Free energy of an inhomogeneous superconductor: A wave-function approach

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A method for calculating the free energy of an inhomogeneous superconductor is presented. This method is based on the quasiclassical limit (or Andreev approximation) of the Bogoliubov–de Gennes (or wave function) formulation of the theory of weakly coupled superconductors. The method is applicable to any pure bulk superconductor described by a pair potential with arbitrary spatial dependence, in the presence of supercurrents and external magnetic field. We find that both the local density of states and the free energy density of an inhomogeneous superconductor can be expressed in terms of the diagonal resolvent of the corresponding Andreev Hamiltonian, which obeys the so-called Gelfand-Dikii equation. Also, the connection between the well known Eilenberger equation for the quasiclassical Green's function and the less known Gelfand-Dikii equation for the diagonal resolvent of the Andreev Hamiltonian is established. These results are used to construct a general algorithm for calculating the (gauge invariant) gradient expansion of the free energy density of an inhomogeneous superconductor at arbitrary temperatures. [S0163-1829(98)05138-8]

I. INTRODUCTION

The most interesting, and also most difficult, problems in the theory of weak coupling (BCS) superconductivity[1] are those in which the pair potential (order parameter) has both spatial and time dependence. Examples of such problems are the electromagnetic response of superconductors,[2] relaxation phenomena and collective modes in superconductors,[3] vortex motion in bulk superconductors,[4–6] quantum tunneling of vortices,[7] phase slips in quasi-one-dimensional superconducting wires,[8–12] fluctuation effects above T_c,[13] etc. In principle all these phenomena can be described in the framework of the microscopic theory of BCS superconductivity in one of its formulations based on either Green's functions,[14] functional integrals,[15] or the Bogoliubov–de Gennes (BdG) equations,[16] i.e., the wave function formulation. Unfortunately, such an approach is impractical due to formidable technical difficulties of solving the corresponding microscopic equations. The existence of the two well separated energy scales in the problem, namely, the Fermi energy E_F and the magnitude of the gap function Δ makes the problem even more difficult as far as numerical calculations are concerned. However, if we are interested only in the low-energy (or long wavelength) physics of superconductors then the significant difference between these two energy scales allows us to employ the quasiclassical limit of the above mentioned microscopic theories. The quasiclassical Green's function method[17] is probably the most efficient method developed so far for solving problems involving inhomogeneous, nonequilibrium superconductors. Nevertheless, this method has its own limitations too (besides the fact that it is valid only on sufficiently long length and time scales, for example, the complicated and counterintuitive boundary conditions used in this method need to be determined from the underlying microscopic theory, which often relies on questionable approximations). Therefore, it is highly desirable to develop an effective theory of weak coupling superconductivity which technically is fairly simple and at the same time is general enough to allow for a correct description of the above mentioned phenomena. Such an effective theory exists only close to the critical temperature T_c, where the superconducting order parameter is small, and a time-dependent Ginzburg-Landau (TDGL) theory is well established.[18,19] Recently, attempts to develop a viable TDGL theory valid at all temperatures[20–22] yielded some promising results but controversy concerning this subject persist.[23–26]

So far, all derivations of TDGL theories have been done by using Green's functions and functional integrals. Although these methods are suitable for describing inhomogeneous superconductors in the presence of impurities, supercurrents, and electromagnetic fields, they usually resort to uncontrollable approximations during the decoupling of the higher order Green's functions. These approximations may lead to unphysical solutions corresponding to states which cannot be described by any wave function. In fact, it is known that the Green's function method as is usually formulated does not provide a complete dynamical description of the superconducting system and, therefore, it needs to be extended by some extra criterion (different from a variational principle) in order to eliminate the spurious, unphysical solutions from the correct one.[27,28] A typical example in this respect is related to the ground state of the superfluid He^3. Starting from the same BCS reduced Hamiltonian, one can use at least two different forms (or, equivalently, decoupling schemes) for the second order correlation function which, in general, lead to different ground states and quasiparticle excitation spectrum: (1) Gor'kov and Galitskii[29] have obtained an isotropic ground state and excitation spectrum, whereas (2) Anderson and Morel,[30] whose approach corresponds to a BCS type of second order correlation function, have obtained an anisotropic ground state and excitation spectrum. Interestingly, the ground state energy corresponding to the isotropic state is lower than the ground state energy of the anisotropic state, however, the former does not correspond to any state wave function and therefore must be rejected.[27] Note that there exist other examples as well, where the Green's function method can lead to an unphysical ground state with energy smaller than the one obtained by solving the corresponding Schrödinger equation.[27]

In view of this fact it is natural to consider the wave

function, or BdG, formulation of weak coupling superconductivity to develop a TDGL theory. A first step in this respect is to derive an expression for the free energy functional for an inhomogeneous superconductor in the time-independent (stationary) situation. Such a derivation is the subject of the present work. In this paper we present a method for calculating the free energy density of an inhomogeneous superconductor by employing the quasiclassical limit of the wave function formulation of the theory of superconductivity. The method is applicable to any pure bulk superconductor described by a pair potential with arbitrary spatial dependence, in the presence of supercurrents and external magnetic field. We show that neither the eigenvalues nor the corresponding eigenfunctions of the BdG Hamiltonian are needed to calculate the free energy density, which can be expressed solely in terms of the diagonal resolvent of the corresponding Andreev Hamiltonian, resolvent which obeys the so-called Gelfand-Dikii equation.[31] One of the main features of our method is that it provides a rather simple and systematic way to derive the (gauge invariant) gradient expansion of the free energy density at arbitrary temperatures.

The BdG method has been applied previously in the literature to study the physical properties of inhomogeneous superconductors. The first attempt in this respect has been undertaken by the Orsay group.[32,16] They have determined by solving the BdG equations in the quasiclassical (WKBJ or Andreev) approximation the low-energy excitations in the core of an isolated vortex. Also, de Gennes[16] has shown that close to T_c the BdG equations can be solved by employing the Rayleigh-Schrödinger perturbation theory and as a result one obtains the Ginzburg-Landau (GL) equations. Mathews[34] has also developed a systematic method of solving the BdG equations within the WKBJ approximation which he applied to study the normal-superconductor boundary in the intermediate state. Later on, he used the BdG method to address the subtle issue of quasiparticle, charge and energy conservation in weak-coupling superconductors.[35] Mathews' method has been further extended by Bardeen *et al.*[33] (BKJT) in their systematic and detailed analysis of the structure of an isolated vortex core. BKJT assumed a variational form for both the pair potential and the vector potential and the variational parameters have been determined by minimizing the corresponding free energy. Clearly[36] applied the theory of BKJT in the vicinity of superconducting transition temperature T_c and, quite surprisingly, besides the expected Ginzburg-Landau terms in the free energy functional he obtained several anomalous terms as well. These findings have been received with great interest by the superconductivity community and several authors have tried to explain the origin of these anomalous terms.[37] As a result of these research efforts it has been found that apart from the vortex problem anomalous terms in the free energy density also appear in other problems involving inhomogeneous superconducting systems, such as the healing-length problem,[38,39] the *N-S* proximity junction problem,[40] etc. Soon after the original work of Bar-Sagi and Kuper,[41] who managed to find analytically a self-consistent solution of the BdG equations in the Andreev approximation (i.e., the Andreev equations) by using a model pair potential $\Delta(z) \propto \tanh(\alpha z)$, an intense search has been started to discover other, practically more useful pair potentials which are self-consistent solutions of the corresponding Andreev equations.[42–44] In fact the existence of these self-consistent pair potentials are related to the supersymmetric property of the properly transformed Andreev Hamiltonian (see Sec. V) where the pair potential has the role of superpotential.[45] In can be shown that whenever the pair of potential energies generated by the superpotential are shape invariant the eigenstates of the corresponding supersymmetric Hamiltonians can be determined analytically by means of simple harmonic oscillator such as operator algebra. Apparently this simple but rather important observation has not been recognized in the literature. The problem of anomalous terms in the gradient expansion of the free energy density has been reconsidered by Hu[46] and Eilenberger and Jacobs[43] (EJ) by using the exact self-consistent solution of certain inhomogeneous superconducting systems. These authors demonstrated that the actual origin of these anomalous terms are related to surface terms and terms originating from the possible discontinuities of the pair potential or its derivatives. EJ have also developed a beautiful theory for calculating the free energy density of a quasi-one-dimensional inhomogeneous superconductor in the clean limit and in the absence of supercurrents and magnetic field. Also, in a recent work Waxman[47] starting from the Fredholm (functional) determinant expression of the free energy of an inhomogeneous superconductor has shown that the later can be expressed in terms of the determinant of a finite 4×4 matrix. However, no viable method for calculating this determinant has been proposed.

The paper is organized as follows. We begin with a brief review of the BdG method of superconductivity (Sec. II). Next, we express the free energy of a bulk superconductor in terms of the spectrum of the BdG Hamiltonian and the distribution function of the quasiparticles (Sec. III). The quasiclassical (Andreev) approximation and the expression of the free energy in this limit are presented in Sec. IV. Next, by using the wave function formulation of the theory of superconductivity, we describe two different methods for calculating the free energy density and the local density of states of an inhomogeneous superconductor. Both methods are based on expressing the free energy density of the superconductor in terms of the diagonal resolvent of the so-called Gelfand-Dikii equation. The first method, which is applicable only in the absence of the magnetic field and for a real pair potential with arbitrary spatial dependence, is presented in Sec. V, while the second method, which is more general and applicable for superconductors in the presence of supercurrents and magnetic field, is presented in Sec. VI. Finally, Sec. VII is reserved for conclusions. Also, the derivation of both *scalar* and *matrix* Gelfand-Dikii equations, which play a key role in our calculations of the free energy, are provided in two appendixes.

II. THE BOGOLIUBOV–de GENNES EQUATIONS

The Bogoliubov–de Gennes (BdG), or wave function, formulation of the microscopic theory of weak coupling superconductors represents an attractive alternative to the widely used Green's function and functional integral methods. The BdG method is conceptually simple, requires only knowledge of elementary quantum mechanics, yet it is gen-

eral and powerful. In what follows we apply this method to evaluate the free energy density of an inhomogeneous conventional *s*-wave superconductor.

Mainly to establish notations, we begin with a brief review of the basic equations of the BdG method.[16] Consider a pure bulk superconductor in the presence of a static magnetic field. The system is described by the effective mean field Hamiltonian[16]

$$\mathcal{H}_{\rm eff}=\int d^3\boldsymbol{r}\Big[\psi_\sigma^\dagger(\boldsymbol{r})H_0(\boldsymbol{r})\psi_\sigma(\boldsymbol{r})+\Delta(\boldsymbol{r})\psi_\uparrow^\dagger(\boldsymbol{r})\psi_\downarrow^\dagger(\boldsymbol{r}) +\Delta^*(\boldsymbol{r})\psi_\downarrow(\boldsymbol{r})\psi_\uparrow(\boldsymbol{r})+\frac{|\Delta(\boldsymbol{r})|^2}{V}\Big], \tag{2.1}$$

where $\Delta(\boldsymbol{r})$ is the (mean-field) pair potential, V is the Gor'kov contact pairing interaction [i.e., $V(\boldsymbol{r}-\boldsymbol{r}')=V\delta(\boldsymbol{r}-\boldsymbol{r}')$], the field operators $\psi_\sigma(\boldsymbol{r})$ and $\psi_\sigma^\dagger(\boldsymbol{r})$ destroy and create, respectively, an electron at position $\boldsymbol{r}$ with spin orientation $\sigma=\uparrow,\downarrow$, and obey the usual fermionic anticommutation relations

$$\{\psi_\sigma(\boldsymbol{r}),\psi_{\sigma'}(\boldsymbol{r}')\}=0,\quad \{\psi_\sigma^\dagger(\boldsymbol{r}),\psi_{\sigma'}^\dagger(\boldsymbol{r}')\}=0,\quad \{\psi_\sigma(\boldsymbol{r}),\psi_{\sigma'}^\dagger(\boldsymbol{r}')\}=\delta_{\sigma\sigma'}\delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{2.2}$$

and, finally, the kinetic energy operator, measured with respect to the Fermi energy $E_{\rm F}$, is given by

$$H_0(\boldsymbol{r})=\frac{1}{2m}\left(\hat{\boldsymbol{p}}-\frac{e}{c}\boldsymbol{A}\right)^2-E_{\rm F},\quad \hat{\boldsymbol{p}}=-i\hbar\nabla, \tag{2.3}$$

where the vector potential $\boldsymbol{A}(\boldsymbol{r})$ is related to the total magnetic field $\boldsymbol{H}(\boldsymbol{r})$ through the equation $\boldsymbol{H}(\boldsymbol{r})=\nabla\times\boldsymbol{A}(\boldsymbol{r})$. In Eq. (2.1), and throughout this paper, implicit summation over repeated spin or pseudospin indices is assumed.

The effective Hamiltonian (2.1) can be diagonalized by using the Bogoliubov transformations[16]

$$\psi_\uparrow(\boldsymbol{r})=\sum_i\,[u_i(\boldsymbol{r})\gamma_{i\uparrow}-v_i^*(\boldsymbol{r})\gamma_{i\downarrow}^\dagger],\qquad \psi_\downarrow(\boldsymbol{r})=\sum_i\,[u_i(\boldsymbol{r})\gamma_{i\downarrow}+v_i^*(\boldsymbol{r})\gamma_{i\uparrow}^\dagger], \tag{2.4}$$

where i labels a complete set of quantum states in the relevant Hilbert space, the γ and $\gamma^\dagger$ are the Bogoliubov quasiparticle annihilation and creation operators, respectively, and satisfy the fermionic anticommutation rules

$$\{\gamma_{i\alpha},\gamma_{j\beta}\}=0,\quad \{\gamma_{i\alpha},\gamma_{j\beta}^\dagger\}=\delta_{ij}\delta_{\alpha\beta}. \tag{2.5}$$

The Bogoliubov amplitudes u_i and v_i ought to be determined by the condition that the transformations (2.4) diagonalize $\mathcal{H}_{\rm eff}$; they obey the so-called Bogoliubov–de Gennes (BdG) equations[16] which can be written in compact form

$$\mathcal{H}_{\rm BdG}\Psi_i(\boldsymbol{r})\equiv\begin{pmatrix}H_0(\boldsymbol{r}) & \Delta(\boldsymbol{r})\\ \Delta^*(\boldsymbol{r}) & -H_0^*(\boldsymbol{r})\end{pmatrix}\Psi_i(\boldsymbol{r})=E_i\Psi_i(\boldsymbol{r}), \tag{2.6}$$

where $\Psi_i\equiv(u_i,v_i)^T$ is a pseudospinor in particle-hole space. Thus, the pair potential mixes coherently the particle and hole states and, as a result, the Bogoliubov quasiparticles have a mixed particle and holelike character. After diagonalization, Eq. (2.1) reads

$$\mathcal{H}_{\rm eff}=E_g+\sum_i\,E_i\gamma_{i\alpha}^\dagger\gamma_{i\alpha}, \tag{2.7}$$

where the ground state energy is given by

$$E_g=-2\sum_i\,E_i\int d^3\boldsymbol{r}|v_i(\boldsymbol{r})|^2+\int d^3\boldsymbol{r}\,\frac{|\Delta(\boldsymbol{r})|^2}{V}. \tag{2.8}$$

According to the expression (2.7) our system is equivalent to an ''ideal gas'' of Bogoliubov quasiparticles with energies E_i, which are the eigenvalues of the BdG equations (2.6). For an arbitrary pair potential $\Delta(\boldsymbol{r})$ the eigenvalue problem determined by Eq. (2.6), subject to suitable boundary conditions, is difficult to solve even numerically.

III. FREE ENERGY

By definition, the free energy is given by[48]

$$\mathcal{F}=\langle\mathcal{H}_{\rm eff}\rangle-T\mathcal{S}+\mathcal{F}_H, \tag{3.1}$$

where $\mathcal{S}$ is the entropy, and

$$\mathcal{F}_H=\int d^3\boldsymbol{r}F_H(\boldsymbol{r}),\quad F_H(\boldsymbol{r})=\frac{|\boldsymbol{H}(\boldsymbol{r})-\boldsymbol{H}_a|^2}{8\pi}, \tag{3.2}$$

is the positive magnetic field exclusion energy due to the screening supercurrents induced by the applied field $\boldsymbol{H}_a$. Also, we have assumed that the temperature distribution across the system is homogeneous. The notation $\langle\cdots\rangle\equiv{\rm Tr}\{\hat{\rho}\cdots\}$ indicates the average over some statistical ensemble described by the density matrix $\hat{\rho}$. In thermal equilibrium

$$\hat{\rho}=\frac{\exp(-\mathcal{H}_{\rm eff}/T)}{{\rm Tr}\{\exp(-\mathcal{H}_{\rm eff}/T)\}}. \tag{3.3}$$

One defines the mean occupation number of level ''i'' corresponding to spin orientation α by

$$f_{i\alpha}=\langle\gamma_{i\alpha}^\dagger\gamma_{i\alpha}\rangle, \tag{3.4}$$

and one assumes that there is no magnetic ordering in the system such that both spin orientations are equally likely, i.e.,

$$f_i\equiv f_{i\uparrow}=f_{i\downarrow}. \tag{3.5}$$

It is known that the entropy of an ideal gas of fermionic (quasi)particles, which is not necessarily in equilibrium, can be expressed in terms of the mean occupation numbers f_i as[49]

$$\mathcal{S}=-2\sum_i\,[f_i\,\ln\,f_i+(1-f_i)\ln(1-f_i)], \tag{3.6}$$

where the factor of 2 accounts for the two independent spin orientations.

Thus, inserting Eqs. (2.7), (3.4), (3.6) into Eq. (3.1), the free energy of the system, which is a functional of the pair

potential $\Delta(\boldsymbol{r})$, the mean occupation numbers f_i, and the vector potential $\boldsymbol{A}(\boldsymbol{r})$, can be written as

$$\mathcal{F}[\Delta(\boldsymbol{r}),f_i,\boldsymbol{A}(\boldsymbol{r})] \equiv \mathcal{F}=E_g+2\sum_i E_i f_i - 2T\sum_i [f_i \ln f_i+(1-f_i)\ln(1-f_i)]+\mathcal{F}_H. \tag{3.7}$$

In thermodynamic equilibrium one requires the free energy to be stationary with respect to Δ, f_i, and $\boldsymbol{A}$. Hence, stationarity with respect to (i) the pair potential yields the so-called *gap equation* (i.e., the self-consistency condition for the pair potential)

$$\Delta(\boldsymbol{r})=V(\boldsymbol{r})\langle\psi_\uparrow(\boldsymbol{r})\psi_\downarrow(\boldsymbol{r})\rangle=V\sum_i u_i(\boldsymbol{r})v_i^*(\boldsymbol{r})(1-2f_i), \tag{3.8}$$

(ii) the mean occupation number of the state i (for either two spin orientations) yields the usual Fermi distribution function

$$f_i=[\exp(E_i/T)+1]^{-1}, \tag{3.9}$$

and (iii) the vector potential yields the Maxwell equation

$$\nabla\times[\nabla\times\boldsymbol{A}(\boldsymbol{r})]=\frac{4\pi}{c}\boldsymbol{j}(\boldsymbol{r}), \tag{3.10}$$

where the supercurrent density is given by

$$\boldsymbol{j}(\boldsymbol{r})=2\frac{e}{m}\,\mathrm{Re}\sum_i [f_i u_i^*(\boldsymbol{r})\hat{\boldsymbol{P}}u_i(\boldsymbol{r}) + (1-f_i)v_i(\boldsymbol{r})\hat{\boldsymbol{P}}v_i^*(\boldsymbol{r})], \quad \hat{\boldsymbol{P}}\equiv\hat{\boldsymbol{p}}-\frac{e}{c}\boldsymbol{A}(\boldsymbol{r}). \tag{3.11}$$

In the absence of the magnetic field, the BdG equations (2.6) together with Eqs. (3.8) and (3.9) yield the standard BCS result corresponding to a uniform and real pair potential $\Delta(\boldsymbol{r})=\Delta_0$; the eigenstates i are plane wave states $|\boldsymbol{k}\rangle$ and

$$E_k=\sqrt{\xi_k^2+\Delta_0^2},\quad \xi_k=\frac{\hbar^2k^2}{2m}-E_\mathrm{F}$$

$$u_k=\sqrt{\frac{1}{2}\left(1+\frac{\xi_k}{E_k}\right)},\quad v_k=\sqrt{\frac{1}{2}\left(1-\frac{\xi_k}{E_k}\right)}, \tag{3.12}$$

$$\frac{1}{VN_0}=\int_0^{\omega_c}d\xi_k\,\frac{\tanh(E_k/2T)}{E_k}=2\pi T\sum_{\omega_n>0}^{\omega_c}(\omega_n^2+\Delta_0^2)^{-1/2},$$

where N_0 is the normal state density of states (for both spin orientations) at the Fermi level, ω_c is a cutoff frequency of the order of the Debye frequency, and $\omega_n=\pi T(2n+1)$ are fermionic Matsubara frequencies.

In what follows we will be interested in calculating the free energy $\mathcal{F}$ for a spatially varying pair potential and magnetic field which do not necessarily obey the self-consistency equations (3.8) and (3.10), (3.11). For the moment, we assume that the relation (3.9) is valid but, later on, we will relax this condition as well (see Sec. V D). So, we consider a superconductor in which the quasiparticles are in thermal equilibrium but the pair potential and the magnetic field may have an arbitrary spatial variation. In this case the expression of the free energy can be further simplified. Inserting Eq. (3.9) into Eq. (3.7), and by taking into account Eq. (2.8), after some straightforward algebra one obtains

$$\mathcal{F}=-2T\sum_i \ln\left(2\cosh\frac{E_i}{2T}\right)+\int d^3\boldsymbol{r}\,\frac{|\Delta(\boldsymbol{r})|^2}{V}+\mathcal{F}_H. \tag{3.13}$$

Apparently, in order to calculate the free energy (3.13) it is necessary to know the spectrum $\{E_i\}$ of the BdG Hamiltonian $\mathcal{H}_\mathrm{BdG}$ for a given pair potential $\Delta(\boldsymbol{r})$ (and boundary condition). Fortunately, this is not the case as several authors have already shown,[47,43] albeit in the absence of any magnetic field and by assuming that $\Delta(\boldsymbol{r})$ depends only on a single spatial coordinate. Indeed, by employing the identity[50]

$$\cosh^2\left(\frac{x}{2}\right)=\prod_{m=-\infty}^{\infty}\left[1+\frac{x^2}{\pi^2(2m+1)^2}\right], \tag{3.14}$$

the free energy (3.13) can be recast as

$$\mathcal{F}=-2T\sum_i \ln\left(2\prod_{\omega_m>0}\frac{\omega_m^2+E_i^2}{\omega_m^2}\right)+\int d^3\boldsymbol{r}\,\frac{|\Delta(\boldsymbol{r})|^2}{V}+\mathcal{F}_H, \tag{3.15}$$

where ω_m are fermionic Matsubara frequencies. The formal divergence of the above expression of the free energy can be eliminated by subtracting from $\mathcal{F}$ (i.e., by measuring $\mathcal{F}$ with respect to) the free energy $\mathcal{F}_N$ of the corresponding normal state. Thus, by denoting $\delta\mathcal{F}\equiv\mathcal{F}-\mathcal{F}_N$, we have

$$\begin{aligned}\delta\mathcal{F}&=-2T\sum_i \ln\prod_{\omega_m>0}\frac{\omega_m^2+E_i^2}{\omega_m^2+\epsilon_i^2}+\int d^3\boldsymbol{r}\,\frac{|\Delta(\boldsymbol{r})|^2}{V}+\mathcal{F}_H\\ &=-2T\sum_{\omega_m>0}\ln\mathrm{Det}\left(\frac{\omega_m^2+\mathcal{H}_\mathrm{BdG}^2}{\omega_m^2+\mathcal{H}_0^2}\right)+\int d^3\boldsymbol{r}\,\frac{|\Delta(\boldsymbol{r})|^2}{V}+\mathcal{F}_H,\end{aligned} \tag{3.16}$$

where $\mathcal{H}_0$ is the BdG Hamiltonian corresponding to the normal state of the system (i.e., $\Delta=0$), and $\{\epsilon_i\}$ denote the spectrum of $\mathcal{H}_0$.

Waxman[47] has shown that the infinite Fredholm (functional) determinant in Eq. (3.16), which contains in an encapsulated form all the information on the one-particle excitation spectrum of the superconductor, can be expressed, at least in the case of a quasi-one-dimensional inhomogeneous superconductor and in the absence of the magnetic field, in terms of a finite 4×4 matrix M. However, the actual evaluation of this matrix $M(x)$, which transports eigenfunctions of $\mathcal{H}_\mathrm{BdG}$ from $x=0$ to $x=L$ (L is the size of the system in the relevant x direction) is quite complicated and analytical results are possible only for layered systems with a piecewise constant pair potential. In the work by Eilenberger and Jacobs[43] the Fredholm determinant is calculated in terms of a function $\mathcal{E}(x)$ which obeys an integral equation of Volterra

type. This method seems to be somewhat simpler than Waxman's and allows for analytical results (in the quasiclassical limit) in several nontrivial cases and, furthermore, provides a viable procedure to obtain the gradient expansion of the free energy density about its equilibrium value.

In contrast to both above mentioned methods, which are only applicable when $\Delta(\boldsymbol{r})$ varies along a given direction, in the absence of any external field, and with the Bogoliubov quasiparticles in thermal equilibrium with the superconducting condensate, our method of calculating the free energy of an inhomogeneous superconductor is valid for an arbitrary $\Delta(\boldsymbol{r})$, in the presence of an arbitrary static magnetic field, and it can be generalized for an arbitrary distribution function f_i of the quasiparticles. Our method is based on the *quasiclassical approximation* of the BdG equations which we describe next.

IV. QUASICLASSICAL (ANDREEV) APPROXIMATION

Superconductors are characterized by two different energy scales, namely, the Fermi energy $E_{\rm F}$ and the amplitude of the pair potential (gap function) Δ_0 at zero temperature. The length scales corresponding to these energies are the Fermi wavelength $\lambda_{\rm F}\sim k_{\rm F}^{-1}\sim\hbar v_{\rm F}/E_{\rm F}$ which gives the mean inter-particle distance in the system, and the superconducting coherence length $\xi_0\sim\hbar v_{\rm F}/\Delta_0$ which determines the spatial extent of the pair correlation. Since in conventional superconductors $E_{\rm F}\gg\Delta_0$ (or $\lambda_{\rm F}\ll\xi_0$), as long as we are interested only in the low-energy (or long wavelength) properties of the system it is legitimate to employ the quasiclassical approximation of the theory of superconductivity. The BdG equations are valid on atomic scale and therefore the spinor wave functions $\Psi_i(\boldsymbol{r})$, which vary on a length scale set by $k_{\rm F}^{-1}$, contain more information than it is necessary to calculate, for example, the free energy and free energy density of an inhomogeneous superconductor. In general, this excess of information is eliminated at the end of the calculations by integrating out the irrelevant high-energy (of rapidly oscillating) degrees of freedom. A more practical approach is, however, to eliminate these irrelevant degrees of freedom right at the beginning of the calculations by replacing the BdG equations by their quasiclassical limit, i.e., the so-called Andreev equations.[51] For this purpose, one writes the spinor wave function Ψ_i as a rapidly oscillating phase factor (which changes on atomic length scale) times a slowly varying amplitude (which changes on a length scale set by the coherence length), i.e.,[52]

$$\Psi_i(\boldsymbol{r})\approx\Phi_n(\boldsymbol{r};\hat{\boldsymbol{u}})\exp(ik_{\rm F}\hat{\boldsymbol{u}}\boldsymbol{r}). \tag{4.1}$$

Thus, in the quasiclassical approximation, the quasiparticles are moving along classical trajectories which are straight lines determined by the unit vector $\hat{\boldsymbol{u}}$ and the ''impact parameter'' $r_\perp$ (which gives the distance of the quasiclassical trajectory from the origin of the coordinate system); the position vector in Eq. (4.1) reads

$$\boldsymbol{r}=x\hat{\boldsymbol{u}}+\boldsymbol{r}_\perp, \tag{4.2}$$

where the impact parameter vector $\boldsymbol{r}_\perp$ is normal to $\hat{\boldsymbol{u}}$. Nevertheless, the motion along the quasiclassical trajectories is quantized and the corresponding eigenstates are labeled in Eq. (4.1) by the quantum number n. So, in the quasiclassical approximation the state i is specified by the quantum number n and the continuously varying parameters $\hat{\boldsymbol{u}}$ and $\boldsymbol{r}_\perp$ which uniquely determine the position of the trajectory. Hence, the trace with respect to the original states i must be evaluated according to the formula

$$\sum_i\cdots=\pi\hbar v_{\rm F}N_0\int d^2r_\perp\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\sum_n\cdots. \tag{4.3}$$

Furthermore, we have (for brevity we omit the arguments)

$$\nabla^2\Psi_i=(\nabla^2\Phi_n+2ik_{\rm F}\hat{\boldsymbol{u}}\nabla\Phi_n-k_{\rm F}^2\Phi_n)\exp(ik_{\rm F}\hat{\boldsymbol{u}}\boldsymbol{r}), \tag{4.4}$$

and therefore, by using Eq. (2.3) in zero magnetic field, one obtains

$$\begin{aligned}H_0\Psi_i&=-\frac{\hbar^2}{2m}(\nabla^2\Phi_n+2ik_{\rm F}\hat{\boldsymbol{u}}\nabla\Phi_n)\exp(ik_{\rm F}\hat{\boldsymbol{u}}\boldsymbol{r})\\&\approx v_{\rm F}\hat{\boldsymbol{u}}\cdot(\hat{\boldsymbol{p}}\Phi_n)\exp(ik_{\rm F}\hat{\boldsymbol{u}}\boldsymbol{r}),\end{aligned} \tag{4.5}$$

where we have neglected the term involving the Laplacian of Φ_n (Andreev approximation) because

$$\left|\frac{\nabla^2\Phi_n}{k_{\rm F}\hat{\boldsymbol{u}}\nabla\Phi_n}\right|\sim(k_{\rm F}\xi_0)^{-1}\ll 1. \tag{4.6}$$

According to the notion of minimal coupling, in finite magnetic field in Eq. (4.5) one needs to replace $\hat{\boldsymbol{p}}$ with $\hat{\boldsymbol{P}}=\hat{\boldsymbol{p}}-(e/c)\boldsymbol{A}$.

Note that condition (4.6) may not hold for a small fraction of the total number of quasiclassical trajectories characterized by $\hat{\boldsymbol{u}}$ oriented almost perpendicular to $\nabla\Phi_n$. The Andreev approximation also fails in spatial regions where the pair potential (and/or its derivatives) has discontinuities, e.g., at interfaces, boundaries, etc. These nonanalyticities in $\Delta(\boldsymbol{r})$ reflect the fact that in such regions the pair potential changes rapidly on atomic scale. Within the quasiclassical approximation this kind of behavior of $\Delta(\boldsymbol{r})$ can be described by (nonintuitive) effective boundary conditions which must be derived starting from the underlying microscopic theory which is valid on atomic scale. It seems to be well established by now that if one does not account properly for the possible discontinuities in the pair potential (and or its derivatives) these can lead to unphysical *anomalous* terms in the corresponding Ginzburg-Landau free energy functional.[36,40,43]

Finally, inserting Eq. (4.1) into the BdG equations (2.6) and by taking into account Eq. (4.5), one arrives at the so-called Andreev equations[51]

$$\begin{aligned}\mathcal{H}_{\rm A}\Phi_n(\boldsymbol{r})&\equiv\begin{pmatrix}H(x)&\Delta(x;\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)\\\Delta^*(x;\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)&-H^*(x)\end{pmatrix}\Phi_n(x;\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)\\&=E_n(\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)\Phi_n(x;\hat{\boldsymbol{u}},\boldsymbol{r}_\perp),\end{aligned} \tag{4.7}$$

where

$$H\equiv H(x)=v_{\rm F}\hat{\boldsymbol{u}}\cdot\left(\hat{\boldsymbol{p}}-\frac{e}{c}\boldsymbol{A}\right)=-i\hbar v_{\rm F}\partial_x-v_{\rm F}\frac{e}{c}\hat{\boldsymbol{u}}\cdot\boldsymbol{A}(x). \tag{4.8}$$

Note that in Eq. (4.8) only the directional derivative $\hat{\boldsymbol{u}}\cdot\nabla$ enters which is equivalent to the ordinary derivative ∂_x along the quasiclassical trajectory. Hence, the Andreev equations (4.7), (4.8) are effectively one dimensional; the independent variable is x (the position along the quasiclassical trajectory), and the other degrees of freedom $(\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)$ enter the equation (and, therefore, the eigenvalues E_n and eigenfunctions Φ_n) only as parameters through the spatial dependence of the pair potential $\Delta(\boldsymbol{r})$. This is a key observation which allows us to treat inhomogeneous superconductors characterized by a pair potential with arbitrary spatial dependence.

In terms of the energy spectrum of the Andreev Hamiltonian $\mathcal{H}_{\rm A}$ the free energy $\delta\mathcal{F}$ can be written as [cf. Eq. (3.16)]

$$\begin{aligned}\delta\mathcal{F}&=-2T\pi\hbar v_{\rm F}N_0\int d^2r_\perp\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\\&\quad\times\sum_n\ \ln\prod_{\omega_m>0}\frac{\omega_m^2+E_n^2(\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)}{\omega_m^2+\epsilon_n^2(\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)}\\&\quad+\int d^3\boldsymbol{r}\,\frac{|\Delta(\boldsymbol{r})|^2}{V}+\mathcal{F}_H\\&=-2T\pi\hbar v_{\rm F}N_0\int d^2r_\perp\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\\&\quad\times\sum_{\omega_m>0}\ \ln\mathrm{Det}\left(\frac{\omega_m^2+\mathcal{H}_{\rm A}^2}{\omega_m^2+\mathcal{H}_0^2}\right)+\int d^3\boldsymbol{r}\,\frac{|\Delta(\boldsymbol{r})|^2}{V}+\mathcal{F}_H.\end{aligned}\tag{4.9}$$

In the above expression of the free energy the Fredholm determinant involves only the quantum states along an individual quasiclassical trajectory.

In what follows we derive a relatively simple formula for calculating the logarithm of the above Fredholm determinant and, consequently, the free energy. We begin with the case of an inhomogeneous superconductor in the absence of supercurrents and magnetic field, where the Andreev equations can be decoupled and, therefore, the calculations are fairly simple. The more complicated case of a superconductor in the presence of the magnetic field and supercurrents requires a completely different method for calculating the free energy density. This method is presented in Sec. VI.

V. SUPERCONDUCTOR IN ZERO MAGNETIC FIELD

A. Free energy

A key step in our derivation of the free energy of an inhomogeneous superconductor in zero magnetic field is the observation, due originally to Bar-Sagi and Kuper,[41,53] that the square of the Andreev Hamiltonian (4.7), (4.8) can be diagonalized and, therefore, the corresponding Andreev equations for the spinor wave function Φ_n decouple into two independent Schrödinger-like equations. Indeed, by dropping all the arguments for brevity, and assuming without any loss of generality a real pair potential, one can write

$$\begin{aligned}\Omega_{\rm A}\equiv\mathcal{H}_{\rm A}^2&=\begin{pmatrix}H^2+\Delta^2 & [H,\Delta]\\ -[H,\Delta] & H^2+\Delta^2\end{pmatrix}\\&=\begin{pmatrix}-\hbar^2v_{\rm F}^2\partial_x^2+\Delta^2 & -i\hbar v_{\rm F}(\partial_x\Delta)\\ i\hbar v_{\rm F}(\partial_x\Delta) & -\hbar^2v_{\rm F}^2\partial_x^2+\Delta^2\end{pmatrix},\end{aligned}\tag{5.1}$$

$\Omega_{\rm A}$ can be brought to diagonal form by employing the unitary transformation

$$\mathcal{U}=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ i & -i\end{pmatrix},\quad \mathcal{U}^\dagger=\mathcal{U}^{-1}=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & -i\\ 1 & i\end{pmatrix},\tag{5.2}$$

i.e.,

$$\Omega_{\rm A}'=\mathcal{U}^{-1}\Omega_{\rm A}\mathcal{U}=\begin{pmatrix}H_+ & 0\\ 0 & H_-\end{pmatrix},\tag{5.3}$$

where

$$H_\pm=H^2+\Delta^2\pm\hbar v_{\rm F}\Delta'=-\hbar^2v_{\rm F}^2\partial_x^2+\Delta^2\pm\hbar v_{\rm F}(\partial_x\Delta).\tag{5.4}$$

Thus, the spectrum of $\mathcal{H}_{\rm A}^2$ is given by the combined spectra of the two independent one-dimensional Schrödinger-like operators $H_\pm$.

It is worthwhile noticing that the Hamiltonian $\Omega_{\rm A}'$ is supersymmetric (SUSY) with $\Delta(x)$ playing the role of superpotential.[45] In the language of SUSY quantum mechanics, H_+ and H_- correspond to the fermionic and bosonic sectors, respectively, and supersymmetry means that the interchange of these two sectors of $\Omega_{\rm A}'$ leaves the dynamics of the system unchanged. The most useful properties which result from the SUSY of the Hamiltonian $\Omega_{\rm A}'$ can be summarized as follows.[54,45,55]

(1) The Hamiltonians $H_\pm$ can be expressed in terms of the ladder operators

$$Q\equiv-\hbar v_{\rm F}\partial_x+\Delta,\quad Q^\dagger=\hbar v_{\rm F}\partial_x+\Delta,\tag{5.5}$$

as

$$H_+=Q^\dagger Q,\quad H_-=QQ^\dagger.\tag{5.6}$$

(2) The Hamiltonians $H_\pm$ are positive-semidefinite isospectral (up to a zero mode) operators, i.e.,

$$H_\pm\phi_{\pm,n}=E_n^2\phi_{\pm,n},\tag{5.7}$$

where the eigenfunctions $\phi_{+,n}$ and $\phi_{-,n}$ are related through

$$\phi_{-,n}=\frac{1}{|E_n|}\,Q\phi_{+,n},\quad \phi_{+,n}=\frac{1}{|E_n|}\,Q^\dagger\phi_{-,n},\quad |E_n|>0.\tag{5.8}$$

(3) The pairing of the eigenstates of $H_\pm$ fails when $E_n=0$. A zero mode (eigenstate with zero energy) exists whenever one of the wave functions

$$\phi_{\pm,0}=\mathcal{N}\exp\left(\pm\int^x dy\,\Delta(y)\right)\tag{5.9}$$

is normalizable. Since at most one of the above wave functions is normalizable it is clear that one may have only one

zero mode belonging to the spectrum of either H_+ or H_-. Indeed, assuming, e.g., that $\phi_{+,0}$ exists, i.e., $H_+\phi_{+,0}=0$, then

$$\langle\phi_{+,0}|H_+|\phi_{+,0}\rangle=\langle\phi_{+,0}|Q^\dagger Q|\phi_{+,0}\rangle$$
$$=\|Q|\phi_{+,0}\rangle\|=0\Rightarrow\phi_{-,0}\propto Q\phi_{+,0}=0,$$

and similarly in the opposite case. The necessary condition that one of $\phi_{\pm,0}$ to be normalizable is that $\Delta(x)$ has different signs at $x=\pm\infty$ along the corresponding quasiclassical trajectory. While for conventional s-wave superconductors this condition is difficult to be met in zero magnetic field,[56] in the case of, e.g., unconventional d-wave superconductors $\Delta(x)$ can have different signs at the two opposite sides of a quasiclassical trajectory which connects two different lobes of the order parameter.[57–59] When the zero mode is absent we say that supersymmetry is spontaneously broken and the ground state of $\Omega'_{\rm A}$ is degenerate (for a given $\hat{\boldsymbol{u}}$ and $\boldsymbol{r}_\perp$). When the zero mode exists one has a good SUSY and the zero mode is the ground state of $\Omega'_{\rm A}$.

(4) Probably the most useful feature of SUSY quantum mechanics is that it allows us to calculate analytically both the spectrum and the eigenfunctions of the partner Hamiltonians $H_\pm$ by means of simple algebraic manipulations, provided that the partner potentials $U_\pm(x;a_0)\equiv\Delta^2(x;a_0)\pm\hbar v_{\rm F}\Delta'(x;a_0)$ are *shape invariant*,[60] i.e., when they obey the condition[45]

$$U_+(x;a_0)=U_-(x;a_1)+R(a_1),\tag{5.10}$$

where a_1 is a new set of parameters uniquely determined from the old ones a_0 via the mapping $a_1=F(a_0)$, and the residual term $R(a_1)$ is independent of x. A few examples of superpotentials which yield shape invariant potentials $U_\pm$ are (i) $\Delta(x;a_0)\propto a_0\tanh(\eta x)$, (ii) $\Delta(x;a_0)\propto 1+a_0\exp(-\eta x)$, (iii) $\Delta(x;a_0)\propto a_0/[1+\exp(-\eta x)]$, and (iv) $\Delta(x;a_0)\propto a_0(1+\eta x)$. For all these model pair potentials the eigenstates of the Andreev Hamiltonian can be determined analytically by using the machinery of SUSY quantum mechanics.[45] Once the eigenstates of $\mathcal{H}_{\rm A}$ have been determined it is possible to evaluate numerically the value of the parameter η by imposing the self-consistency condition (3.8). Successful calculations along this line have been reported by Bar-Sagi and Kuper[41,53] for the pair potential (i), by Clinton[42] for case (ii), and by Eilenberger and Jacobs[43] for cases (iii), (iv). Of course, in principle, it is possible to obtain analytical results for all known nontrivial superpotentials [i.e., $\Delta(x)$ in our case] which lead to shape invariant (or factorizable, in the language of Infeld and Hull[61]) potentials $U_\pm(x)$ with the possibility of even satisfying the self-consistency (gap) equation (3.8). Unfortunately none of these ''super'' pair potentials correspond to real physical situations and, therefore, we will not pursue here this issue in any further details. Nevertheless, it is fair to recognize the potential usefulness of the application of SUSY quantum mechanics in the study of inhomogeneous superconductors within the framework of the Andreev approximation, a fact which to our knowledge has not been fully realized so far in the literature.

Before proceeding any further it is useful to introduce new units for length $\mathcal{L}\equiv\hbar v_F/\Delta_0\sim\xi_0$, and for energy $\mathcal{E}\equiv\Delta_0$, where Δ_0 is a suitably chosen constant pair potential, e.g., the equilibrium BCS gap parameter at the considered temperature T. One can express $H_\pm$ in these new units by performing the following transformations in Eq. (5.4): $x\to x\mathcal{L}$, $\Delta\to\Delta\Delta_0$, and $H_\pm\to H_\pm\Delta_0$; one obtains

$$H_\pm=H^2+\Delta^2\pm\Delta'=-\partial_x^2+\Delta^2\pm\partial_x\Delta.\tag{5.11}$$

It is also convenient to measure the free energy density in units of $N_0\Delta_0^2$. We shall use these units throughout this section, except where otherwise stated.

In what follows, the fact that $H_\pm$ are supersymmetric will play no special role. The important thing is that $H_\pm$ are decoupled and Schrödinger-like.

Now we introduce the diagonal resolvents $R_\pm$ of the operators $H_\pm$ which will play the central role in our method for evaluating the free energy of an inhomogeneous superconductor in zero field. By definition

$$R_\pm(x;\lambda)\equiv R_\pm(x;\lambda;\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)=-\langle x|(\lambda-H_\pm)^{-1}|x\rangle.\tag{5.12}$$

Hence

$$\int_{-\infty}^{\infty}dx R(x;\lambda)=-\sum_n\ \frac{1}{\lambda-E_n^2},\tag{5.13}$$

and a similar relation holds for R_0 corresponding to the reference state described by the Hamiltonian $\mathcal{H}_0$. In Eq. (5.13) we have used the shorthand notation

$$R\equiv R_+ + R_-.\tag{5.14}$$

Next, one integrates both sides of Eq. (5.13) with respect to the spectral variable λ

$$\int^{\lambda}d\lambda\int_{-\infty}^{\infty}dx R(x;\lambda)=-\sum_n\ \ln|\lambda-E_n^2|+\text{const.}\tag{5.15}$$

The integration constant on the right-hand side (RHS) of Eq. (5.15) can be eliminated by subtracting from this equation the one corresponding to the reference state. By introducing the notation

$$\delta R\equiv R-R_0,\tag{5.16}$$

we get

$$\int_{-\infty}^{\lambda}d\lambda\int_{-\infty}^{\infty}dx\,\delta R(x;\lambda)=-\sum_n\ \ln\left|\frac{\lambda-E_n^2}{\lambda-\epsilon_n^2}\right|.\tag{5.17}$$

Finally, by setting $\lambda=-\omega_m^2$ in this last equation, the logarithm of the Fredholm determinant in Eq. (4.9) can be written in terms of the diagonal resolvent δR as

$$\ln\,\mathrm{Det}\left(\frac{\omega_m^2+\mathcal{H}_{\rm A}^2}{\omega_m^2+\mathcal{H}_0^2}\right)=\sum_n\ \ln\left(\frac{\omega_m^2+E_n^2}{\omega_m^2+\epsilon_n^2}\right)$$
$$=-\int_{-\infty}^{-\omega_m^2}d\lambda\int_{-\infty}^{\infty}dx\,\delta R(x;\lambda).\tag{5.18}$$

Thus, the free energy (4.9) becomes

$$\delta\mathcal{F}=2T\pi\int d^2r_\perp\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\sum_{\omega_m>0}\int_{-\infty}^{-\omega_m^2}d\lambda \times\int_{-\infty}^{\infty}dx\,\delta R(x;\lambda;\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)+\int d^3\boldsymbol{r}\,\frac{[\Delta(\boldsymbol{r})]^2}{V}, \tag{5.19}$$

where, for clarity, we have listed all the arguments of the diagonal resolvent.

Now the free energy density

$$\delta F=\frac{d(\delta\mathcal{F})}{d^3\boldsymbol{r}}=\frac{d(\delta\mathcal{F})}{dxd^2r_\perp}, \tag{5.20}$$

as a functional of the inhomogeneous pair potential, can be readily extracted from Eq. (5.19)

$$\delta F\equiv\delta F[\Delta(\boldsymbol{r})]=\left\langle 2\pi T\sum_{\omega_m>0}\int_{-\infty}^{-\omega_m^2}d\lambda\,\delta R\right\rangle+\frac{[\Delta(\boldsymbol{r})]^2}{V}, \tag{5.21}$$

where $\langle\cdots\rangle=\int d\Omega_{\hat{\boldsymbol{u}}}/4\pi\cdots$ means averaging over the directions of the quasiclassical trajectories. Note that the only difference between the cases, when the pair potential depends only on one coordinate and when it has an arbitrary $\boldsymbol{r}$ dependence, is that in the former case the diagonal resolvent does not depend on the impact parameter $\boldsymbol{r}_\perp$ whereas in the latter case it does. The above expression of the free energy density does not contain explicitly either the eigenvalues or the eigenfunctions of the Andreev Hamiltonian $\mathcal{H}_{\mathrm{A}}$. All the information about the superconductor is encapsulated in the diagonal resolvent δR which, however, needs to be determined first in order to make Eq. (5.21) useful.

Since $R_\pm$ are the diagonal resolvents of the one-dimensional Schrödinger operators $H_\pm=-\partial_x^2+U_\pm$, with $U_\pm=\Delta^2\pm\Delta'$, they obey the so-called Gelfand-Dikii equation[62,31]

$$-2R_\pm R_\pm''+R_\pm'^2+4R_\pm^2(U_\pm-\lambda)=1. \tag{5.22}$$

For completeness a simple derivation of this equation is provided in Appendix A (see also Ref. 63). Equations (5.21) and (5.22) tell us that the free energy density of an inhomogeneous superconductor can be expressed solely in terms of the solution of a nonlinear second order ordinary differential equation. Unfortunately the Gelfand-Dikii equation cannot be solved analytically for an arbitrary pair potential. However, both the diagonal resolvent and the free energy density can be calculated numerically once some appropriate boundary conditions have been specified. In this respect our method of calculating δF is similar to the ones considered by Waxman[47] and Eilenberger and Jacobs.[43] However, while their methods are applicable *only* to superconductors described by a pair potential which depends on a single spatial coordinate and in the absence of supercurrents and magnetic field, our method is valid for pair potentials with *arbitrary* spatial dependence, at any temperature and in the presence of supercurrents and magnetic field (see Sec. VI). Another important feature of our approach is that it provides a simple and systematic way for obtaining the gradient expansion of δF for an inhomogeneous superconductor with $\Delta(\boldsymbol{r})$ varying slowly on a length scale $l\gg\xi_0$.

B. Gradient expansion

For the normal state the pair potential $U_\pm=0$, and Eq. (5.22) yields

$$R_{0,\pm}=\frac{1}{2\sqrt{-\lambda}}. \tag{5.23}$$

For an arbitrary pair potential the general solution of the Gelfand-Dikii equation (5.22) can be sought as an asymptotic series expansion

$$R_\pm(x;\lambda)=\frac{1}{2}\sum_{k=0}^{\infty}R_k^\pm(x)(\Delta^2-\lambda)^{-k-1/2}, \tag{5.24}$$

where $\Delta\equiv\Delta(x)$ is the pair potential of the inhomogeneous superconductor, and $R_k^\pm(x)$ are expansion coefficients which ought to be determined. For the uniqueness (up to a sign) of this expansion see, e.g., Ref. 31. Equation (5.24) is the main ingredient in our derivation of the gradient expansion of δF. Our strategy is to express first δF in terms of $R_k^\pm(x)$, $k=0,1,\ldots$, and then to evaluate these expansion coefficients. The latter task can be accomplished in a systematic way by inserting Eq. (5.24) into the Gelfand-Dikii equation (5.22) and equating the coefficients of the different integer powers of $\zeta\equiv\Delta^2-\lambda$ in the resulting equation. Although this method can be used to derive a cumbersome analytical expression for the recursion relation obeyed by the coefficients $R_k^\pm(x)$, in practice it is more convenient to carry out the calculations by employing a computer software which is suitable for sophisticated symbolical calculations, such as MATHEMATICA.[64]

It is easy to see that the first coefficient $R_0^\pm=1$. Clearly, for the normal state $R_{0,0}^\pm=1$ and the rest of the coefficients vanish identically [cf. Eqs. (5.23) and (5.24)], i.e., $R_{0,k}^\pm=0$, $k=1,2,\ldots$. Thus, if one defines $\delta R_k\equiv R_k^+ + R_k^-$, $k=1,2,\ldots$, one can write

$$\delta R(x;\lambda)=\left(\frac{1}{\sqrt{\Delta^2-\lambda}}-\frac{1}{\sqrt{-\lambda}}\right)+\frac{1}{2}\sum_{k=1}^{\infty}\delta R_k(x)(\Delta^2-\lambda)^{-k-1/2}, \tag{5.25}$$

and

$$\begin{aligned}\int_{-\infty}^{-\omega_m^2}d\lambda\,\delta R(x;\lambda)&=\int_{-\infty}^{-\omega_m^2}d\lambda\left(\frac{1}{\sqrt{\Delta^2-\lambda}}-\frac{1}{\sqrt{-\lambda}}\right)+\frac{1}{2}\sum_{k=1}^{\infty}\delta R_k(x)\int_{-\infty}^{-\omega_m^2}\frac{d\lambda}{(\Delta^2-\lambda)^{k+1/2}}\\&=2(|\omega_m|-\sqrt{\omega_m^2+\Delta^2})+\frac{1}{2}\sum_{k=1}^{\infty}\frac{\delta R_k(x)}{(k-1/2)(\omega_m^2+\Delta^2)^{k-1/2}}.\end{aligned} \tag{5.26}$$

Inserting Eq. (5.26) into Eq. (5.21) yields

$$\delta F = 4\pi T \sum_{\omega_m>0} (|\omega_m| - \sqrt{\omega_m^2+\Delta^2}) + \frac{\Delta^2}{V} + \left\langle \sum_{k=1}^{\infty} \left[2\pi T \sum_{\omega_m>0} (\omega_m^2+\Delta^2)^{-k+1/2} \right] \frac{\delta R_k(x)}{2k-1} \right\rangle. \tag{5.27}$$

The first two terms on the RHS of Eq. (5.27) give the well known bulk term contribution to the free energy density of the superconducting state with respect to the normal state, while the third term gives the actual gradient expansion in term of asymptotic power series of the derivatives of the real pair potential $\Delta(x)$.

Following the above mentioned strategy for calculating the expansion coefficients $R_{\pm}$, we wrote a MATHEMATICA code which evaluates analytically, in a systematic fashion, these coefficients. Here we apply our results to calculate the gradient expansion of δF up to the fourth order terms, i.e.,

$$\delta F \approx \delta F_0 + \delta F_2 + \delta F_4, \tag{5.28}$$

where δF_0 is given by the first two terms on the RHS of Eq. (5.27). Since $\delta R_1 = 0$ there is no first order correction to δF. In fact one can easily show, based on symmetry arguments, that all odd order contributions to the gradient expansion vanishes identically. This does not mean, of course, that all odd order expansion coefficients δR_{2k+1} are equal to zero.

To calculate δF_2 one needs the following coefficients:

$$\delta R_2 = \frac{1}{4}(\Delta^2 - 2\Delta\Delta''), \tag{5.29a}$$

$$\delta R_3 = \frac{1}{16}(20\Delta^2\Delta'^2 - \Delta''^2 + 2\Delta'\Delta^{(3)} - 2\Delta\Delta^{(4)}). \tag{5.29b}$$

Note that while δR_2 contains only terms of second order in the small parameter ξ_0/l, the coefficient δR_3 contains both second and fourth order terms as well. None of the higher order coefficients δR_k contain other second order terms in ξ_0/l. One of the main features of our method is that it can automatically collect all the terms of a given order in the various relevant expansion coefficients δR_k. Inserting all the second order terms from Eqs. (5.29) into Eq. (5.27) one obtains

$$\delta F_2 = \frac{1}{12} \left\langle 2\pi T \sum_{\omega_m>0} \left[\frac{\Delta'^2 - 2\Delta\Delta''}{(\omega_m^2+\Delta^2)^{3/2}} + 5\frac{\Delta^2\Delta'^2}{(\omega_m^2+\Delta^2)^{5/2}} \right] \right\rangle. \tag{5.30}$$

One can easily see that the second term (proportional to Δ'') on the RHS of Eq. (5.30) can also be expressed in terms of Δ'^2. Indeed, we have

$$\frac{\Delta\Delta''}{(\omega_m^2+\Delta^2)^{3/2}} = \frac{\Delta}{(\omega_m^2+\Delta^2)^{3/2}} \frac{d\Delta'}{dx} = \frac{d}{dx}\left[\frac{\Delta\Delta'}{(\omega_m^2+\Delta^2)^{3/2}} \right] - \frac{\Delta'^2}{(\omega_m^2+\Delta^2)^{3/2}} + \frac{3\Delta^2\Delta'^2}{(\omega_m^2+\Delta^2)^{5/2}}. \tag{5.31}$$

Upon integration with respect to x, the total derivative on the RHS yields a surface term in the free energy which, for a bulk superconductor with natural boundary conditions, vanishes. Therefore, this total derivative can be dropped in δF_2. In more complex superconductivity problems such surface terms may lead to anomalous terms in the free energy functional.[43] Nevertheless, it is important to notice that it is always possible to express the gradient expansion of the free energy density in terms of even powers of the pair potential and its derivatives. Another virtue of the computer implementation of our method is that it can automatically perform these partial integrations and return the final result for δF_k in the desired form.

Thus, Eq. (5.30) can be rewritten as

$$\delta F_2 = \frac{1}{4} \left\langle 2\pi T \sum_{\omega_m>0} \left[\frac{\Delta'^2}{(\omega_m^2+\Delta^2)^{3/2}} - \frac{\Delta^2\Delta'^2}{(\omega_m^2+\Delta^2)^{5/2}} \right] \right\rangle. \tag{5.32}$$

Next, we perform the average over $\hat{\boldsymbol{u}}$, i.e., the directions of the quasiclassical trajectories; the relevant expression is

$$\langle f(\Delta)\Delta'^2 \rangle = \langle f(\Delta)(\hat{\boldsymbol{u}}\cdot\nabla\Delta)^2 \rangle = \langle n_i n_j \rangle f(\Delta)(\partial_i\Delta)(\partial_j\Delta) = \frac{1}{3} f(\Delta)\delta_{ij}(\partial_i\Delta)(\partial_j\Delta) = \frac{1}{3} f(\Delta)(\nabla\Delta)^2, \tag{5.33}$$

where $f(\Delta)$ is an arbitrary function of the pair potential. This last result clearly depends on dimensionality; in d dimensions $\langle n_i n_j \rangle = (1/d)\delta_{ij}$. Inserting the above results into Eq. (5.32), and restoring the original units, one obtains

$$\delta F_2 = \frac{1}{12} \pi T N_0 (\hbar v_F)^2 \sum_{\omega_m>0} \frac{\omega_m^2}{(\omega_m^2+\Delta^2)^{5/2}} (\nabla\Delta)^2, \tag{5.34}$$

This expression coincides with the well known Werthamer result [Eq. (129) in Ref. 65] for a clean superconductor in the absence of supercurrents and magnetic field, obtained by means of many-body Green's functions.

The complexity of calculating the successive terms in the gradient expansion of δF increases exponentially with the order of the term. Nevertheless, by using the computer implementation of our method we were able to compute in matter of minutes the fourth order term δF_4. For this purpose one needs to evaluate the expansion coefficients δR_k, $k=3,\ldots,6$ and then filter out all the fourth order terms in the small parameter ξ_0/l. After collecting all these terms, we obtain the following expression for the fourth order term in the gradient expansion of δF

$$\delta F_4=\frac{1}{16}\left\langle 2\pi T\sum_{\omega_m>0}\left[\frac{7}{4}\left(\frac{5\Delta^2\omega_m^2}{(\omega_m^2+\Delta^2)^{11/2}}-\frac{\omega_m^2}{(\omega_m^2+\Delta^2)^{9/2}}\right)\Delta'^4-\frac{\omega_m^2}{(\omega_m^2+\Delta^2)^{7/2}}\Delta''^2\right]\right\rangle. \tag{5.35}$$

This result has been obtained after dropping irrelevant total derivatives in order to express the final result only in terms of even powers of the first and second derivatives of Δ, the only ones which contribute to the fourth order term in the gradient expansion. To obtain the final expression for δF_4 all we need to do is to average over the directions of the quasiclassical trajectories and to restore the original units.

Apparently, in the derivation of the results presented so far, the particular form of the Fermi-Dirac distribution function of the quasiparticles together with formula (3.14) were crucial. In what follows we show that this is not the case and that our method of evaluating the free energy of an inhomogeneous superconductor can be formulated in a more general form which is also applicable for a nonequilibrium distribution function f_i of the quasiparticles. The basic idea is to express the free energy density in terms of the *local density of states* corresponding to the Andreev Hamiltonian (i.e., along an individual quasiclassical trajectory).

C. Local density of states

In this section we present an alternative derivation of the expressions (5.27) of the free energy density for the case of thermal equilibrium without invoking formula (3.14) but rather rewriting the summation (4.3) over the complete set of states i as

$$\sum_i \cdots=\pi\hbar v_F N_0\int d^2r_\perp\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\sum_n\cdots$$

$$=\pi\hbar v_F N_0\int d^2r_\perp\left\langle\int_0^\infty\rho(E)dE\cdots\right\rangle, \tag{5.36}$$

where the density of states (DOS) along the quasiclassical trajectory determined by $(\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)$ is given by

$$\rho(E)\equiv\rho(E;\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)=\sum_n\delta[E-E_n(\hat{\boldsymbol{u}},\boldsymbol{r}_\perp)]. \tag{5.37}$$

Here $\{E_n\}$ represent the energy spectrum of the Andreev Hamiltonian. Next, let us define the DOS corresponding to the SUSY Hamiltonians $H_\pm$

$$\tilde{\rho}(E)=\rho_+(E)+\rho_-(E)\equiv\sum_n\delta(E^2-E_n^2)$$

$$=\frac{1}{2E}\sum_n\delta(E-E_n)=\frac{\rho(E)}{2E}. \tag{5.38}$$

Thus, from Eqs. (5.38) and (5.13), by employing the formula

$$\frac{1}{x\pm i0^+}\equiv\lim_{\varepsilon\to0^+}\frac{1}{x\pm i\varepsilon}=\mp i\pi\delta(x)+\mathcal{P}\frac{1}{x},$$

the DOS $\rho(E)$ can be expressed in terms of the diagonal resolvent $R=R_+ +R_-$ as

$$\rho(E)=2E\tilde{\rho}(E)=-\frac{2E}{\pi}\,\mathrm{Im}\sum_n\frac{1}{E^2-E_n^2+i0^+}$$

$$=\frac{2E}{\pi}\lim_{\varepsilon\to0^+}\mathrm{Im}\int_{-\infty}^{\infty}dx R(x;E^2+i\varepsilon). \tag{5.39}$$

Now combining equations (3.13), (5.36), and (5.39) lead us to the following expression for the free energy density:

$$F=-2\pi T\int_0^\infty dE\rho(E;\boldsymbol{r})\ln\left(2\cosh\frac{E}{2T}\right)+\frac{\Delta^2}{V}$$

$$=-4T\lim_{\varepsilon\to0^+}\mathrm{Im}\int_0^\infty EdE\,\ln\left(2\cosh\frac{E}{2T}\right)\langle R(x;E^2+i\varepsilon)\rangle+\frac{\Delta^2}{V}, \tag{5.40}$$

where, by definition, the local DOS is given by

$$\rho(E;\boldsymbol{r})\equiv\frac{2E}{\pi}\,\mathrm{Im}\langle R(x;E^2+i0^+)\rangle, \tag{5.41a}$$

or in conventional units [cf. Eq. (5.36)]

$$\rho(E;\boldsymbol{r})=2\hbar v_F N_0 E\,\mathrm{Im}\langle R(x;E^2+i0^+)\rangle. \tag{5.41b}$$

The next step is to subtract from Eq. (5.40) the free energy density corresponding to the reference normal state and to replace δR in the resulting expression by its asymptotic series expansion (5.25), i.e.,

$$\delta R(x;E^2+i\varepsilon)=\left(\frac{1}{\sqrt{\Delta^2-E^2-i\varepsilon}}-\frac{1}{\sqrt{-E^2-i\varepsilon}}\right)+\frac{1}{2}\sum_{k=1}^{\infty}\delta R_k(x)(\Delta^2-E^2-i\varepsilon)^{-k-1/2}. \tag{5.42}$$

Thus, the free energy density $\delta F=F-F_N$ becomes

$$\delta F=\delta F_0-2T\sum_{k=1}^{\infty}\lim_{\varepsilon\to0^+}\mathrm{Im}\int_0^\infty EdE\times\frac{\ln[2\cosh(E/2T)]}{(\Delta^2-E^2-i\varepsilon)^{k+1/2}}\langle\delta R_k(x)\rangle, \tag{5.43}$$

where, the zeroth order term in the gradient expansion of δF is given by

$$\delta F_0=-4T\lim_{\varepsilon\to0^+}\mathrm{Im}\int_0^\infty EdE\,\ln\left(2\cosh\frac{E}{2T}\right)\times\left(\frac{1}{\sqrt{\Delta^2-E^2-i\varepsilon}}-\frac{1}{\sqrt{-E^2-i\varepsilon}}\right)+\frac{\Delta^2}{V}. \tag{5.44}$$

By employing contour integration in the complex plane, it can be shown (see Appendix C) that Eq. (5.44) coincides

precisely with the first two terms on the RHS of Eq. (5.27). Equation (5.43) can be further simplified through integration by parts

$$\int_0^\infty \frac{EdE}{(1-E^2-i\varepsilon)^{k+1/2}} \ln\left(2\cosh\frac{E}{2T}\right) = -\frac{1}{2T(2k-1)} \int_0^\infty dE \frac{\tanh(E/2T)}{(1-E^2-i\varepsilon)^{k-1/2}}. \tag{5.45}$$

Hence

$$\delta F = \delta F_0 + \sum_{k=1}^{\infty} \frac{\langle \delta R_k(x)\rangle}{2k-1} \lim_{\varepsilon\to 0^+} \mathrm{Im} \int_0^\infty dE \times \frac{\tanh(E/2T)}{(1-E^2-i\varepsilon)^{k-1/2}}. \tag{5.46}$$

By using complex contour integration, it can be shown that (see Appendix C)

$$\begin{aligned} c_k(T) &\equiv \lim_{\varepsilon\to 0^+} \mathrm{Im} \int_0^\infty dE \frac{\tanh(E/2T)}{(1-E^2-i\varepsilon)^{k-1/2}} \\ &= 2\pi T \sum_{\omega_m>0} (\omega_m^2+1)^{-k+1/2} \\ &= \lim_{\varepsilon\to 0^+} \mathrm{Re} \int_0^\infty dE \frac{\tanh(E/2T)}{\sqrt{\tilde{E}^2-1}(1-\tilde{E}^2)^{k-1}}, \quad k=2,3,\ldots, \end{aligned} \tag{5.47}$$

where $\tilde{E}\equiv E+i\varepsilon$. Finally, inserting Eq. (5.47) into Eq. (5.46) leads to our previous result (5.27) and, therefore, to Eq. (5.27) which can be also written as

$$\delta F = \delta F_0 + \sum_{k=2}^{\infty} \frac{c_k(T)}{2k-1} \langle \delta R_k(x)\rangle. \tag{5.48}$$

The coefficients $c_k(T)$ can be calculated by using their integral representation (5.47). By employing the identity $\tanh(E/2T)=1-2f(E)$, where $f(E)$ is the Fermi function, one can separate $c_k(T)$ into a temperature independent and a temperature dependent part; the T-independent part can be calculated analytically and $c_k(T)$ becomes

$$\begin{aligned} c_k(T) &= \lim_{\varepsilon\to 0^+} \mathrm{Re} \int_0^\infty dE \frac{1-2f(E)}{\sqrt{\tilde{E}^2-1}(1-\tilde{E}^2)^{k-1}} \\ &= \frac{2^{k-2}(k-2)!}{(2k-3)!!} \\ &\quad - \lim_{\varepsilon\to 0^+} \mathrm{Re} \int_0^\infty dE \frac{2f(E)}{\sqrt{\tilde{E}^2-1}(1-\tilde{E}^2)^{k-1}}. \end{aligned} \tag{5.49}$$

Furthermore, by repeated partial integration, the second term on the RHS of Eq. (5.49) can be expressed as an improper definite integral involving the derivatives of the Fermi function and the familiar BCS DOS

$$\rho_0(E) = \frac{E\Theta(E-1)}{\sqrt{E^2-1}}. \tag{5.50}$$

For convenience we list below the expressions of the coefficients $c_k(T)$ for $k=2$ and 3

$$c_2(T) = 1-2\int_0^\infty \rho_0(E)dE\left(-\frac{\partial f}{\partial E}\right) = \frac{\rho_s(T)}{\rho_s(0)}, \tag{5.51}$$

$$c_3(T) = \frac{2}{3} - \frac{2}{3}\int_0^\infty \rho_0(E)dE\left(-\frac{\partial f}{\partial E}\right) - \frac{1}{3}\int_0^\infty \rho_0(E)dE\left(\frac{\partial f}{\partial E}\right)^2, \tag{5.52}$$

where $\rho_s(T)$ is the superfluid density at temperature T.

As we have already mentioned, this second method of calculating the free energy of an inhomogeneous superconductor by means of the effective local density of states (5.41a) is quite general and in fact it is applicable for an arbitrary distribution f_i of the Bogoliubov quasiparticles, as we show in the next section.

D. Nonequilibrium free energy density

Consider a superconducting state in which the quasiparticles are out of equilibrium with the condensate. We also assume that the superconducting state can be described by the effective mean-field Hamiltonian (2.1), with a pair potential $\Delta(\boldsymbol{r})$ and a nonequilibrium quasiparticle distribution function $f(E;\boldsymbol{r})$. Then, the local DOS $\rho(E;\boldsymbol{r})$ given by Eq. (5.41b) is applicable with the same diagonal resolvent $R_\pm$ studied in the previous sections. Thus, one can immediately write down the expressions for the energy (W) and entropy (S) densities of the system

$$W = \frac{[\Delta(\boldsymbol{r})]^2}{V} - \int_0^\infty EdE\rho(E;\boldsymbol{r})[1-2f(E;\boldsymbol{r})] \tag{5.53}$$

and

$$S = \int_0^\infty dE\rho(E;\boldsymbol{r})\{f(E;\boldsymbol{r})\ln f(E;\boldsymbol{r}) + [1-f(E;\boldsymbol{r})]\ln[1-f(E;\boldsymbol{r})]\}. \tag{5.54}$$

The usefulness of these equations depends on the problem at hand. For example, if the system is in local thermal equilibrium, such that a local temperature $T(\boldsymbol{r})$ can be defined and the distribution function of the quasiparticles can be expressed, e.g., as $f(E;\boldsymbol{r})=(\exp[E/T(\boldsymbol{r})]+1)^{-1}$, then it make sense to define a free energy density through the usual thermodynamic relation $F=W-TS$. Furthermore, assuming that the considered superconducting state is close to the equilibrium BCS state, it is straightforward to derive a gradient expansion formula for δF along the line discussed in the previous sections.

VI. SUPERCONDUCTOR IN THE PRESENCE OF THE MAGNETIC FIELD AND SUPERCURRENTS

A. Free energy

For $\Delta(\mathbf{r})=|\Delta|e^{i\theta}$ complex, with a general spatial dependence of the phase θ, and in the presence of a static magnetic field the squared Hamiltonian $\mathcal{H}_A^2$ cannot be rotated into a matrix with second-order differential operators on the diagonal and off-diagonal terms equal to zero. Consequently we will go back to the expression for the free energy (4.9), but now written as

$$\mathcal{F}=-2T\pi\hbar v_F N_0\int d^2r_\perp\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\sum_{\omega_m}\ \ln\mathrm{Det}(i\omega_m+\mathcal{H}_A)+\int d^3\boldsymbol{r}\,\frac{|\Delta(\mathbf{r})|^2}{V}+\mathcal{F}_H. \tag{6.1}$$

Here we use the factorization $\omega_m^2+E_n^2=(i\omega_m+E_n)(-i\omega_m+E_n)$, so the sum now goes over both positive and negative Matsubara frequencies.

The determinant stays unchanged when we make the unitary transformation

$$\mathcal{H}_A\equiv\begin{pmatrix}-i\hbar v_F\partial_x-v_F\dfrac{e}{c}A_{\boldsymbol{u}} & |\Delta|e^{i\theta}\\ |\Delta|e^{-i\theta} & i\hbar v_F\partial_x-v_F\dfrac{e}{c}A_{\boldsymbol{u}}\end{pmatrix}$$

$$\to\tilde{\mathcal{H}}_A\equiv\begin{pmatrix}e^{-i\theta/2}&0\\0&e^{i\theta/2}\end{pmatrix}\mathcal{H}_A\begin{pmatrix}e^{i\theta/2}&0\\0&e^{-i\theta/2}\end{pmatrix}=\begin{pmatrix}-i\hbar v_F\partial_x+v_F m v_{s_{\boldsymbol{u}}} & |\Delta|\\ |\Delta| & i\hbar v_F\partial_x+v_F m v_{s_{\boldsymbol{u}}}\end{pmatrix}. \tag{6.2}$$

Here

$$A_{\boldsymbol{u}}\equiv\hat{\boldsymbol{u}}\cdot\mathbf{A}$$

and

$$v_{s_{\boldsymbol{u}}}\equiv\hat{\boldsymbol{u}}\cdot\boldsymbol{v}_s\equiv\hat{\boldsymbol{u}}\cdot\frac{\hbar}{2m}\left(\nabla\theta-\frac{2e}{\hbar c}\mathbf{A}\right),$$

are, respectively, the components of the vector potential and the superfluid velocity in the direction of the quasiclassical trajectory. In what follows, it is more convenient to use the Hamiltonian $\tilde{\mathcal{H}}_A$ instead of $\mathcal{H}_A$.

As in the absence of the magnetic field and supercurrents, the Fredholm determinant in Eq. (6.1) can be calculated from the trace of the *matrix* resolvent [cf. Eq. (5.18)]

$$G(x,y;\mathbf{r}_\perp,\hat{\boldsymbol{u}};\lambda)\equiv\langle x|(\tilde{\mathcal{H}}_A-\lambda)^{-1}|y\rangle.$$

We have

$$\begin{aligned}\ln\mathrm{Det}(i\omega_m+\tilde{\mathcal{H}}_A)&=\sum_n\ \ln(i\omega_m+E_n)\\&=-\sum_n\int^{-i\omega_m}\frac{d\lambda}{E_n-\lambda}\\&=-\int^{-i\omega_m}d\lambda\ \mathrm{Tr}\,G(\lambda)\\&=-\int^{-i\omega_m}d\lambda\int dx\ \mathrm{tr}\,G(x,x;\mathbf{r}_\perp,\hat{\boldsymbol{u}};\lambda).\end{aligned} \tag{6.3}$$

In Eq. (6.3) the notation Tr means the trace of the differential operator, and so involves integration over x, while the symbol tr means a summation over the two spin indices only. In the following, for brevity we will omit the arguments $\mathbf{r}_\perp$ and $\hat{\boldsymbol{u}}$.

As shown in Appendix B, the 2×2 matrix $G(x,x;\lambda)$ is obtained from the matrix function $g(x;\lambda)\equiv G(x,x;\lambda)\sigma_3$, which satisfies the Eilenberger equation

$$i\hbar v_F g'+\left[\begin{pmatrix}\lambda-v_F m v_{s_{\boldsymbol{u}}} & -|\Delta|\\ |\Delta| & -\lambda+v_F m v_{s_{\boldsymbol{u}}}\end{pmatrix},g\right]=0. \tag{6.4}$$

The Eilenberger (or quasiclassical Green's) function $g(x;\lambda)$ also satisfies

$$\mathrm{tr}\,g=0,\quad g^2=-\frac{1}{4\hbar^2v_F^2}\sigma_0. \tag{6.5}$$

In terms of $g(x;\lambda)$, the free-energy density is given by

$$F=2T\pi\hbar v_F N_0\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\sum_{\omega_m}\int^{-i\omega_m}d\lambda\ \mathrm{tr}\{g(x;\lambda)\sigma_3\}+\frac{|\Delta(\boldsymbol{r})|^2}{V}+F_H. \tag{6.6}$$

B. Gradient expansion

To obtain the gradient expansion of the free energy density F, we rewrite the Eilenberger equation (6.4) in the form

$$i\hbar v_F g'+[V,g]+[A,g]=0, \tag{6.7}$$

where

$$A=\begin{pmatrix}\lambda & -|\Delta|\\ |\Delta| & -\lambda\end{pmatrix}$$

is of the zeroth order and

$$V=\begin{pmatrix}-v_F m v_{s_{\boldsymbol{u}}} & 0\\ 0 & v_F m v_{s_{\boldsymbol{u}}}\end{pmatrix}$$

is of the first order in gradients of the order parameter.

The contribution of the zeroth order to g satisfies the equation

$$[A,g_0]=0, \tag{6.8}$$

and so it is at every point the Eilenberger function for a homogeneous superconductor with constant real order parameter that would be equal to $|\Delta|$ at that point. This may be calculated explicitly from the resolvent. We find

$$g_0(x;\lambda)=\frac{i}{2\hbar v_F\sqrt{\lambda^2-|\Delta|^2}}\begin{pmatrix}\lambda & -|\Delta|\\ |\Delta| & -\lambda\end{pmatrix}, \tag{6.9}$$

which indeed satisfies Eq. (6.8).

To obtain the higher-order terms, it is convenient to transform to the basis of eigenvectors of A. That is we find a matrix B such that $B^{-1}AB=\mathrm{diag}$. The eigenvalues of A are $\pm\zeta$ with $\zeta\equiv\sqrt{\lambda^2-|\Delta|^2}$, and

$$B=\begin{pmatrix}\lambda+\zeta & |\Delta|\\ |\Delta| & \lambda+\zeta\end{pmatrix}. \tag{6.10}$$

A general matrix $M=M^{(0)}\sigma_0+\cdots+M^{(3)}\sigma_3$ (where σ_α, $\alpha=1,2,3$, are the Pauli matrices, and σ_0 is the 2×2 identity matrix) transforms into $\hat{M}\equiv\hat{M}^{(0)}\sigma_0+\cdots+\hat{M}^{(3)}\sigma_3\equiv B^{-1}MB$, where

$$\hat{M}^{(0)}=M^{(0)}, \tag{6.11a}$$

$$\hat{M}^{(1)}=M^{(1)}, \tag{6.11b}$$

$$\begin{pmatrix}\hat{M}^{(2)}\\ \hat{M}^{(3)}\end{pmatrix}=\frac{1}{\zeta}\begin{pmatrix}\lambda & i|\Delta|\\ -i|\Delta| & \lambda\end{pmatrix}\begin{pmatrix}M^{(2)}\\ M^{(3)}\end{pmatrix}. \tag{6.11c}$$

This transformation is complex-orthogonal rather than unitary, because it was supposed to rotate $-i|\Delta|\sigma_2+\lambda\sigma_3$ with one component purely imaginary into $\zeta\sigma_3$, as it, indeed, does.

Next we define

$$R(x;\lambda)\equiv B^{-1}g(x;\lambda)B. \tag{6.12}$$

Then

$$B^{-1}g'B=R'+[B^{-1}B',R]. \tag{6.13}$$

From Eq. (6.10), we obtain

$$B^{-1}B'=\frac{\lambda|\Delta|'}{2\zeta^2}\,\sigma_1+B_0,$$

where B_0 is proportional to the unit matrix σ_0 and, therefore, contributes nothing to the commutator with R in Eq. (6.13). Hence, in this new basis, Eq. (6.7) reads

$$i\hbar v_F R'(x;\lambda)+[U,R(x;\lambda)]+\zeta[\sigma_3,R(x;\lambda)]=0, \tag{6.14}$$

where $U\equiv B^{-1}VB+i\hbar v_F(B^{-1}B')^{(1)}$ is given by

$$U^{(1)}=\frac{i\hbar v_F\lambda|\Delta|'}{2\zeta^2}, \tag{6.15a}$$

$$U^{(2)}=-\frac{i|\Delta|v_F m v_{s_u}}{\zeta}, \tag{6.15b}$$

$$U^{(3)}=-\frac{\lambda v_F m v_{s_u}}{\zeta}, \tag{6.15c}$$

and R satisfies the conditions

$$\mathrm{tr}\,R(x;\lambda)\equiv0,\quad R^2\equiv-\frac{1}{4\hbar^2v_F^2}\,\sigma_0. \tag{6.16}$$

It is this matrix function $R(x;\lambda)$ that is the analog of the *scalar* resolvent (5.12); hence we denote it by the same letter. The function R can be expanded into the asymptotic series[31]

$$R=\sum_{n=0}^{\infty}R_n\zeta^{-n}, \tag{6.17}$$

where

$$R_0\equiv B^{-1}g_0B=\frac{i}{2\hbar v_F}\,\sigma_3. \tag{6.18}$$

We have somewhat generalized Dikii's work,[31] because the expansion parameter ζ^{-1} is x dependent, and has to be, therefore, differentiated too when we substitute Eq. (6.17) into Eq. (6.14). The derivative of the nth order term in the expansion is

$$(R_n\zeta^{-n})'=R_n'\zeta^{-n}-nR_n\zeta'\zeta^{-n-1}.$$

If we multiply ζ by a constant C, both terms will be multiplied by C^{-n}, so they are both of the order n in ζ^{-1}. Equating the nth order term in Eq. (6.14) to zero, we obtain the recurrence relation

$$i\hbar v_F\left(R_n'-n\,\frac{\zeta'}{\zeta}\,R_n\right)+[U,R_n]+[\sigma_3,R_{n+1}]=0. \tag{6.19}$$

If we write $R_n=R_n^{(0)}\sigma_0+\cdots+R_n^{(3)}\sigma_3$, then $R_n^{(0)}=0$ since $\mathrm{tr}\,R=0$, and the remaining components satisfy the following recurrence relations:

$$R_{n+1}^{(1)}=-\frac{1}{2}\,\hbar v_F\left(R_n^{(2)\prime}-n\frac{\zeta'}{\zeta}\,R_n^{(2)}\right)+U^{(1)}R_n^{(3)}-U^{(3)}R_n^{(1)}, \tag{6.20a}$$

$$R_{n+1}^{(2)}=\frac{1}{2}\,\hbar v_F\left(R_n^{(1)\prime}-n\frac{\zeta'}{\zeta}\,R_n^{(1)}\right)+U^{(2)}R_n^{(3)}-U^{(3)}R_n^{(2)}, \tag{6.20b}$$

$$(R_n^{(3)}\zeta^{-n})'=2\frac{\zeta^{-n}}{\hbar v_F}(U^{(2)}R_n^{(1)}-U^{(1)}R_n^{(2)}). \tag{6.20c}$$

Note that there is no recurrence relation for the coefficients $R_n^{(3)}$, but only for the derivative of $R_n^{(3)}\zeta^{-n}$. For $\zeta=\mathrm{const}$, the theory in Ref. 31 guarantees that the right-hand side of Eq. (6.20c) is always a derivative of a polynomial in entries of U and their derivatives. The integration is, therefore, always possible, but it leaves an undetermined constant in every $R_n^{(3)}$. These constants together with the constants in $R_n^{(0)}$ (which are set to zero in our case since $\mathrm{tr}\,R=0$) determine the solution of Eq. (6.14) uniquely. The product of two such solutions again solves Eq. (6.14), so all the solutions of Eq. (6.14) form an infinitely dimensional commutative algebra over the field of complex numbers. Equivalently, they

form a two-dimensional algebra over the field of formal series in ζ^{-1} with constant coefficients.

For ζ spatially dependent, a simple extension of Dikii's theory shows that the right-hand side of Eq. (6.20c) can still be integrated; now it will contain also powers and derivatives of ζ^{-1}. However, the spatial dependence of ζ forces all the constants on the diagonal of R_n to be zero for $n>0$, so the solution of Eq. (6.14) is completely determined by constants on the diagonal of R_0. Moreover, the only solution with $R_0=\sigma_0$ is σ_0 itself, so an arbitrary solution can be written as

$$R=R_0^{(0)}\sigma_0+R_0^{(3)}\tilde{R},$$

where $R_0^{(0)}$ and $R_0^{(3)}$ are complex numbers, and $\tilde{R}$ is the *unique* solution with $\tilde{R}_0=\sigma_3$. Hence, the spatial dependence of ζ keeps the algebra two-dimensional, but reduces the coefficient field from formal infinite series to complex numbers. The algebra is therefore reduced to the two-dimensional Clifford algebra Cl(1,C). In our case, $R=(i/2\hbar v_F)\tilde{R}$. The algebra structure then *forces* $R^2=-(1/4\hbar^2 v_F^2)\sigma_0$, in agreement with Eq. (6.16).

In terms of the expansion coefficients $R_n^{(\alpha)}$ the free-energy density has the form

$$F=4T\pi\hbar v_F N_0\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\sum_{\omega_m}\int^{-i\omega_m}d\lambda \times\sum_{n=0}^{\infty}\frac{i|\Delta|R_n^{(2)}(x;\lambda)+\lambda R_n^{(3)}(x;\lambda)}{\zeta^{n+1}}+\frac{|\Delta|^2}{V}+F_H. \tag{6.21}$$

So, to evaluate the free energy density we just need to find the coefficients R_n^{α} from the recurrence relations (6.20) with the initial condition (6.18), substitute them into Eq. (6.21), and perform the Matsubara sum and the λ and $\hat{\boldsymbol{u}}$ integrations. All the λ integrals are of the form

$$I_{\lambda,k}\equiv\int^{-i\omega_m}d\lambda\,\frac{i\lambda}{(\sqrt{\lambda^2-|\Delta|^2})^{2k+1}}, \tag{6.22}$$

where k is a non-negative integer.

For $k=0$, the integral diverges, and therefore needs special treatment. If we subtract from Eq. (6.21) the free-energy density of a normal metal F_N then the difference of the corresponding integrals becomes finite

$$I_{\lambda,0}=\int^{-i\omega_m}d\lambda\left(\frac{i\lambda}{\sqrt{\lambda^2-|\Delta|^2}}-\frac{i\lambda}{\sqrt{\lambda^2}}\right)=|\omega_m|-\sqrt{\omega_m^2+|\Delta|^2}. \tag{6.23}$$

Using $R_0^{(3)}=i/2\hbar v_F$, we find the zeroth-order contribution to the free energy density

$$F_0(\mathbf{r})-F_N=4\pi TN_0\sum_{\omega_m>0}^{\omega_D}(\omega_m-\sqrt{\omega_m^2+|\Delta|^2})+\frac{|\Delta|^2}{V}+F_H, \tag{6.24}$$

where the spurious divergence of the infinite frequency sum can be eliminated, as usually, by cutting it off at the Debye frequency ω_D.

The first-order term $F_1(\boldsymbol{r})$ vanishes because it contains one vector $\hat{\boldsymbol{u}}$ to be averaged over the unit sphere which gives zero. For $k>1$,

$$I_{\lambda,k}=\frac{i^{-2k}}{2k-1}(\omega_m^2+|\Delta|^2)^{-k+1/2}. \tag{6.25}$$

Finally, for the average over the direction $\hat{\boldsymbol{u}}$, we use the symmetric integration formula

$$\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}(\boldsymbol{v}_{(1)}\cdot\hat{\boldsymbol{u}})\cdots(\boldsymbol{v}_{(2k)}\cdot\hat{\boldsymbol{u}}) =\frac{\Sigma_{\pi=\mathrm{perm}}(\boldsymbol{v}_{(\pi_1)}\cdot\boldsymbol{v}_{(\pi_2)})\cdots(\boldsymbol{v}_{(\pi_{2k-1})}\cdot\boldsymbol{v}_{(\pi_{2k})})}{(2k+1)!}. \tag{6.26}$$

In this expression many of the terms will be the same. Indeed when vectors $\boldsymbol{v}_{(j)}$ are all different the numerator on the RHS of Eq. (6.26) contains only $(2k)!/k!2^k$ distinct terms rather than $(2k)!$. Note that for an odd number of vectors, the $\hat{\boldsymbol{u}}$ integral vanishes.

Using MATHEMATICA, we obtained the expansion of the free energy density functional up to the eighth order in gradients of the order parameter. The terms are getting progressively longer, so we list them below only up to the fourth order. To make the formula shorter, we do not perform the $\hat{\boldsymbol{u}}$ averaging in the fourth order, just denote it by $\langle\cdots\rangle$ around the 21 fourth-order terms. Leaving the explicit directional averaging to the reader has been customary in the literature. Also, in the fourth-order terms we write primes instead of gradients. As an example, $\langle\mathbf{v}_s|\Delta|'\mathbf{v}_s'\rangle$ means

$$\frac{1}{15}\sum_{i,j}\{v_{si}(\mathbf{r})[\partial_i|\Delta(\mathbf{r})|]\partial_j v_{sj}(\mathbf{r})+v_{si}(\mathbf{r})[\partial_j|\Delta(\mathbf{r})|]\partial_i v_{sj}(\mathbf{r}) +v_{si}(\mathbf{r})[\partial_j|\Delta(\mathbf{r})|]\partial_j v_{si}(\mathbf{r})\}.$$

In this notation, the expansion up to the fourth order reads

$$F(\mathbf{r})-F_N=4\pi TN_0\sum_{\omega_m>0}^{\omega_D}(\omega_m-\sqrt{\omega_m^2+|\Delta|^2})+\frac{|\Delta|^2}{V}+F_H +F_2(\mathbf{r})+F_4(\mathbf{r}), \tag{6.27a}$$

where

$$F_2(\mathbf{r})=\frac{1}{3}\pi TN_0m^2v_F^2\sum_{\omega_m}\frac{|\Delta|^2}{(\omega_m^2+|\Delta|^2)^{3/2}}v_s^2 +\frac{1}{12}\pi TN_0\hbar^2v_F^2\sum_{\omega_m}\frac{\omega_m^2}{(\omega_m^2+|\Delta|^2)^{5/2}}(\nabla|\Delta|)^2 \tag{6.27b}$$

and

$$F_4(\mathbf{r})=N_0\pi T\sum_{\omega_m}\left\langle \frac{5}{4}\frac{v_F^4m^4|\Delta|^4\boldsymbol{v}_s^4}{(\omega_m^2+|\Delta|^2)^{7/2}}-\frac{v_F^4m^4|\Delta|^2\boldsymbol{v}_s^4}{(\omega_m^2+|\Delta|^2)^{5/2}}-\frac{25}{8}\frac{v_F^4\hbar^2m^2|\Delta|^2\boldsymbol{v}_s^2|\Delta|'^2}{(\omega_m^2+|\Delta|^2)^{7/2}}-\frac{1}{2}\frac{v_F^4\hbar^2m^2\boldsymbol{v}_s^2|\Delta|'^2}{(\omega_m^2+|\Delta|^2)^{5/2}}\right.$$
$$+\frac{35}{8}\frac{v_F^4\hbar^2m^2|\Delta|^4\boldsymbol{v}_s^2|\Delta|'^2}{(\omega_m^2+|\Delta|^2)^{9/2}}+\frac{105}{64}\frac{v_F^4\hbar^4|\Delta|^4|\Delta|'^4}{(\omega_m^2+|\Delta|^2)^{11/2}}-\frac{3}{64}\frac{v_F^4\hbar^4|\Delta|'^4}{(\omega_m^2+|\Delta|^2)^{7/2}}-\frac{49}{96}\frac{v_F^4\hbar^4|\Delta|^2|\Delta|'^4}{(\omega_m^2+|\Delta|^2)^{9/2}}$$
$$-\frac{5}{2}\frac{v_F^4\hbar^2m^2|\Delta|^3\boldsymbol{v}_s|\Delta|'\boldsymbol{v}_s'}{(\omega_m^2+|\Delta|^2)^{7/2}}+\frac{v_F^4\hbar^2m^2|\Delta|\boldsymbol{v}_s|\Delta|'\boldsymbol{v}_s'}{(\omega_m^2+|\Delta|^2)^{5/2}}+\frac{1}{4}\frac{v_F^4\hbar^2m^2|\Delta|^2\boldsymbol{v}_s'^2}{(\omega_m^2+|\Delta|^2)^{5/2}}-\frac{5}{4}\frac{v_F^4\hbar^2m^2|\Delta|^3\boldsymbol{v}_s^2|\Delta|''}{(\omega_m^2+|\Delta|^2)^{7/2}}$$
$$+\frac{v_F^4\hbar^2m^2|\Delta|\boldsymbol{v}_s^2|\Delta|''}{(\omega_m^2+|\Delta|^2)^{5/2}}+\frac{3}{16}\frac{v_F^4\hbar^4|\Delta||\Delta|'^2|\Delta|''}{(\omega_m^2+|\Delta|^2)^{7/2}}-\frac{77}{48}\frac{v_F^4\hbar^4|\Delta|^3|\Delta|'^2|\Delta|''}{(\omega_m^2+|\Delta|^2)^{9/2}}+\frac{3}{16}\frac{v_F^4\hbar^4|\Delta|^2|\Delta|''^2}{(\omega_m^2+|\Delta|^2)^{7/2}}$$
$$\left.-\frac{1}{80}\frac{v_F^4\hbar^4|\Delta|''^2}{(\omega_m^2+|\Delta|^2)^{5/2}}+\frac{1}{2}\frac{v_F^4\hbar^2m^2|\Delta|^2\boldsymbol{v}_s\boldsymbol{v}_s''}{(\omega_m^2+|\Delta|^2)^{5/2}}+\frac{1}{4}\frac{v_F^4\hbar^4|\Delta|^2|\Delta|'|\Delta|'''}{(\omega_m^2+|\Delta|^2)^{7/2}}+\frac{1}{40}\frac{v_F^4\hbar^4|\Delta|'|\Delta|'''}{(\omega_m^2+|\Delta|^2)^{5/2}}-\frac{1}{40}\frac{v_F^4\hbar^4|\Delta||\Delta|''''}{(\omega_m^2+|\Delta|^2)^{5/2}}\right\rangle. \tag{6.27c}$$

The second order term (6.27b) is identical with Werthamer's result [Eq. (129) in Ref. 65] for a clean superconductor in finite magnetic field, and for $\boldsymbol{v}_s=0$ this reduces to our previous result (5.34). In the same limiting case $\boldsymbol{v}_s=0$ the expression (6.27c) of the fourth order term gives, up to a total derivative, the same result as Eq. (5.35). The fact that the two methods we used to calculate F_4 are fully independent of one another gives us confidence in the validity of our results. However, the formula (6.27c) apparently disagrees with the result obtained by Tewordt.[66] Work is in progress to locate and understand the difference between these two results and we hope to report our findings in this regard in a future publication.

C. Local density of states

As we have seen in Sec. V C, an alternative route for calculating the free energy density of an inhomogeneous superconductor is based on the local DOS. The free energy of a bulk superconductor can be written

$$\mathcal{F}=-2T\sum_{E_i\geqslant 0}\ln\left(2\cosh\frac{E_i}{2T}\right)+\int d^3\boldsymbol{r}\,\frac{|\Delta|^2}{V}+\mathcal{F}_H$$
$$=-2\pi T\int_0^\infty dE\,\rho(E)\ln\left(2\cosh\frac{E}{2T}\right)+\int d^3\boldsymbol{r}\,\frac{|\Delta|^2}{V}+\mathcal{F}_H, \tag{6.28}$$

where the DOS $\rho(E)$ in the quasiclassical approximation reads

$$\rho(E)=\frac{1}{\pi}\,\mathrm{Im}\left[2\hbar v_FN_0\int d^2r_\perp\int dx\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\,\mathrm{tr}\,G(x,x;\tilde{E})\right], \tag{6.29}$$

and $\tilde{E}=E+i\varepsilon$. Furthermore, Eqs. (6.12) and (6.10) allow us to express the trace in Eq. (6.29) in terms of the diagonal resolvent $R(x;\lambda)$

$$\mathrm{tr}\,G(x,x;\tilde{E})=\mathrm{tr}[g(x;\tilde{E})\sigma_3]=\mathrm{tr}[BR(x;\tilde{E})B^{-1}\sigma_3]$$
$$=2\frac{i|\Delta|R^{(2)}(x;\tilde{E})+ER^{(3)}(x;\tilde{E})}{\sqrt{\tilde{E}^2-|\Delta|^2}}. \tag{6.30}$$

Hence, by employing the asymptotic expansion (6.17) the local DOS $\rho(\boldsymbol{r};E)$ and the corresponding free energy density $F(\boldsymbol{r})$ can be written, respectively, in the following form;

$$\rho(\boldsymbol{r};E)=\frac{4}{\pi}\hbar v_FN_0$$
$$\times\mathrm{Im}\left[\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\sum_{n=0}^\infty\frac{i|\Delta|R^{(2)}(x;\tilde{E})+ER^{(3)}(x;\tilde{E})}{(\sqrt{\tilde{E}^2-|\Delta|^2})^{n+1}}\right] \tag{6.31}$$

and

$$F(\boldsymbol{r})=-8T\hbar v_FN_0\,\mathrm{Im}\left[\int_0^\infty dE\,\ln\left(2\cosh\frac{E}{2T}\right)\int\frac{d\Omega_{\hat{\boldsymbol{u}}}}{4\pi}\right.$$
$$\left.\times\sum_{n=0}^\infty\frac{i|\Delta|R^{(2)}(x;\tilde{E})+ER^{(3)}(x;\tilde{E})}{(\sqrt{\tilde{E}^2-|\Delta|^2})^{n+1}}\right]+\frac{|\Delta|^2}{V}+F_H(\boldsymbol{r}). \tag{6.32}$$

Similarly to Eq. (6.21), first we need to determine the relevant coefficients R_n^α from the recurrence relations (6.20) with the initial condition (6.18), then substitute them into Eq. (6.32), and finally perform the E and $\hat{\boldsymbol{u}}$ integrations. All the E integrals are of the form

$$J_{E,k}=\mathrm{Im}\int_0^\infty dE\ \ln 2\cosh\frac{E}{2T}\frac{iE}{(\sqrt{\tilde{E}^2-|\Delta|^2})^{2k+1}}$$
$$=\mathrm{Re}\int_0^\infty dE\ \ln 2\cosh\frac{E}{2T}\frac{E}{(\sqrt{\tilde{E}^2-|\Delta|^2})^{2k+1}}. \quad (6.33)$$

In Appendix C we show that the integrals defined by Eqs. (6.22) and (6.33) are related through

$$\sum_{\omega_m} I_{\lambda,k}=-\frac{2}{\pi}J_{E,k},\quad k=0,1,2,\ldots . \quad (6.34)$$

By employing this identity, a direct comparison between Eqs. (6.21) and (6.32) shows that the two routes to the free energy density give the same result.

VII. CONCLUSIONS

In this paper we have presented a general method, based on the semiclassical limit of the Bogoliubov–de Gennes (or wave function) formulation of the theory of weak coupling superconductivity, for calculating the (gauge invariant) free energy density of an inhomogeneous superconductor with a pair potential with arbitrary spatial variation and in the presence of supercurrents and magnetic field. We have shown that the free energy density can be expressed in terms of the diagonal resolvent of the Andreev Hamiltonian, the semiclassical limit of the BdG Hamiltonian, which obey the so-called Gelfand-Dikii equation. Since the solution of the Gelfand-Dikii equation can be easily expressed in terms of an asymptotic series, our method is most suitable for obtaining the gradient expansion of the free energy density when the superconducting order parameter has slow spatial variations on a length scale set by the BCS coherence length. To the best of our knowledge, this is the first time that the gradient expansion of the free energy of a clean inhomogeneous superconductor, in the general three-dimensional case and in the presence of supercurrents and external magnetic field, has been obtained by employing the wave function (BdG) formulation of the theory of superconductivity. Our result for the second order term in the gradient expansion of the free energy density coincides with the result of Werthamer[67,65] obtained more than three decades ago by using Green's functions. However, our expression of the fourth order term appears to be somewhat different from Tewordt's Green's function result[66] and further investigation is needed to establish the origin of this discrepancy. Nevertheless, since in the zero-field case we have arrived at the same result for the fourth order term in the gradient expansion of the free energy by using two essentially different methods, we are confident in the viability of our approach and results. We have also shown that our method for calculating the free energy of an inhomogeneous superconductor is applicable for states far from equilibrium characterized by an arbitrary temperature field and quasiparticle distribution function.

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APPENDIX A: THE GELFAND-DIKII EQUATION

Consider the one-dimensional Schrödinger operator

$$\hat{H}_S(x)=-\partial_x^2+U(x), \quad (A1)$$

defined on the interval $x\in[a,b]$ (any of a and b may be infinite), and the associated eigenvalue problem

$$\hat{H}_S(x)\psi_n(x)=E_n\psi_n(x), \quad (A2)$$

corresponding to the homogeneous boundary condition

$$\alpha\psi(x)+\beta\psi'(x)=0 \quad \text{for } x=a,b. \quad (A3)$$

Let us denote by ψ_a (ψ_b) the solution of the equation

$$\hat{H}_S(x)\psi(x)=[-\partial_x^2+U(x)]\psi(x)=E\psi(x), \quad (A4)$$

where E is an arbitrary real number, which obeys the boundary condition (A3) only at $x=a$ ($x=b$) but not at the other end of the interval. Then the Wronskian of ψ_a and ψ_b

$$W(E)=\psi_a'(x)\psi_b(x)-\psi_a(x)\psi_b'(x) \quad (A5)$$

does not depend on x and it is only a function of E. Note that $W(E)$ vanishes only for $E=E_n$.

The Green's function $G(x,y;E)$ associated to $\hat{H}_S$ is defined through

$$\hat{H}_S(x)G(x,y;E)=\hat{H}_S(y)G(x,y;E)=\delta(x-y), \quad (A6)$$

and can be expressed in terms of the Wronskian (A5) as

$$G(x,y;E)=\left\langle x\left|\frac{1}{\hat{H}_S-E}\right|y\right\rangle$$
$$=\frac{1}{W(E)}[\Theta(x-y)\psi_b(x)\psi_a(y)$$
$$+\Theta(y-x)\psi_a(x)\psi_b(y)], \quad (A7)$$

where $\Theta(x)$ is the step function. One can easily check that Eq. (A7) obeys Eq. (A6) and, because by construction satisfies the boundary condition (A3), $G(x,y;E)$ is indeed the Green's function associated to $\hat{H}_S$.

The diagonal resolvent of $\hat{H}_S$ for a given energy E is defined in terms of the Green's function as

$$R(x;E)=\left\langle x\left|\frac{1}{\hat{H}_S-E}\right|x\right\rangle$$

$$=\lim_{\delta\to 0^+}\frac{1}{2}[G(x,x+\delta;E)+G(x+\delta,x,E)]$$

$$=\frac{\psi_a(x)\psi_b(x)}{W(E)}. \tag{A8}$$

By taking into account Eqs. (A8) and (A4), the first two derivatives of $R_E\equiv R(x;E)$ can be written as (for brevity we drop the arguments)

$$R_E'=\frac{\psi_a'\psi_b+\psi_a\psi_b'}{W} \tag{A9}$$

and

$$R_E''=2(U-E)R_E+2\frac{\psi_a'\psi_b'}{W}. \tag{A10}$$

Then, combining Eqs. (A5), (A10), and (A8) we arrive at

$$\psi_a'\psi_b'=\frac{W}{4R_E}(R_E'^2-1). \tag{A11}$$

Finally, inserting Eq. (A11) into Eq. (A10) and after some rearrangements one obtains the desired Gelfand-Dikii equation

$$-2R_ER_E''+R_E'^2+4R_E^2(U-E)=1. \tag{A12}$$

APPENDIX B: THE MATRIX GELFAND-DIKII EQUATION

In this appendix we will study the Andreev Hamiltonian

$$\hat{H}_A=-i\sigma_3\partial_x+\Delta\sigma_1 e^{i\sigma_3\theta} \tag{B1}$$

and obtain a relation, analogous to the Gelfand-Dikii equation, obeyed by the diagonal part of its resolvent

$$G_{\alpha\beta}(x,y;E)=\left\langle \alpha,x\left|\frac{1}{\hat{H}_A-E}\right|\beta,y\right\rangle. \tag{B2}$$

Here the indices α and β label components in the two-dimensional Nambu space.

To derive the Gelfand-Dikii analog we must first write $G_{\alpha\beta}(x,y;E)$ in a form similar to the expression we used earlier for the resolvent $G(x,y;E)$ of the Schrödinger Hamiltonian. Recall that there we had

$$G(x,y;E)=\frac{1}{W(E)}\,\psi_a(x)\psi_b(y), \tag{B3}$$

where $W(E)=W(\psi_a,\psi_b)=\psi_a'\psi_b-\psi_b'\psi_a$ is the Wronskian of the two solutions ψ_a, ψ_b of the homogeneous Schrödinger equation $\hat{H}\psi_{a,b}=E\psi_{a,b}$, and is independent of x.

We will begin by constructing the resolvent $G_{\alpha\beta}(x,y;E)$ for the Andreev Hamiltonian on a finite interval $[a,b]$. If required, the limit of an infinite domain can be taken later. To specify the problem completely we must impose boundary conditions on the wave functions at a, b in such a way that the Hamiltonian is self-adjoint. This requires that the condition for hermiticity

$$\langle\psi_1|\hat{H}_A\psi_2\rangle-\langle\hat{H}_A\psi_1|\psi_2\rangle=-i\psi_1^\dagger\sigma_3\psi_2|_a^b=0 \tag{B4}$$

be satisfied in a manner that treats ψ_1 and ψ_2 on an equal footing, thus ensuring that the domain of $\hat{H}_A$ and $\hat{H}_A^\dagger$ coincide. We impose the vanishing condition at each end separately. Thus

$$\psi_{1u}^*\psi_{2u}-\psi_{1l}^*\psi_{2l}=0,\quad x=a,b, \tag{B5}$$

where u and l refer to the upper and lower components of ψ, respectively. We disentangle ψ_1, ψ_2 by dividing by $\psi_{1u}^*\psi_{2l}$ and find, for example,

$$\left.\frac{\psi_{2u}}{\psi_{2l}}\right|_{x=a}=\left.\left(\frac{\psi_{1l}}{\psi_{1u}}\right)^*\right|_{x=a}. \tag{B6}$$

Equation (B6) requires that all ψ in the domain of $\hat{H}_A$ obey

$$\left.\frac{\psi_u}{\psi_l}\right|_{x=a}=e^{i\theta_a} \tag{B7}$$

for some real angle θ_a. Similarly

$$\left.\frac{\psi_u}{\psi_l}\right|_{x=b}=e^{i\theta_b}. \tag{B8}$$

These boundary angles $\theta_{a,b}$ parametrize the family of possible self-adjoint boundary conditions. Physically one may think of them as the phases of the order parameter of a superconductor with an infinitely large energy-gap abutting the ends of the interval.

We now notice that, for any two solutions ψ_1, ψ_2 of the equation

$$(-i\sigma_3\partial_x+\Delta\sigma_1 e^{i\sigma_3\theta})\psi_{1,2}=E\psi_{1,2}, \tag{B9}$$

where E is real, the quantity

$$w(\psi_1,\psi_2)\equiv\psi_1^\dagger(x)\sigma_3\psi_2(x) \tag{B10}$$

is independent of x. To prove this, simply differentiate w and use Eq. (B9). We will see that $w(\psi_1,\psi_2)$ plays the same role for the Andreev equation as the Wronskian plays for the Schrödinger equation. For example, using the boundary condition we see that $\psi_1^\dagger\sigma_3\psi_1=0=\psi_2^\dagger\sigma_3\psi_2$. Combining this with the constancy of $w(\psi_1,\psi_2)$, we see that w must vanish identically if the two solutions ψ_1, ψ_2 are proportional to one another. Conversely, if for two solutions of $\hat{H}_A\psi=E\psi$ we have $w(\psi_1,\psi_2)=0$ at some point (and hence at all points) in the interval, then

$$(\psi_{u1}^*\psi_{u2}-\psi_{l1}^*\psi_{l2})|_a=0 \tag{B11}$$

or

$$\left.\left(\frac{\psi_{u1}}{\psi_{l1}}\right)^*\right|_{x=a}=\left.\frac{\psi_{l2}}{\psi_{u2}}\right|_{x=a}. \tag{B12}$$

The two solutions therefore satisfy the same differential equation with the same initial boundary condition, and so

must be proportional. We have therefore shown that $w(\psi_1,\psi_2)$ provides the same test for linear independence as the Wronskian $W(\psi_1,\psi_2)$.

The resolvent $G_{\alpha\beta}(x,y;E)$ will have the form

$$G_{\alpha\beta}(x,y;E)=A^L_\beta(y)\Psi^L_\alpha(x) \quad \text{for } x<y,$$
$$=A^R_\beta(y)\Psi^R_\alpha(x) \quad \text{for } x>y, \tag{B13}$$

where $\Psi^L_\alpha(x)$, $\Psi^R_\alpha(x)$ are solutions of the homogeneous equation and satisfy the boundary condition on the left (L) or right (R) hand boundary, respectively. The jump-condition obtained by integrating

$$(-i\sigma_3\partial_x+\Delta\sigma_1 e^{i\sigma_3\theta}-E)G(x,y;E)=\sigma_0\delta(x-y) \tag{B14}$$

across the point $x=y$ is

$$i(\sigma_3)_{\alpha\alpha'}[\Psi^L_{\alpha'}(y)A^L_\beta-\Psi^R_{\alpha'}(y)A^R_\beta]=\delta_{\alpha\beta}. \tag{B15}$$

To solve Eq. (B15) we define $W=\Psi^{\dagger L}\sigma_3\Psi^R$ and use the conditions $\Psi^{\dagger L}\sigma_3\Psi^L=\Psi^{\dagger R}\sigma_3\Psi^R=0$. For example, on multiplying Eq. (B15) by $\Psi^{\dagger L}_\alpha$ we find

$$i\Psi^{\dagger L}_\alpha(\sigma_3)_{\alpha\alpha'}\Psi^L_{\alpha'}A^L_\beta-i\Psi^{\dagger L}_\alpha(\sigma_3)_{\alpha\alpha'}\Psi^R_{\alpha'}A^R_\beta=\Psi^{\dagger L}_\beta. \tag{B16}$$

This collapses to

$$-iWA^R_\beta=\Psi^{\dagger L}_\beta(y). \tag{B17}$$

In this manner we obtain

$$G_{\alpha\beta}(x,y;E)=-\frac{i}{W^*}\Psi^L_\alpha(x)\Psi^{\dagger R}_\beta(y) \quad \text{for } x<y,$$
$$=\frac{i}{W}\Psi^R_\alpha(x)\Psi^{\dagger L}_\beta(y) \quad \text{for } x>y. \tag{B18}$$

Notice that $G_{\alpha\beta}(x,y;E)=G^*_{\beta\alpha}(y,x;E)$ as befits the resolvent of a self-adjoint operator.

For the Schrödinger problem the Gelfand-Dikii equation applies to the diagonal $x=y$ entry in the resolvent. Our matrix-valued $G_{\alpha\beta}(x,y;E)$ is discontinuous at $x=y$ and, as explained in earlier sections, we must define $G_{\alpha\beta}(x,x;E)$ by taking an average of the left- and right-hand limits

$$G_{\alpha\beta}(x,x;E)=\frac{i}{2}\left[\frac{1}{W}\Psi^R_\alpha(x)\Psi^{\dagger L}_\beta(x)-\frac{1}{W^*}\Psi^L_\alpha(x)\Psi^{\dagger R}_\beta(x)\right]. \tag{B19}$$

It turns out that $G_{\alpha\beta}(x,x;E)$ is not quite the most convenient quantity to work with. Instead we use the matrix

$$g_{\alpha\beta}(x;E)=G_{\alpha\beta'}(x,x;E)(\sigma_3)_{\beta'\beta}. \tag{B20}$$

The utility of this modification is related to the coefficient of ∂_x in the Andreev equation being σ_3 instead of the identity.

If one takes the square of the matrix $g_{\alpha\beta}$, again using $\Psi^{\dagger L}\sigma_3\Psi^L=\Psi^{\dagger R}\sigma_3\Psi^R=0$, one finds that

$$g^2_{\alpha\beta}=\frac{1}{4}\left[-\frac{1}{W}\Psi^R_\alpha\Psi^{\dagger L}_{\beta'}(\sigma_3)_{\beta'\beta}-\frac{1}{W^*}\Psi^L_\alpha\Psi^{\dagger R}_{\beta'}(\sigma_3)_{\beta'\beta}\right]. \tag{B21}$$

Now

$$g^2_{\alpha\beta}\Psi^L_\beta=-\frac{1}{4W^*}\Psi^L_\alpha\Psi^{\dagger R}_{\beta'}(\sigma_3)_{\beta'\beta}\Psi^L_\beta=-\frac{1}{4}\Psi^L_\alpha. \tag{B22}$$

Similarly

$$g^2_{\alpha\beta}\Psi^R_\beta=-\frac{1}{4}\Psi^R_\alpha. \tag{B23}$$

Provided that E is not an eigenvalue we have $W\neq 0$, so the two column vectors Ψ^R_α and Ψ^L_α are linearly independent and together span the two-dimensional vector space at each point x. Consequently these last two equations are telling us that

$$g^2_{\alpha\beta}=-\frac{1}{4}\delta_{\alpha\beta}. \tag{B24}$$

We also see that the trace of g vanishes;

$$g_{\alpha\alpha}=\frac{1}{2}\left(\frac{i}{W}W-\frac{i}{W^*}W^*\right)=0. \tag{B25}$$

We can therefore find three (generally complex) numbers a_1, a_2, a_3 such that

$$a_1^2+a_2^2+a_3^2=1 \tag{B26}$$

and

$$g_{\alpha\alpha}=\frac{i}{2}(a_1\sigma_1+a_2\sigma_2+a_3\sigma_3). \tag{B27}$$

After inserting Eq. (B19) into Eq. (B20) we may now seek the Andreev-equation analog of the Gelfand-Dikii relation. Because the Andreev equation is first-order, we have only to differentiate once with respect to x before we are able eliminate the $\partial_x\Psi$'s using Eq. (B9). We immediately find that

$$i\partial_x g=[g,\sigma_3(E-\Delta\sigma_1 e^{i\sigma_3})]. \tag{B28}$$

The equation (B28) is well-known in the superconductivity literature as a form of the Eilenberger equation. The present derivation is much simpler than those usually adduced. In particular the normalization condition Eq. (B24) appears automatically and does not have to be introduced by hand. It also has the added advantage of demonstrating that the Eilenberger equation should be regarded as the Andreev problem analog of the Gelfand-Dikii equation.

Notice that the position dependent matrix $g_{\alpha\beta}(x)$ is the diagonal part of $[\sigma_3(\hat{H}_A-E)]^{-1}$. Equation (B28) asserts that it commutes with $\sigma_3(\hat{H}_A-E)$, i.e.,

$$0=[\sigma_3(\hat{H}_A-E),g]. \tag{B29}$$

In this appendix we have so far assumed that E is real. Under this condition it is easy to show that

$$\psi^\dagger=\psi^T\sigma_1, \tag{B30}$$

so for example, we could also define the Wronskian analog as

$$w(\psi_1,\psi_2)=\psi_1^T(-i\sigma_2)\psi_2. \tag{B31}$$

In this form the antisymmetry $w(\psi_1,\psi_2)=-w(\psi_2,\psi_1)$ is manifest. More importantly after replacing $\psi^\dagger$ by $\psi^T\sigma_1$ in the appropriate places the expression (B18) continues to be valid for complex values of E.

APPENDIX C: RELATIONSHIP BETWEEN $I_{\lambda,k}$ AND $J_{E,K}$

To prove Eq. (6.34) we examine the integrals in Eq. (6.33). Again, for $k=0$, the integral diverges. By subtracting the contribution of the normal metal from the free-energy density, the integral takes the form

$$J_{E,0}=\mathrm{Re}\int_0^\infty dE\ \ln 2\cosh\frac{E}{2T}\left(\frac{E}{\sqrt{\tilde{E}^2-|\Delta|^2}}-1\right). \tag{C1}$$

This integral still diverges logarithmically. We can formally integrate by parts

$$J_{E,0}=\mathrm{Re}\left[(\sqrt{\tilde{E}^2-|\Delta|^2}-E)\ln 2\cosh\frac{E}{2T}\right]_0^\infty - \mathrm{Re}\int_0^\infty\frac{dE}{2T}\tanh\frac{E}{2T}(\sqrt{\tilde{E}^2-|\Delta|^2}-E). \tag{C2}$$

At $E=0$, the boundary term vanishes (as $\varepsilon\to 0+$, the contribution from the square root is pure imaginary; the second term is zero altogether). As $E\to\infty$, the boundary term goes to $-|\Delta|^2/4T$. To do the regularization consistently, we have to discard the boundary term. In the remaining integral, we can replace E by $\tilde{E}$ in the argument of tanh, so we can write

$$J_{E,0}=\frac{1}{2}\ \mathrm{Re}\int_{0+i\varepsilon}^{\infty+i\varepsilon}\frac{dE}{T}\tanh\frac{E}{2T}(\sqrt{E^2-|\Delta|^2}-E). \tag{C3}$$

We note that the integrand becomes complex conjugate upon $E\to E^*$. Thus, by extending the lower limit of integration to $-\infty+i\varepsilon$, we automatically obtain just the real part

$$J_{E,0}=\frac{1}{4}\int_{-\infty+i\varepsilon}^{\infty+i\varepsilon}\frac{dE}{T}\tanh\frac{E}{2T}(\sqrt{E^2-|\Delta|^2}-E). \tag{C4}$$

We can now formally close the contour of integration around the imaginary upper half axis where $\tanh(E/2T)$ has simple poles at the (positive) fermionic Matsubara frequencies, and obtain the result

$$J_{E,0}=-\pi\sum_{\omega_m>0}(\omega_m-\sqrt{\omega_m^2+|\Delta|^2}). \tag{C5}$$

This result together with Eq. (6.23) yield Eq. (6.34) for $k=0$.

For $k\geqslant 1$ everything is straightforward. The integral $J_{E,1}$ does not contribute because the first-order term is zero due to symmetry discussed above. For $k>1$, $J_{E,k}$ converges. Integrating by parts and extending the contour gives

$$J_{E,k}=\mathrm{Re}\left[\frac{-1}{2k-1}\frac{\ln 2\cosh(E/2T)}{(\sqrt{\tilde{E}^2-|\Delta|^2})^{2k-1}}\right]_0^\infty + \frac{1}{4(2k-1)}\int_{-\infty+i\varepsilon}^{\infty+i\varepsilon}\frac{dE}{T}\frac{\tanh(E/2T)}{(\sqrt{E^2-|\Delta|^2})^{2k-1}}. \tag{C6}$$

The integrated out term vanishes. To perform the integral we again close the contour in the upper half plane and obtain

$$J_{E,k}=\frac{1}{4(2k-1)}\sum_{\omega_m>0}2\pi i\frac{2}{(\sqrt{-\omega_m^2-|\Delta|^2})^{2k-1}} =\frac{\pi}{2(2k-1)}\sum_{\omega_m}\frac{1}{(i)^{2k-2}(\sqrt{\omega_m^2+|\Delta|^2})^{2k-1}} \tag{C7}$$

By comparing this result with Eq. (6.25) one can infer that Eq. (6.34) holds for any positive integer k.

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