

Clearly, we have $\mathcal{K}(\mathbf{q}, \omega_0) = \det_2 W(\mathbf{q}, \omega_0)$.

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