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<sup>1</sup>C. A. Hamilton and Sidney Shapiro, Phys. Rev. Letters 26, 426 (1971).

<sup>2</sup>E. Riedel, Z. Naturforsch. <u>19a</u>, 1634 (1964).

<sup>3</sup>B. D. Josephson, Phys. Letters 1, 251 (1962); Rev. Mod. Phys. 36, 216 (1964); Advan. Phys. 14, 419 (1965).

<sup>4</sup>S. Shapiro, A. R. Janus, and S. Holly, Rev. Mod. Phys. <u>36</u>, 223 (1964).

<sup>5</sup>C. C. Grimes and Sidney Shapiro, Phys. Rev. 169, 397 (1968).

<sup>6</sup>N. R. Werthamer, Phys. Rev. <u>147</u>, 255 (1966).

<sup>7</sup>M. Abramowitz and I. Stegun, Handbook of Mathematical Functions (Dover, New York, 1965), Eq. 9.1.75.

<sup>8</sup>The result given in Eq. (8) was first derived by

P. K. Tien and J. P. Gordon, Phys. Rev. 129, 647 (1963).

<sup>9</sup>A. H. Dayem and R. J. Martin, Phys. Rev. Letters <u>8</u>, 246 (1962). <sup>10</sup>C. F. Cook and G. E. Everett, Phys. Rev. <u>159</u>,

374 (1967).

<sup>11</sup>S. Teller and B. Kofoed, Solid State Commun. <u>8</u>,

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# 235 (1970).

<sup>12</sup>C. A. Hamilton and Sidney Shapiro, Phys. Rev. B 2, 4494 (1970).

<sup>13</sup>Andrew Longacre, Jr. and Sidney Shapiro, Bull. Am. Phys. Soc. <u>16</u>, 399 (1971).

<sup>14</sup>J. C. Swihart, J. Appl. Phys. <u>32</u>, 461 (1961).

<sup>15</sup>S. A. Buckner, J. T. Chen, and D. N. Langenberg, Phys. Rev. Letters 25, 738 (1970).

<sup>16</sup>J. N. Sweet and  $\overline{G}$ . I. Rochlin, Phys. Rev. B 2, 656 (1970).

<sup>17</sup>We have made an analysis of the spatial-variation problem for the Josephson steps similar to that discussed in Ref. 12 for the quasiparticle steps. This analysis suggests that when the spatial variation becomes significant ( $\Delta \alpha \simeq 3$ ), only the highest steps ( $N \simeq 2\alpha$ ) should be observed. This result is consistent with our experimental data.

<sup>18</sup>D. J. Scalapino and T. M. Wu, Phys. Rev. Letters 17, 315 (1966). <sup>19</sup>D. G. McDonald, V. E. Kose, K. M. Evenson, J. S.

Wells, and J. D. Cupp, Appl. Phys. Letters 15, 121

(1969); D. G. McDonald, K. M. Evenson, J. S. Wells,

and J. D. Cupp, J. Appl. Phys. 42, 179 (1971).

<sup>20</sup>I. Giaever and H. R. Zeller, Phys. Rev. B 1, 4278 (1971).

<sup>21</sup>J. M. Rowell and W. L. Feldman, Phys. Rev. <u>172</u>, 393 (1968).

 $^{22}\mathrm{S.}$  A. Buckner and T. F. Finnegan, Bull. Am. Phys. Soc. <u>16</u>, 399 (1971).

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## Pair Propagator Approach to Fluctuation-Induced Diamagnetism in Superconductors-**Effects of Impurities**

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We have obtained, within the ladder approximation, expressions for the electron pair propagator of a dilute superconducting alloy (i.e., subject to the condition  $\omega_D \tau \gg 1$ ) in the presence of strong magnetic field and above the transition temperature. We then proceed to calculate microscopically the free energy and the magnetization. The procedure used in an earlier work on pure superconductors is justified, but important additional contributions are found for alloys.

#### I. INTRODUCTION

Recently, Gollub, Beasley, and Tinkham<sup>1</sup> (GBT) reported observation of universal behavior in the fluctuation-induced diamagnetism of superconductors above the transition temperature. Owing to the fact that fluctuations of very short wavelength contribute to the diamagnetism, the data deviate markedly from the calculation by Prange<sup>2</sup> which is exact within the framework of the Ginsburg-Landau (GL) theory. Patton, Ambegaokar, and

Wilkins<sup>3</sup> (PAW) have attempted to deal with the problem by introducing an ad hoc cutoff energy Einto the fluctuation spectrum. However, it is found that the parameter E required to fit the experimental data for clean materials is about ten times smaller than expected from physical arguments.<sup>1</sup> In a recent work<sup>4</sup> (hereafter referred to as I) we pointed out that for pure samples in the presence of a strong magnetic field the usual replacement  $\vec{q} \rightarrow \vec{q} + 2e \vec{A}/c$  assumed by previous authors is no longer valid. We calculated the mag-

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netization by constructing a free-energy functional  $f(\Delta)$  which reduced to the GL free-energy functional in the appropriate limit but which led to the linearized Gorkov equation when its variation was set equal to zero. Following Schmid, <sup>5</sup> the partition function was then calculated as a functional integral of  $e^{-\beta f(\Delta)}$ . We were able to evaluate the partition function and hence the magnetization while including nonlocal effects due to the presence of a uniform magnetic field *B* in detail. By including nonlocal effects accurately results were obtained which are in reasonable agreement with experiments on clean superconductors.<sup>1</sup>

In the present work we approach the problem by studying the electron pair propagator. We obtain an explicit expression for the pair propagator in the presence of a strong magnetic field and nonmagnetic impurities and from it we derive microscopically the free energy and the magnetization. We find that in the clean case the physical argument we used to obtain the free energy is justified. whereas in the dirty case important corrections occur. Furthermore, in the clean case the theory predicts universal behavior in the sense that a graph of  $-M/B^{1/2}TV$  vs lnb is the same for different materials with the same  $T/T_{c0}$  value ( $T_{c0}$  is the transition temperature,  $b = \alpha_0^2 e B/\hbar c$ , and  $\alpha_0$  $= \hbar v_F / 4\pi kT$ ). We find that universal behavior is only approximate for alloys with different degrees of dirtiness.

After the writing of I, several other preprints on fluctuation-induced diamagnetism have appeared.<sup>6-8</sup> A recent phenomenological theory by Nam<sup>6</sup> assumes the existence of bosonlike excitations. His theory is mathematically equivalent to a PAW theory with a field-dependent cutoff energy E(H). As anticipated by GBT he finds that if E(H)is chosen to be  $\alpha H^{1/2}$  and  $\alpha$  is used as an adjustable parameter, he can fit the GBT data for pure superconductors very well. However, his argument for a  $H^{1/2}$  behavior of E is unconvincing to us; particularly in view of the fact that if his arguments were taken seriously it actually predicts a value of  $\alpha$ that has little to do with the  $\alpha$  he uses to fit the data ( $\alpha$  is finally chosen so that his theory goes through the point where  $-M/B^{1/2}TV$  is reduced to one-half the Prange value). Nonlocal effects are not included in Nam's work. More recently, we have received a preprint from Kurkijärvi, Ambegaokar, and Eilenberger.<sup>7</sup> The latter workers have arrived independently at many of the results reported in I and in the present work by using Hubbard's method<sup>9</sup> to express the partition function as a functional integral. A recent work by Maki and Takayama<sup>8</sup> treating the extremely dirty case contradicts the conclusions reached by Kurkijärvi et al. and the present work and will be discussed in Sec. III.

#### **II. PAIR PROPAGATOR**

We would like to study the propagator of an electron pair under the influence of an interaction Hamiltonian<sup>10</sup>

$$\hat{H}_{1} = -\lambda \int \Phi^{\dagger}(\vec{\mathbf{r}}) \Phi(\vec{\mathbf{r}}) d^{3}r \quad , \qquad (2.1)$$

where  $\Phi(\vec{\mathbf{r}}) = \psi_1(\vec{\mathbf{r}})\psi_1(\vec{\mathbf{r}})$ ,  $\psi_1(\vec{\mathbf{r}})$  being the electron destruction operator and  $\lambda$  the coupling constant times the volume V. It is understood that the interaction is not truly  $\delta$ -function-like, but that in momentum space, only electrons within  $\hbar\omega_D$  of the Fermi surface participate in the interaction. We will also include the effect of nonmagnetic impurities and a strong magnetic field by taking

$$\hat{H}_{0} = \int d^{3} \boldsymbol{\gamma} \sum_{\sigma} \psi^{\dagger}_{\sigma}(\vec{\mathbf{r}}) \left( \frac{(\vec{\mathbf{p}} + e\vec{\mathbf{A}}/c)^{2}}{2m} + \sum_{i} u_{i}(\vec{\mathbf{r}}) \right) \psi_{\sigma}(\vec{\mathbf{r}}),$$
(2.2)

where  $u_i(\mathbf{r})$  is a short-range potential due to the *i*th impurity. The pair propagator for a particular impurity configuration is defined as

$$D(1, 2) = \langle T(\Phi(1) \Phi^{\dagger}(2)) \rangle, \qquad (2.3)$$

where

$$\Phi(1) = e^{(\hat{H}_0 + \hat{H}_1 - \mu \hat{N})\tau_1} \Phi(\tilde{\mathbf{r}}) e^{-(\hat{H}_0 + \hat{H}_1 - \mu \hat{N})\tau_1}$$

By summing the ladder diagrams<sup>11</sup> we obtain an approximate D(1, 2) satisfying the Dyson equation:

$$D(1, 2) = G_0(1, 2)G_0(1, 2) + \lambda \int_0^\beta d\tau_3 \int d^3r_3 D(1, 3)G_0(3, 2)G_0(3, 2) ,$$
(2.4)

where  $G_0(1, 2) = \langle T(\psi_1^T(1)\psi_1^{\dagger\dagger}(2)) \rangle_0$  is the Green's function for a single electron moving under the influence of  $\hat{H}_0$ . Performing an impurity average<sup>11,12</sup> on Eq. (2.4), we obtain an approximate equation for  $\overline{D}(1, 2)$ , where the bar indicates the average over impurity configurations,

$$\overline{D}(\mathbf{1},\mathbf{2}) = \overline{Q}(\mathbf{1},\mathbf{2}) + \lambda \int d(\mathbf{3}) \overline{D}(\mathbf{1},\mathbf{3}) \overline{Q}(\mathbf{3},\mathbf{2}) , \qquad (\mathbf{2},\mathbf{5})$$

where

$$\overline{Q}(1,2) = \langle G_0(1,2) G_0(1,2) \rangle_{av} .$$
(2.6)

 $\overline{D}$  and  $G_0$  depend only on time differences and satisfy well-known boundary conditions.<sup>13</sup> We then introduce Fourier series for  $\overline{D}$  and  $G_0$ ,

$$\overline{D}(1,2) = (1/\beta) \overline{\sum}_{m} e^{-i\nu_{m} (\mathbf{r}_{1}-\mathbf{r}_{2})} D(\mathbf{\tilde{r}}_{1},\mathbf{\tilde{r}}_{2};\nu_{m}),$$

$$\nu_{m} = 2\pi k T m \quad (2.7)$$

and

$$G_{0}(1,2) = (1/\beta) \sum_{s} e^{-i\omega_{s} (r_{1} - r_{2})} G_{0}(\vec{r}_{1}, \vec{r}_{2}; \omega_{s})$$
$$\omega_{s} = 2\pi k T(s + \frac{1}{2}) . \quad (2.8)$$

The Fourier coefficients satisfy the equation

$$D(\mathbf{\vec{r}}_1, \mathbf{\vec{r}}_2, \nu_m) = Q_m(\mathbf{\vec{r}}_1, \mathbf{\vec{r}}_2)$$
$$+ \lambda \int d^3 r_3 D(\mathbf{\vec{r}}_1, \mathbf{\vec{r}}_3, \nu_m) Q_m(\mathbf{\vec{r}}_3, \mathbf{\vec{r}}_2)$$

where

$$Q_m(\mathbf{r}_1,\mathbf{r}_2) = \sum_s Q_m^s(\mathbf{r}_1,\mathbf{r}_2)$$

and

$$Q_m^s(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) = (1/\beta) \langle G_0(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2; -\omega_s) G_0(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2; \omega_s + \nu_m) \rangle_{av}.$$

(2.10)

(2.9)

In general, Eq. (2.9) can be solved once the eigenvalues and eigenfunctions of the integral operator with kernel  $Q_m(\vec{r}_1,\vec{r}_2)$  are found. To solve this eigenvalue problem we note that if we include only s-wave scattering,<sup>12</sup>

$$Q_{m}^{s}(\vec{\mathbf{r}}_{1},\vec{\mathbf{r}}_{2}) = \tilde{Q}_{m}^{s}(\vec{\mathbf{r}}_{1},\vec{\mathbf{r}}_{2}) + [\hbar/2\pi\tau N(0)] \\ \times \int d^{3}r_{3} \tilde{Q}_{m}^{s}(\vec{\mathbf{r}}_{1},\vec{\mathbf{r}}_{3}) Q_{m}^{s}(\vec{\mathbf{r}}_{3},\vec{\mathbf{r}}_{2}) ,$$
(2.11)

where  $\tau = l/v_F$  (*l* is the mean free path), N(0) is the density of states at the Fermi surface, and

$$\tilde{Q}_{m}^{s}(\vec{\mathbf{r}}_{1},\vec{\mathbf{r}}_{2}) = \overline{G}_{0}(\vec{\mathbf{r}}_{1},\vec{\mathbf{r}}_{2}; -\omega_{s})\overline{G}_{0}(\vec{\mathbf{r}}_{1},\vec{\mathbf{r}}_{2}; \omega_{s}+\nu_{m}).$$
(2.12)

Our task is now reduced to solving the eigenvalue problem

$$\int \tilde{Q}_{m}^{s}(\vec{r}_{1},\vec{r}_{2})\psi_{m,\eta}^{s}(\vec{r}_{1}) d^{3}r_{1} = \tilde{P}_{m}^{s}(\eta)\psi_{m,\eta}^{s}(\vec{r}_{2}) , \quad (2.13)$$

where  $\eta$  indexes the eigenvalues and eigenfunctions. In I we solved a special case of Eq. (2.13) where we treated only clean superconductors and considered only the m = 0 case. It turns out that the same technique can be used to solve the more general Eq. (2.13). The details are given in the Appendix. The eigenvectors are simply the Landau states  $\phi_{n,k,q}(\mathbf{\dot{r}})$  for a doubly charged particle moving in a uniform magnetic field and are independent of s and m,

$$\psi_{m,\eta}^{s} = \phi_{n,k,q}(\mathbf{\dot{r}}) = \langle \mathbf{\dot{r}} | n, k, q \rangle , \qquad (2.14)$$

and the eigenvalue is given by

$$P_{m}^{s}(\eta) = P_{m}^{s}(n, k)$$

$$= \frac{N(0)}{2} \frac{(-1)^{n}}{2} \int dx \, e^{-x^{2}} L_{n}(x)$$

$$\times \frac{\tan^{-1}[\alpha_{0}(k^{2} + b'x)^{1/2}/(s + \frac{1}{2} + \frac{1}{2}|m| + \rho)]}{\alpha_{0}(k^{2} + b'x)^{1/2}},$$
(2.15)

where  $L_n$  is the Laguerre polynomial,  $b' = eB/\hbar c$ ,  $\alpha_0 = \hbar v_F/4\pi kT$ , and  $\rho = \alpha_0/l$ . Equation (2.15) is valid subject to the condition  $\omega_D \tau \gg 1$  and the understanding that a cutoff is required in any sum over *s* involving  $P_m^s(n, k)$ . We shall return to this point in Sec. IV. We can now solve Eq. (2.11) in terms of  $\phi_{n,k,q}$  and  $P_m^s$ . Furthermore, since  $\phi_{n,k,q}$  is independent of s we obtain the following expression for  $Q_m(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2)$ :

$$Q_{m}(\mathbf{\dot{r}}_{1}, \mathbf{\dot{r}}_{2}) = \sum_{n,k,q} \Pi_{m}(n,k) \phi_{n,k,q}^{*}(\mathbf{\dot{r}}_{1}) \phi_{n,k,q}(\mathbf{\dot{r}}_{2}),$$
(2.16)

where

$$\Pi_{m}(n,k) = \sum_{s} P_{m}^{s}(n,k) / \left( 1 - \frac{\hbar}{2\pi\tau N(0)} P_{m}^{s}(n,k) \right) .$$
(2.17)

The pair propagator can now be written as

$$D(\vec{\mathbf{r}}_{1}, \vec{\mathbf{r}}_{2}, \nu_{m}) = \sum_{n, k, q} \frac{\prod_{m}(n, k) \phi_{n, k, q}^{*}(\vec{\mathbf{r}}_{1}) \phi_{n, k, q}(\vec{\mathbf{r}}_{2})}{1 - \lambda \prod_{m}(n, k)}$$
(2.18)

For m = n = k = 0,  $1 - \lambda \Pi_0(0, 0) = 0$  determines the temperature at which a pole first occurs in the pair propagator. This of course determines  $T_{c2}(H)$  and we recover the results of Helfand and Werthamer.<sup>14</sup> It is useful to write

$$g_{n,k}(\nu_m) \equiv 1 - \lambda \Pi_m(n,k) \tag{2.19}$$

in terms of the zero-field transition temperature  $T_{c0}$  given by

$$N(0) \lambda \ln\left(\frac{T}{T_{c0}}\right) = 1 - 2N(0) \lambda \sum_{s=0}^{\Lambda} \frac{1}{2s+1} , \qquad (2.20)$$

where  $\Lambda = \hbar \omega_D / 2\pi k T$  is the usual BCS cutoff. After some algebra, we obtain

$$g_{n,k}(\nu_{m}) = N(0) \\ \times \lambda \left[ \ln \left( \frac{T}{T_{c0}} \right) + \sum_{s=0}^{\Lambda_{m}} \frac{(s + \frac{1}{2} + \rho) h_{s,m}(n,k) + \frac{1}{2} |m|}{(s + \frac{1}{2}) \left[ s + \frac{1}{2} + \frac{1}{2} |m| + \rho h_{s,m}(n,k) \right]} \right],$$

$$(2.21)$$

where

 $h_{s,m}(n,k) = \frac{1}{2}(-1)^n \int_0^\infty dx \, e^{-x^2} L_n(x) \left[ 1 - (\tan^{-1} v) / v \right]$ 

and

$$v = \alpha_0 (k^2 + b'x)^{1/2} / (s + \frac{1}{2} + \frac{1}{2} |m| + \rho).$$

The cutoff  $\Lambda_m = \hbar \omega_D / 2\pi kT - \frac{1}{2}|m|$  is discussed in the Appendix. The quantity  $g_{n,k}(\nu_m)$  is of special importance because the contribution to the free energy due to  $\hat{H}_1$  can be expressed in terms of it. The latter property of  $g_{n,k}(\nu_m)$  will be discussed in detail in Sec. III.

It is worthwhile to point out two limiting forms of Eq. (2.21). In both cases we assume that  $\Lambda_m$  is large enough or that  $\rho$ , n, and k are small enough so that we can let  $\Lambda_m$  be infinite.

(a.) Clean limit and m = 0. In this case  $\rho = 0$  and Eq. (2.20) becomes

$$g_{n,k}(0) = N(0) \lambda \{ \ln (T/T_{c0}) + \frac{1}{2} (-1)^n \}$$

$$\times \int_0^\infty e^{-x^2} L_n(x) K \left[ (k^2 + b'x)^{1/2} \right] dx \}, \qquad (2.22)$$

where

$$K(y) = \sum_{s=0}^{\infty} \frac{1}{s+\frac{1}{2}} - \frac{\tan^{-1}(\alpha_0 y / (s+\frac{1}{2}))}{\alpha_0 y}$$

The latter form of  $g_{n,k}(0)$  was used in I where fluctuation diamagnetism was calculated for pure superconductors with  $T > T_{c2}(H)$ .

(b.) Dirty limit. In this case  $\rho$  is so large that for all relevant k and n,  $v \ll 1$  for the contributing x values and we can approximate

$$\begin{split} h_{s,m}(n,k) &\to \frac{1}{2}(-1)^n \int_0^\infty dx \, e^{-x^2} L_n(x) v^2 / 3 \\ &= \frac{1}{3} \, \alpha_0^2 \left[ k^2 + 4b' (n + \frac{1}{2}) \right] / \left( s + \frac{1}{2} + \frac{1}{2} \right| m \left| + \rho \right|^2 \,. \end{split}$$

Thus the nonlocal electrodynamics effect discussed in I is not important for very dirty materials. For large  $\rho$  the sum in Eq. (2.21) converges before  $s + \frac{1}{2}|m|$  becomes comparable with  $\rho$ , and we obtain

 $g_{n,k}(\nu_m) \approx N(0) \lambda \left[ \ln\left(\frac{T}{T_{c0}}\right) + \sum_{s=0}^{\infty} \frac{q^2/3\rho + \frac{1}{2} |m|}{(s + \frac{1}{2})(s + \frac{1}{2} + \frac{1}{2} |m| + q^2/3\rho)} \right]$  $= N(0) \lambda \left[ \ln\left(\frac{T}{T_{c0}}\right) + \psi\left(\frac{1}{2} + \frac{1}{2} |m| + \frac{q^2}{3\rho}\right) - \psi\left(\frac{1}{2}\right) \right], \quad (2.24)$ 

where  $q^2 = \alpha_0^2 [k^2 + b'(4n + 2)]$  and  $\psi$  is the digamma function. The latter limiting form has been used extensively by de Gennes<sup>15</sup> and co-workers, as well as by Maki.<sup>16</sup> For most materials the use of an effective Hamiltonian with a BCS cutoff in the presence of impurities becomes incorrect long before  $\rho$ becomes large enough for this derivation to hold. In particular Anderson's arguments<sup>17</sup> indicate that one must have  $\hbar/\tau \ll \hbar\omega_p$  if one is to obtain correct results from a theory based on the Hamiltonian used here. In terms of  $\rho$  the condition becomes  $\rho \ll \hbar \omega_{\rm D}/$  $4\pi kT = \Theta_D/4\pi T$ . For most superconductors this condition limits  $\rho$  to be less than 10 and this is not sufficiently large for the dirty limit to be reached. Even though the present derivation of the dirty limit of  $g_{n,k}(\nu_m)$  fails unless  $\Theta_D/4\pi T_c \gtrsim 30$  the final result may conceivably have a wider range of validity. The reader should look at de Gennes's book<sup>15</sup> for a derivation that proceeds from a different point of view.

It is well known<sup>11</sup> that the pole of  $D(\mathbf{r}, \mathbf{r}', \tau)$  that appears at  $T = T_{c2}(H)$  is due to the Cooper instability which signals the onset of superconductivity. Thus we expect that a propagator calculated in the ladder approximation does contain the pair correlations which should dominate any physical effects due to electron-phonon interaction in the region just above  $T_{c2}(H)$ . For a more general discussion of the use of similar approximations to describe fluctuations in the region just above phase transitions the reader should consult Brout's lectures.<sup>18</sup> The propagator derived here may have wider applications, but in the present work we will concentrate on fluctuation-induced diamagnetism.

## III. CONTRIBUTION TO FREE ENERGY BY PAIR FLUCTUATIONS

We consider the grand potential

$$\Omega(\lambda') = -kT \ln \left[ \operatorname{Tr} \left( e^{-\beta(\hat{H}_0 + \hat{H}_1(\lambda') - \mu \hat{N})} \right) \right], \qquad (3.1)$$

where we have replaced  $\lambda$  in  $\hat{H}_1$  by the variable  $\lambda'$ . Then

$$\frac{d\Omega}{d\lambda'} = -\int d^3r \, \langle \Phi^{\dagger}(\vec{\mathbf{r}}) \, \Phi(\vec{\mathbf{r}}) \rangle_{\lambda'} \,, \qquad (3.2)$$

where the average is over the ensemble described by the Hamiltonian with the variable  $\lambda'$ . We can write Eq. (3.2) in terms of the pair propagator  $D_{\lambda'}$ as follows:

$$\frac{d\Omega}{d\lambda'} = -\int d^3r D_{\lambda'}(\mathbf{\dot{r}}, 0; \mathbf{\dot{r}}, \delta)$$
$$= (1/\beta) \sum_m e^{i\nu_m \delta} \int d^3r D_{\lambda'}(\mathbf{\dot{r}}, \mathbf{\dot{r}}; \nu_m), \quad (3.3)$$

where  $\delta = 0_{\star}$ . Within the ladder approximation for  $D_{\lambda'}$  we can use Eq. (2.18) and the fact that  $\phi_{n,k,q}$  are normalized to unity to write Eq. (3.3) as

$$\frac{d\Omega}{d\lambda'} = -\frac{V}{\pi\beta} \left(\frac{eB}{hc}\right) \times \sum_{m} \sum_{n} \int dk \, e^{i\nu_{m}\delta} \, \Pi_{m}(n,k) / [1 - \lambda' \Pi_{m}(n,k)] \,,$$
(3.4)

where we have inserted the degeneracy factor for the Landau states. Equation (3.4) can be integrated with respect to  $\lambda'$  and we obtain the contribution to the free energy due to the pair interaction;

$$\Omega_{\lambda} - \Omega_{0} = \frac{VkT}{\pi} \left(\frac{eB}{hc}\right) \sum_{m} e^{i\nu_{m}\delta} \sum_{n} \int dk \ln[1 - \lambda \Pi_{m}(n, k)] .$$
(3.5)

Within the ladder approximation of the BCS interaction it is well known that  $D_{\lambda}(\vec{\mathbf{r}}, \vec{\mathbf{r}}, \nu_m)$  is a function only of  $|\nu_m|$ . This can be seen by direct computation as is done in Eq. (A4) and is actually a consequence of particle-hole symmetry. Writing

$$D_{\lambda}(\vec{\mathbf{r}},\vec{\mathbf{r}};\nu_m) = \begin{cases} f(\nu_m), & \nu_m \ge 0\\ f(-\nu_m), & \nu_m < 0 \end{cases}$$
(3.6)

we obtain the following analytic continuation of  $D_{\lambda}$  to the upper and lower z plane:

$$\tilde{D}(\vec{\mathbf{r}},\vec{\mathbf{r}};iz) = \begin{cases} f(-iz), & \text{Im}z > 0\\ f(iz), & \text{Im}z < 0. \end{cases}$$
(3.7)

There is a discontinuity in  $\tilde{D}$  across the real z axis,

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given by the spectral function

$$A(\mathbf{\dot{r}},\mathbf{\dot{r}};\omega) = i \left[ \tilde{D}(\mathbf{\dot{r}},\mathbf{\dot{r}};-i\omega) - \tilde{D}(\mathbf{\dot{r}},\mathbf{\dot{r}};i\omega) \right]. \quad (3.8)$$

From Eq. (3.8) it is clear that  $A(\vec{\mathbf{r}}, \vec{\mathbf{r}}; \omega)$ =  $A(\vec{\mathbf{r}}, \vec{\mathbf{r}}, -\omega)$ . The sum over m in Eq. (3.3) can be transformed into an integral by standard techniques.<sup>11</sup> A contour integral with the Bose factor  $(e^{\beta\omega}-1)^{-1}$  is introduced with the contour surrounding the poles of the Bose factor. The contour is then distorted so that it runs above and below the real zaxis. The  $e^{i\nu_m\delta}$  factor assures the vanishing of the contribution from the part of the great circle where the Bose factor does not give convergence. We obtain from Eqs. (3.8) and (3.3)

$$\frac{d\Omega}{d\lambda'} = -\frac{eBVkT}{hc\pi} \sum_{n,k} \int d^3r \int_{-\infty}^{\infty} e^{\omega \delta} \frac{d\omega}{2\pi} \frac{A(\mathbf{\dot{r}},\mathbf{\dot{r}};\omega)}{e^{\beta\omega}-1} .$$
(3.9)

Using the antisymmetry property of A, we can write Eq. (3.9) as

$$\frac{d\Omega}{d\lambda'} = -\frac{eBVkT}{\pi hc} \sum_{n,k} \int d^{3}r \int_{0}^{\infty} A(\omega) \frac{d\omega}{2\pi} \left( e^{-\omega \delta} + \frac{2}{e^{\beta \omega} - 1} \right).$$
(3.10)

Using the explicit representation of  $A(\mathbf{r}, \mathbf{r}, \omega)$  in terms of  $\Pi_m(n, k)$  we can integrate over  $\mathbf{r}$  and  $\lambda'$ , and obtain

 $\Omega_{\lambda} - \Omega_{D} = -VkT\left(\frac{eB}{2\pi^{2}hc}\right) \sum_{n} \int dk \int_{0}^{\infty} \left(e^{-\delta \omega} + \frac{2}{e^{\beta \omega} - 1}\right)$ 

× Im 
$$\left[ \ln \left( \frac{g_{n,k}(-i\omega)}{g_{n,k}(i\omega)} \right) \right] d\omega.$$
 (3.11)

It is interesting to observe that if the interaction contained  $\Phi \Phi^{\dagger}$  instead of  $\Phi^{\dagger} \Phi$  we would have had  $\delta = 0_{-}$  and the factor  $-(e^{-\beta\omega}-1)^{-1}$  would have been introduced instead of the Bose factor in order to ensure the validity of distorting the contour. However, owing to the antisymmetry of  $A(\mathbf{r}, \mathbf{r}, \omega)$ , the final result for  $\Omega_s - \Omega_n$  is the same. This shows that within the present approximation there is no discontinuity in  $D(\vec{r}, \vec{r}; \tau)$  at  $\tau = 0$ . It must be emphasized, however, that the above arguments are based on the properties of the approximate expression for  $D_{\lambda}(\mathbf{r}, \mathbf{r}; \nu_m)$ . In particular, the linear term in  $\lambda$  of Eq. (3.5) is clearly just the Hartree contribution to the free energy. In order that this contribution be finite and equal to  $-\lambda n^2$ , where n is the density of the electron gas, it is essential to keep the  $e^{i\nu_m \delta}$  factor. This is related to the fact that the linear term involves a sum over all momenta, and particle-hole symmetry only applies near the Fermi surface. However, higher-order terms in  $\lambda$  involve higher order in  $\Pi_m$ , and the sum over m is then convergent without the  $e^{i\nu_m \delta}$  factor. Hence one should first subtract the linear term and the argument beginning with Eq. (3.6) should be applied to  $\Pi_m[(1-\lambda\Pi_m)^{-1}-1]$  instead of  $D_\lambda$  itself. The conclusion is then that Eq. (3.5) can be written as

$$\Omega_{\lambda} - \Omega_{0} = \frac{VkT}{\pi} \left( \frac{eB}{hc} \right) \left( \sum_{m} \sum_{n} \int dk \left\{ \ln[1 - \lambda \Pi_{m}(n, k)] + \lambda \Pi_{m}(n, k) \right\} - \sum_{m} \sum_{n} e^{i\nu_{m}\delta} \int \lambda \Pi_{m}(n, k) dk \right),$$
(3.12)

where in the first term the factor  $e^{i\nu_m\delta}$  is unnecessary and has been removed. As pointed out earlier the second term is just  $-\lambda n^2$  and does not contribute to any fluctuation-induced property of the system. An expression similar to Eq. (3.12) but in the absence of field and impurities has been obtained by Thouless.<sup>19</sup>

We have also attempted to derive Eq. (3.5) using Hubbard's functional integral method, but we find that the approximations are less transparent and that the derivation is much more difficult unless one starts with a symmetrized interaction<sup>20</sup>

$$\hat{H}_{1}' = \left(\frac{1}{2}\lambda\right) \int d^{3}\gamma \left[\Phi(\vec{\mathbf{r}}) \Phi^{\dagger}(\vec{\mathbf{r}}) + \Phi^{\dagger}(\vec{\mathbf{r}}) \Phi(\vec{\mathbf{r}})\right]$$

As one expects, the symmetrized interaction leads to Eq. (3.5), but with  $e^{i\nu_m\delta}$  replaced by unity. We find the derivation given here more satisfactory.

In the Ginsburg-Landau limit,  $g_{n,k}(\nu_m)$  is approximated by

$$\ln (T/T_{c0}) + A \left[k^2 + 4b \left(n + \frac{1}{2}\right)\right] + B \left|\nu_m\right|$$

where A and B depend on T and  $\rho$ . In this approximation the m = 0 term of Eq. (3.5) is precisely the

expression obtained by Schmid<sup>5</sup> who calculated the partition function as a functional integral of  $e^{-\beta F(\Delta)}$ , where  $F(\Delta)$  is the GL free-energy functional. In the integral form given by Eq. (3.9) the m = 0 term is recovered if the Bose factor is replaced by  $(\beta \omega)^{-1}$ , thus giving rise to a single pole at  $\omega = 0$ . In I we have considered only the m = 0 term. In Sec. IV we shall show that this is a good approximation for clean superconductors, but not for dirty materials unless  $\rho < 1$ .

Recently Maki and Takayama<sup>8</sup> have treated the fluctuation-induced diamagnetism problem in the dirty limit by using a GL approximation for  $\Pi_m(n, k)$ . They then write down an equation for the free energy which is very similar to Eq. (3.11), except the term  $e^{-\omega\delta}$  in the first parentheses is dropped. After dropping this very large term, the remaining term has an exponential convergence factor and the result is a strong suppression of the diamagnetism below Prange's result. We believe that the term dropped by Maki and Takayama would, if evaluated, contribute significantly to the magnetization when B is large. However, it does not appear to change the Prange limit (i.e.,  $B \rightarrow 0$ ). We shall discuss this in greater detail in Sec. IV.

#### IV. CALCULATION OF MAGNETIZATION

The fluctuation-induced magnetization is given by differentiating Eq. (3.5) with respect to B,

$$M = -\frac{VkT}{\pi} \left(\frac{e}{hc}\right) \sum_{m} e^{i\nu_{m}\delta}$$
$$\times \sum_{n} \int dk \left( \ln g_{n,k}(\nu_{m}) + B \frac{\partial}{\partial B} \ln g_{n,k}(\nu_{m}) \right) . \quad (4.1)$$

Using Eq. (2. 20) with  $\Lambda_m \rightarrow \infty$ ,  $g_{n,k}$  is logarithmically divergent for large n and k and the sum over n, k in Eq. (4. 1) is divergent. Even within the spirit of the BCS effective Hamiltonian, it can be shown that

$$g_{n,k} \rightarrow 1 - \frac{1}{2}\pi \Lambda / \alpha_0 \left[ 4b \left( n + \frac{1}{2} \right) + k^2 \right]^{1/2}$$

for  $\alpha_0[4b(n+\frac{1}{2})+k^2]^{1/2} \gg \Lambda$ . In this regime the expression for  $g_{n,k}$  is linearly dependent on the cutoff and should not be trusted; but even with the cutoff the sum over n, k in Eq. (4.1) is still divergent. We assume that a more detailed treatment of the coupled electron-phonon system would show that contributions to M from large quantum-number fluctuations are strongly suppressed so that the sums over n and k are effectively convergent. Thus, we will feel free to rearrange the order of terms in the sum over n in the hope of obtaining a series which converges rapidly enough so that only values of  $g_{n,k}$ for  $\alpha_0 \left[4b\left(n+\frac{1}{2}\right)+k^2\right]^{1/2} \ll \Lambda$  are important. This point of view seems to be implicit in Prange's trick<sup>2</sup> of obtaining convergence by doing partial integrations and neglecting the contribution from the limits.

In I we rearranged the first term in Eq. (4.1) by writing

 $\sum_{n} \ln g_n = -\sum_{n} (n+1) \ln (g_{n+1,k}/g_{n,k}).$ 

We also made use of recursion relations for  $L_n$  to write ( $\rho = 0$ )

$$2B \frac{\partial}{\partial B} g_{n,k} = (n+1)(g_{n+1,k} - g_{n,k}) + n(g_{n,k} - g_{n-1,k}).$$
(4.2)

Shifting the second term on the right-hand side of Eq. (4.2) by one in the sum over n, we obtain the following formula for M ( $\rho = 0$ ):

$$M = \frac{\sqrt{kT}}{\pi} \frac{e}{hc} \sum_{m} \sum_{n=0}^{\infty} \int dk$$
$$\times \frac{(n+1)}{2} \left( 2 \ln \frac{g_{n+1,k}}{g_{n,k}} - \frac{g_{n+1,k}}{g_{n,k}} + \frac{g_{n,k}}{g_{n+1,k}} \right) . \quad (4.3)$$

The integrand in Eq. (4.3) is of order  $\frac{1}{6}(n+1)$  $\times [(g_{n+1,k} - g_{n,k})/g_{n,k}]^3$  and this expression is now convergent. Introducing the new variables  $k' = \alpha_0 k$  and  $b = \alpha_0^2 b'$  we see that  $g_{n,k}(\nu_m)$  depends only on b,  $T/T_{c0}$ , and the dummy variables k' and n. Thus,  $MB^{-1/2}/VT$  is a universal function of b and  $T/T_{c0}$ . Equation (4. 2) is no longer true for  $g_{n,k}(\nu_m)$  when  $\rho \neq 0$ . However, an identical equation is true for  $h_{s,m}(n,k)$  as defined by Eq. (2. 21). Guided by our experience with the clean case we make the same type of rearrangement and obtain the following expression:

$$MB^{-1/2}/VT = \frac{k}{2\pi^2} \left(\frac{e}{\hbar c}\right)^{3/2} b^{-1/2} \sum_{m=-\infty}^{\infty} \int_{-\infty}^{\infty} d(\alpha_0 k) \frac{(n+1)}{2} \times \left(2\ln \frac{g_{n+1,k}(\nu_m)}{g_{n,k}(\nu_m)} - \frac{D_{-}(k,n,m)}{g_{n,k}(\nu_m)} - \frac{D_{+}(k,n,m)}{g_{n+1,k}(\nu_m)}\right),$$
(4.4)

where

$$D_{\pm}(k,n,m)$$

$$= \sum_{s=0}^{\Lambda_m} (s + \frac{1}{2} + \frac{1}{2} |m| + \rho) [h_{s,m}(n+1,k) - h_{s,m}(n,k)] \times [s + \frac{1}{2} + \frac{1}{2} |m| + \rho h_{s,m}(n + \frac{1}{2} + \frac{1}{2}, k)]^{-2}.$$
(4.5)

 $MB^{-1/2}/VT$  can be calculated numerically. For our numerical work we have approximated the function  $1 - (\tan^{-1} v)/v$  by

$$1-\sum_{n=1}^{4} a_n e^{-\gamma_n v^2},$$

where the parameters  $a_n$  and  $\gamma_n$  were chosen so that the percentage error is everywhere smaller than 5%and in fact approaches zero for both small and large v. This approximation enabled us to obtain an analytic expression for  $h_{s,m}(n, k)$  and thereby made the rest of the numerical work rather simple. As discussed in Sec. III, in order to perform the sum over m without worrying about the  $e^{\overline{i}\nu_m \delta}$  factor, one has to remove the contribution that is linear in  $\lambda$ . In the clean case it can be shown that with the particular rearrangement we have chosen the linear term exactly cancels for each m. Hence the m sum can simply be done and in fact we find that the  $m \neq 0$ terms are entirely negligible. In the presence of impurities, however, the linear term in  $\lambda$  does not vanish. It is then necessary to remove the linear term by hand, using Eq. (2.20) for  $\lambda N(0)$ .

In Fig. 1 we show the results of our numerical calculation for  $\rho_c \equiv \rho (T = T_c) = 0$ , 1.38, and 7.04 at  $T = T_{c0}$ . We used  $\Lambda = 5$  for the  $\rho_c = 1.38$  case and  $\Lambda = 20$  for the  $\rho_c = 7.04$  case. Roughly speaking, these are the largest  $\rho_c$  values for which  $\omega_D \tau \gg 1$  for the cases of indium and a typical weakly coupled superconductor, respectively. The  $\rho_c = 1.38$  curve is not changed appreciably for  $b/(2\rho+1) < 0.5$  if  $\Lambda$  is changed to 20. We have also snown the contribution from the m = 0 term for  $\rho_c = 7.04$ . For  $\rho_c = 1.38$  the  $m \neq 0$  contribution is only 15% of the total at  $b/(2\rho+1) = 0.2$  and it becomes smaller as  $b/(2\rho+1)$  is decreased. The linear term



FIG. 1. Field dependence of  $-M(T_c)H^{-1/2}/T_c$  plotted vs the parameter  $b/(1+2\rho)$  for superconductors of different mean free path  $l(\rho=0.44\xi_0/l$  at  $T=T_c)$ . In terms of the magnetic field  $H_c$ 

$$\frac{b}{1+2\rho} = 0.177 \ H \left/ \left( T_c \frac{\partial H_{c2}}{\partial T} \left( 1+2\rho_c \right) \chi \left( \rho_c \right) \right) \right.$$

where  $\chi(\rho_c)$  is the Gorkov function. The dashed line is the m = 0 contribution along for  $\rho = 7.04$ .

in  $\lambda$  has not been subtracted from the graphs in Fig. 1. We expect its contribution to become important for large  $\rho_c$  and large  $b/(1 + 2\rho_c)$ . For  $\rho_c = 1.38$ , the linear term subtracts only 3% at  $b/(1 + 2\rho_c) = 0.08$ . For  $\rho_c = 7.04$ , the linear term subtracts 5, 20, 30% at  $b/(1 + 2\rho_c) = 0.066$ , 0.5, and 2.0, respectively, from the m = 0 contribution. The  $m \neq 0$  terms are affected more strongly as m increases, but it is not a drastic reduction, being never more than 40%.

As was pointed out earlier the m = 0 term is the only one that gives rise to a pole at  $T = T_{c2}(H)$ . From Eq. (2.20) we can see that  $g_{0,0}(\nu_m)$  for  $m \neq 0$ does not vanish at  $T = T_c(H)$  and hence can be interpreted in some sense as being equivalent to  $g_{0,0}(0)$ at an elevated temperature. In the clean case the magnetization decreases rather rapidly with temperature and the  $m \neq 0$  terms can be shown to be entirely negligible. However, in the dirty limit Prange's theory predicts a temperature scaling roughly proportional to  $\rho$ . For  $\rho$  sufficiently large the temperature dependence of the magnetization is so slow that  $m \neq 0$  terms can become important. These observations are borne out by our numerical calculations. In our approximation it is clear that inclusion of the  $m \neq 0$  terms has the effect of enhancing the magnetization. We have also performed numerical calculations using Eq. (3, 11)but using the nonlocal  $g_{n,k}(\nu_m)$  given by Eq. (2.21). If we follow Maki and Takayama and drop the  $e^{-\omega\delta}$ , as discussed earlier, we indeed obtain a suppression of the m = 0 result as expected. However, when we put back this term we obtain a net enhancement to the m = 0 term which is consistent with the results obtained by simply performing the sum over т.

If the value of  $\rho_c$  continues to increase, the contribution of the  $m \neq 0$  term also increases, even

after subtraction of the linear term in the coupling constant. However, we would like to point out that the  $\omega_{p} \tau \gg 1$  condition means that for very large  $\rho_{c}$ our theory is applicable only to materials with extremely large  $\Lambda$ . Furthermore as  $\rho_c$  increases, terms with higher and higher values of m become important and one is sampling the region of  $g_{n,k}(\nu_m)$ for larger and larger n and k, i.e., one is probing fluctuations of shorter and shorter wavelengths. An approximate rule is that the k integral in Eq. (4.4) is important out to  $k^2 \simeq nb$  and the sum over *n* is important out to  $nb/(1+2\rho) \simeq |m|+1$ . Another consideration one has to bear in mind is that for  $m \neq 0$  and for  $b/(1+2\rho)$  so large that  $B > H_{c2}(0)$ , there is no singularity in the pair propagator  $D(r, r', \nu_m)$ . It is then difficult to argue why the ladder approximation to the pair propagator should dominate the physical properties of the system. It is perhaps possible that a large contribution from the  $m \neq 0$  terms is an indication that a wider class of diagrams other than the ladder diagrams needs to be retained.

Finally we would like to discuss the  $\omega_{D} \tau \gg 1$  condition. Physically, when the mean free path is short the energy of an electron is uncertain to order  $\hbar/\tau$ . If  $\omega_{p}\tau \lesssim 1$  this means that the BCS cutoff which requires that only electrons with momentum within  $\hbar\omega_D/v_F$  of the Fermi surface should participate in the interaction is no longer realistic. Actual calculations using an effective Hamiltonian with a BCS cutoff in the presence of impurities indicate that once  $\hbar/\tau \gtrsim \hbar \omega_D$  the calculated transition temperature starts to vary sharply with the impurity concentration. This prediction contradicts experimental measurements which indicate a very weak dependence on  $\hbar/\tau$ .<sup>21</sup> Anderson<sup>17</sup> has pointed out how the slow variation of the transition temperature can be explained for  $\hbar/\tau \gg \hbar\omega_D$ . He shows

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that if one finds the electron energy eigenstates in the presence of impurities and calculates the phonon-mediated intereaction between electrons in such states, then a new truncated effective Hamiltonian can be found that has the pairing occurring between electrons in time-reversed states. The new effective Hamiltonian again has a BCS cutoff which restricts the interaction to particles with energies within  $\hbar\omega_{p}$  of the Fermi surface. The equation for the transition temperature obtained from the new effective Hamiltonian is the same as the one for pure superconductors except for the presence of a new density of states which is weakly dependent on  $\hbar/\tau$ . Anderson<sup>17</sup> has pointed out that once  $\hbar/\tau \geq \hbar\omega_p$  the interaction between pairs with nonzero net momentum is changed more drastically because of the lack of momentum conservation in the presence of impurities. In other words there is no Anderson's theorem for properties of a superconductor involving pairs of finite total momentum. While it is true that the  $\omega_D \tau$  condition is not in evidence in Eq. (2.21), we can find no reason to believe that cutting off the sum over s as done in Eq. (2.21) simulates the energy cutoff if  $\omega_D \tau \leq 1$ .

Recently Beasley, Tinkham, and co-workers<sup>22</sup> have obtained more data for indium alloys with  $\rho_c$ up to about 10. For indium,  $\omega_D/2\pi kT_c \simeq 5$ . We find that for  $\rho_c = 1.38$  our theory is in reasonable agreement with the experiment. However, as  $\rho_c$ is increased the experiment shows that a graph like Fig. 1 saturates for  $\rho_c \simeq 7$  [i.e., when  $T = T_{c0}$ and  $\rho_c > 7$ , all  $\rho_c$  values give the same graph of  $-MB^{-1/2}/VT$  vs  $b/(1+2\rho_c)$ ]. Thus, the  $\rho_c = 7.04$ curve does not agree with the experiment at all. In the absence of a more complete theory we cannot tell whether the violation of the  $\omega_D \tau \gg 1$  condition alone is responsible for the discrepancy. Further experiments on the alloys of materials with larger values of  $\omega_D/2\pi kT$  would be helpful.

If we use Eq. (3.11), but follow Maki and Takayama and throw out the contribution of the  $e^{-\omega\delta}$ term as compared with that from  $2/(e^{\beta\omega}-1)$  factor, we obtain numerical results which have saturated by the time  $\rho_c$  is increased to 7. The saturated curve is not far from what is found experimentally. We know of no reason why the  $e^{-\omega\delta}$  term should be thrown out. However, one cannot help but be impressed by the results obtained once it is discarded. We hope that further experimental and theoretical work will clarify the situation.

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## **APPENDIX: SOLUTION OF EQ. (2.13)**

We make use of the semiclassical phase-integral

approximation for the single-electron Green's function in the presence of a field  $\vec{A}(\vec{r})$ ,

$$\overline{G}_{0}(\mathbf{\dot{r}}_{1}, \mathbf{\dot{r}}_{2}; \omega_{s}) = \overline{G}_{0}(\mathbf{\dot{r}}_{1}, \mathbf{\dot{r}}_{2}; \omega_{s}, B = 0)$$

$$\times \exp[ie/\hbar c) \int_{\mathbf{\ddot{r}}_{2}}^{\mathbf{\ddot{r}}_{1}} d\mathbf{\ddot{s}} \cdot \mathbf{\vec{A}}(\mathbf{\ddot{s}})], \quad (A1)$$

where the line integral is performed along a straight line between  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . Equation (A1) is valid if  $\mu_B B \ll 2\pi kT + \hbar/\tau$ , which is the same as the condition that the single-electron cyclotron orbit is large compared with the range of  $\overline{G}_0$ . For B = 0,  $\tilde{Q}_m^s(\mathbf{r}_1, \mathbf{r}_2)$ depends only on  $|\mathbf{r}_1 - \mathbf{r}_2|$  and we introduce a Fourier transform  $\tilde{Q}_m^s(q)$  which can be written as

$$\widehat{Q}_{m}^{s}\left(q\right) = \int \frac{d^{3}k}{\left(2\pi\right)^{3}} \overline{G}_{0}\left(\vec{k}, -\omega_{s}\right) \widetilde{G}_{0}\left(\vec{k}+\vec{q}, \omega_{s}+\nu_{m}\right), \qquad (A2)$$

where

$$\tilde{G}_{0}(\mathbf{\ddot{k}}, \omega_{s}) = \int d^{3}r \ e^{i\mathbf{\vec{k}}\cdot\mathbf{\vec{r}}} \ \overline{G}_{0}(\mathbf{\ddot{r}}, \omega_{s}) = \frac{1}{\epsilon_{k} + i(\omega_{s} + \hbar\omega_{s}/2 \mid \omega_{s} \mid \tau)}$$
(A3)

is the Fourier transform of the impurity-averaged simple-particle Green's function. The integral in Eq. (A2) is evaluated by replacing  $\int d^3k$  by  $N(0)\int d\epsilon$ , where the energy integral is cut off at  $\epsilon_F \pm \omega_D$  according to the prescription of the BCS interaction. If we extend this cutoff to  $\infty$ ,  $\hat{Q}_{s,m}(q)$  can easily be evaluated,

$$\hat{Q}_{s,m}(q) = \frac{1}{2}N(0)(\alpha_0 q)^{-1} \tan^{-1}[\alpha_0 q/(s + \frac{1}{2} + \frac{1}{2}|m| + \rho)], \quad (A4)$$

where  $\alpha_0 = \hbar v_F / 4\pi k T$  and  $\rho = \alpha_0 / l$ . Equation (A4) behaves like  $s^{-1}$  for large s, and anticipating that we need to calculate  $\sum_{s} \hat{Q}_{s,m}(q)$ , it is clearly important to put in the cutoff. By examining Eq. (A2) for large q, it can be shown that the cutoff in the energy integral is roughly simulated by keeping Eq. (A4) for  $\hat{Q}_{s,m}(q)$  but with the understanding that the sum over s should be cut off when  $s + \frac{1}{2}|m|$ is of order  $\omega_D/2\pi kT$ . However, it is clear that this procedure makes sense only if  $\omega_D \tau \gg 1$ . From Eqs. (A2) and (A3) one easily sees that for  $\tau^{-1} \gtrsim \omega_D$ the integral over  $\epsilon$  has not started to converge at  $\omega_{p}$ . Consequently the value of  $\hat{Q}$  will be extremely sensitive to the cutoff, indicating a break down of the BCS effective Hamiltonian. This the reason why our results are restricted by the condition  $\omega_{p} \tau \gg 1$ . In Sec. IV we give a more physical discussion of this condition, particularly in the light of Anderson's theorem.

We proceed to use an identity derived by Werthamer<sup>23</sup>:

$$\exp[(2ie/\hbar c)\int_{\mathbf{r}_2}^{\mathbf{r}_1} d\mathbf{s} \cdot \mathbf{A}(\mathbf{s})]\psi(\mathbf{r}_1)$$

$$= \exp\left[-i\left(\vec{\mathbf{r}}_1 - \vec{\mathbf{r}}_2\right) \cdot \vec{\Pi}\right] \psi\left(\vec{\mathbf{r}}_2\right), \quad (A5)$$

where  $\vec{\Pi} = -\nabla/i - (2e/\hbar c)\vec{A}(\vec{r})$  and  $\vec{\Pi}$  only operates on the  $\vec{r}$  dependence of  $\psi(\vec{r})$ . Using Eqs. (A1), (A5), and (2.12), the eigenvalue problem (2.13) is transformed into a differential equation of infinite order,

$$\hat{D}_{s,m}\psi_{n}(\vec{\mathbf{r}}) = \lambda_{n}\psi_{n}(\vec{\mathbf{r}}) , \qquad (A6)$$

where the operator  $\hat{D}_{s,m}$  is defined by

$$\hat{D}_{s,m} = \int d^3 \gamma_1 d^3 q \ (2\pi)^{-3} \ e^{i\vec{\mathfrak{q}}\cdot\vec{\mathfrak{r}}_1} \hat{Q}_{s,m}(q) e^{-i\vec{\mathfrak{r}}_1\cdot\vec{\mathfrak{n}}} \ . \tag{A7}$$

It is clear from Eq. (A4) that  $\hat{D}_{s,m}(q)$  has an expansion in even powers of q. Indeed retaining only the constant and the  $q^2$  term yields the usual GL approximation for the pair propagator. To keep higher-order  $q^{2n}$  one must keep the corresponding order in  $(\mathbf{r}_1 \cdot \mathbf{n})^{2n}/(2n)!$ . However, different components of  $\Pi_i$  do not commute, and in fact, in the case of constant field B,

$$[\Pi_x, \Pi_y] = -i(2e/\hbar c)B .$$
 (A8)

Hence higher-order terms will include not only the combination  $\vec{\Pi} \cdot \vec{\Pi} = [\vec{\nabla}/i + (2e/\hbar c)\vec{A}]^2$ , but will contain terms dependent on  $(2eB/\hbar c)^2$  as well. It is thus inconsistent to treat nonlocality in the order parameter (higher orders in  $q^2$ ) without taking into account nonlocal electrodynamics, the expansion parameter being  $\xi_0^2 B (2e/\hbar c)$  in both cases. This is why the PAW form for the free energy is not a good approximation. A direct calculation of the  $\xi_0^2 (2eB/\hbar c)$  dependence is a hard counting problem. However, it is clear that the eigenstates of  $\hat{D}_{s,m}$  are the Landau states  $\langle r | n, k, k' \rangle$ , where

$$[\vec{\nabla}/i + (2e/\hbar c)\vec{A}]^2 \langle \vec{r} | n, k, k' \rangle$$

$$= \left[k^{2} + (4eB/\hbar c)(n+\frac{1}{2})\right] \langle \mathbf{\tilde{r}} | n, k, k' \rangle .$$
 (A9)

The eigenvalues can be calculated using a coherent state representation as follows. We introduce the operator  $a = (\prod_x - i\prod_y)/(4eB/\hbar c)^{1/2}$ . Then  $a, a^{\dagger}$  are

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<sup>1</sup>J. P. Gollub, M. R. Beasley, and M. Tinkham, Phys. Rev. Letters <u>25</u>, 1646 (1970).

<sup>2</sup>R. E. Prange, Phys. Rev. B <u>1</u>, 2349 (1970).

<sup>3</sup>B. R. Patton, V. Ambegaokar, and J. W. Wilkins, Solid State Commun. <u>7</u>, 1287 (1969).

<sup>4</sup>P. A. Lee and M. G. Payne, Phys. Rev. Letters, <u>26</u>, 1537 (1971).

<sup>5</sup>A. Schmid, Phys. Rev. <u>180</u>, 527 (1969).

<sup>6</sup>S. B. Nam, Phys. Rev. Letters <u>26</u>, 1369 (1971).

<sup>7</sup>J. Kurkijärvi, V. Ambegaokar, and G. Eilenberger, this issue, Phys. Rev. B <u>5</u>, 868 (1972).

<sup>8</sup>K. Maki and H. Takayama, J. Low Temp. Phys. <u>5</u>, 313 (1971).

<sup>9</sup>J. Hubbard, Phys. Rev. Letters <u>3</u>, 77 (1959).

<sup>10</sup>L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. <u>34</u>, 735 (1958) [Sov. Phys. JETP <u>7</u>, 182 (1958)].

<sup>11</sup>See, V. Ambegaokar, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969).

<sup>12</sup>S. F. Edwards, Phil. Mag. <u>3</u>, 1020 (1958); A. A.

Abrikosov and L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. <u>36</u>, 319 (1959) [Sov. Phys. JETP <u>9</u>, 220 (1959)]; C. Caroli, P.-G. de Gennes, and J. Matricon, J. Phys. Radium <u>23</u>, 707 (1962).

<sup>13</sup>See, L. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (Benjamin, New York, 1962).

boson operators obeying  $[a, a^{\dagger}] = 1$ . Furthermore, we can write

$$e^{-i\vec{r}_{1}\cdot\vec{\Pi}} = e^{-iz_{1}\Pi_{z}-\mu^{T}a+\mu a^{\dagger}},$$
 (A10)

where  $\mu = b'^{1/2}(y_1 + ix_1)$  and  $b' = eB/\hbar c$ . The operator  $e^{-\mu * a + \mu a^{\dagger}}$  is the generator of a translation in the coherent state, <sup>24</sup>

$$|\alpha\rangle = \sum_{n} \alpha^{n} e^{-|\alpha|^{2}/2} (n!)^{-1/2} |n, k, k'\rangle,$$
 (A11)

i.e.,

$$e^{-\mu *_{a+\mu a^{\dagger}}} | \alpha \rangle = | \alpha + \mu \rangle e^{(\mu a^{*} - \mu * \alpha)/2} .$$
 (A12)

Going into cylindrical coordinates and using Eqs. (A10) and (A12), we obtain

$$N(0) V \int^{-1} D_{s,m} | \alpha \rangle$$

$$= \ln \left( \frac{T}{T_c} \right) | \alpha \rangle + \int r_1 dr_1 d\theta q dq d\phi (2\pi)^{-2}$$

$$\times e^{ir_1 q \cos \phi} \hat{Q}_{|s,m|} ((q^2 + k^2)^{1/2}) e^{-\mu^* \alpha} \sum_n \frac{(\alpha + \mu)^n}{(n!)^{1/2}}$$

$$\times e^{-(|\mu|^2 + |\alpha|^2)/2} | n, k, k' \rangle . \quad (A13)$$

We note that  $\int_0^{2\pi} d\theta e^{-\mu^* \alpha} (\alpha + \mu)^n = 2\pi \alpha^n L_n(|\mu|^2)$ , where  $L_n$  is the Laguerre polynomial. The  $\phi$  and  $r_1$  integrations can be performed<sup>25</sup> and on projecting  $|\alpha\rangle$  onto  $|n, k, k'\rangle$  we obtain the remarkably simple result

$$\hat{D}_{s,m} \langle \mathbf{\dot{r}} | n, k, k' \rangle = P_{s,m}(n,k) \langle \mathbf{\dot{r}} | n, k, k' \rangle, \quad (A14)$$

where

$$P_{s,m}(n,k) = \frac{1}{2}(-1)^n \int_0^\infty e^{-x^2} L_n(x) \hat{Q}_{s,m}[(k^2 + b'x)^{1/2}] dx$$

This is the result given by Eqs. (2.14) and (2.15).

<sup>14</sup>E. Helfand and N. R. Werthamer, Phys. Rev. <u>147</u>, 288 (1966).

<sup>15</sup> P.-G. de Gennes, *Superconductivity of Metals and* Alloys (Benjamin, New York, 1966).

<sup>16</sup>K. Maki, Physics <u>1</u>, 21 (1964).

<sup>17</sup>P. W. Anderson, J. Phys. Chem. Solids <u>11</u>, 26 (1959).

<sup>18</sup>R. Brout, in *Brandeis University Summer Institute* in *Theoretical Physics*, 1966 (Gordon and Breach, New York, 1966), Vol. 1.

<sup>19</sup>D. J. Thouless, Ann. Phys. (N.Y.) <u>10</u>, 553 (1960). <sup>20</sup>This point has apparently been overlooked in the work of T. M. Rice, J. Math. Phys. <u>8</u>, 1581 (1967). We believe the difficulty stems from using the equation

believe the difficulty stems from using the equation  $e^{|A|^2} = \pi^{-1} \int dx_1 dx_2 e^{-|x|^2 + Ax^2 A^* x^*}$  with A as an operator.

This is not correct if  $[A, A^{\dagger}] \neq 0$ , even with time ordering. <sup>21</sup>A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical* 

Physics (Pergamon, New York, 1965), p. 334.
 <sup>22</sup>M. R. Beasley and M. Tinkham (private communication).

<sup>23</sup>N. R. Werthamer, in *Superconductivity*, edited by
 R. D. Parks (Marcel Dekker, New York, 1969).

<sup>24</sup>See, R. J. Glauber, Phys. Rev. <u>131</u>, 2766 (1963).

<sup>25</sup>I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals*, *Series, and Products* (Academic, New York, 1965), Eq. 7.421, p. 847.