Interface-potential approach to surface states in type-I superconductors

R. Blossey and J. O. Indekeu
Laboratorium voor Vaste-Stoffysica en Magnetisme, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium
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We study inhomogeneous surface states in strongly type-I superconductors from the viewpoint of wetting phenomena. The interface-potential approach, known for fluids or magnets, is extended to superconductors. Within the Ginzburg-Landau theory we calculate an interface potential $V(l)$, which describes the interaction between the surface and a parallel superconductor/normal (SC/N) interface, at separation l. Unlike for fluids or magnets, a quantum effect shows up in the form of $V(l)$ for small l. Introducing an interface displacement model, we predict an S-shaped distortion of an inclined SC/N interface near the surface.

The possibility that the superconducting phase "wets" the surface has up to now been largely ignored. Long ago, Pippard argued that the difference of the surface free energies $\gamma_{W,N}$ and $\gamma_{W,\mathrm{SC}}$ of, respectively, superconducting (SC) and normal (N) phases near a surface or wall (W) is much smaller than the interfacial tension $\gamma_{\mathrm{SC},N}$ of a superconductor/normal interface.[1,2] If that were generally true, wetting would not take place, since the wetting condition is $\gamma_{W,N}=\gamma_{W,\mathrm{SC}}+\gamma_{\mathrm{SC},N}$.[3] However, recent calculations in the Ginzburg-Landau (GL) theory have revealed that genuine wetting or "interface delocalization" phase transitions occur, whenever the superconducting order parameter φ is enhanced at the surface.[4] The transitions are of first order for $0<\kappa<0.374$ and critical for $0.374<\kappa<1/\sqrt{2}$, where $\kappa=\lambda/\xi$ is the ratio of the magnetic penetration depth to the coherence length.

Building further on this previous work,[4] we extend the *interface potential* approach, well known for fluids and Ising magnets,[3] to type-I superconductors. We derive a wall-interface potential $V(l)$ for wetting and prewetting transitions and for partial wetting states. For superconductors, $V(l)$ can be defined as the excess free energy per unit area of a uniform superconducting surface sheath of thickness l and represents the effective interaction potential between the SC/N interface and the wall W. The equilibrium sheath thickness is determined by the minimum of $V(l)$. The wall-interface potential is not only interesting from a fundamental viewpoint, but also permits applications to *inhomogeneous* structures, such as three-phase contact regions (Ref. 5, first paper). By inhomogeneous we mean that the wave function and magnetic induction profiles now depend on two coordinates x (perpendicular to the surface) and y (parallel to the surface). A quantitative study of these inhomogeneities is difficult to carry out using the standard GL equations. As a first example, we employ $V(l)$ to predict the distortion of an inclined SC/N interface near the surface in the partial wetting regime.

Our derivation of $V(l)$ starts from the GL surface free energy functional

$$\gamma[\varphi,\mathbf{A}]=\int_0^\infty dx\Bigg[\alpha|\varphi|^2+\frac{\beta}{2}|\varphi|^4+\frac{1}{2m}\left|\left(\frac{\hbar}{i}\boldsymbol{\nabla}-q\mathbf{A}\right)\varphi\right|^2+\frac{|\boldsymbol{\nabla}\times\mathbf{A}-\mu_0\mathbf{H}|^2}{2\mu_0}\Bigg]+\frac{\hbar^2}{2mb}|\varphi(0)|^2. \tag{1}$$

The type-I superconductor fills the half-space $x>0$, so that the surface is at $x=0$. $\mathbf{A}$ is the vector potential, and $\mathbf{H}=H\mathbf{e}_z$ is the applied magnetic field, which is *parallel* to the surface. Furthermore, $\alpha\propto T-T_c$, with T_c the bulk critical temperature. The gauge is chosen so that $\mathbf{A}=(0,A(x),0)$. Because we are at this stage, i.e., for the derivation of the interface potential itself, concerned with *uniform* states (i.e., translationally invariant along y and z), it suffices to work with real functions $\varphi(x)$. The profiles $A(x)$ and $\varphi(x)$ are determined by the GL equations, being the Euler-Lagrange equations of the functional (1).

The surface contribution in (1) plays a crucial role. The parameter b is the extrapolation length of the order parameter $\varphi(x)$ at the surface.[6] Minimization of (1) with respect to $\varphi(0)$ leads to the boundary condition

$$\frac{d\varphi}{dx}(0)=b^{-1}\varphi(0). \tag{2}$$

The sign of b is especially important in the context of wetting.[4] For $b>0$, which pertains to surfaces against normal metals or against insulators or vacuum ($b\to\infty$), φ is suppressed at the surface. For $b<0$, however, φ is enhanced and wetting transitions occur.[4] The significance of the case $b<0$ has been discussed before for cold-worked surfaces[7] and for twinning planes.[8,9] Also, a thin film of a superconductor with a higher T_c, deposited on the surface of the type-I superconductor by, e.g., molecular beam epitaxy, should lead to $b<0$.[10] Following previous works, we take b as a temperature-independent material constant. We furthermore remark that the effect of geometrical disorder at the surface, including strain energies and lattice mismatch due to deposited thin films, is properly taken into account in the

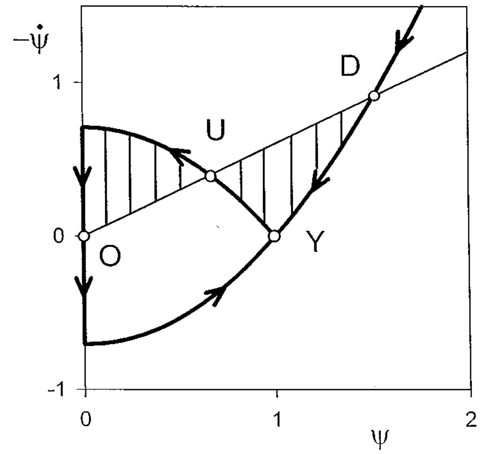

FIG. 1. The method for calculating the superconducting wave function profile $\psi(x)$ makes use of the "phase portrait." Shown here is the phase portrait for bulk two-phase coexistence in the limit $\kappa \to 0$.

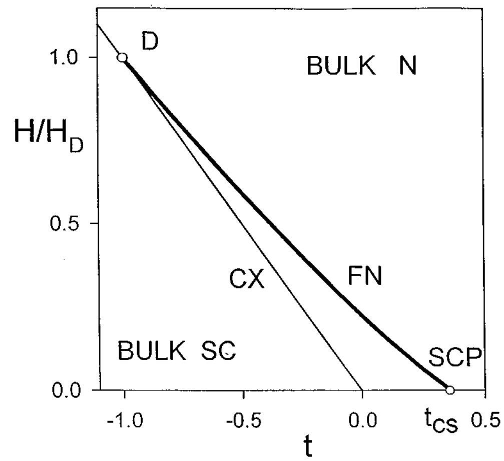

FIG. 2. H-T surface phase diagram of wetting and prewetting transitions in the limit $\kappa \to 0$.

present functional (1), *provided* the disorder does not penetrate into the bulk superconductor over length scales larger than the coherence length ξ, which is large (several 10^3 Å) in these materials.[11]

For clarity of presentation we first recall the wetting phenomena[4] and then give the results for the wall-interface potential and the interface displacement profile. To obtain explicit analytical results, we make the approximation $\lambda \ll \xi$, which is quantitatively correct for strongly type-I superconductors such as, e.g., Al. But as we shall argue at the end, it is *qualitatively* correct for materials with κ up to 0.374, which includes In, Sn, and others.

In the limit $\kappa \to 0$ the magnetic induction dA/dx is a step function, whereas φ is smoothly varying on the scale of ξ, near surfaces or interfaces. The GL equations imply that $\varphi = 0$ in regions with nonzero dA/dx, so that the equations for A and φ decouple. This allows one to obtain a "phase portrait" for determining the trajectories $\dot{\psi}$ versus ψ, with $\psi \equiv \varphi \sqrt{\beta/|\alpha|}$ and the overdot stands for $\xi d/dx$. Here ξ is the zero-field coherence length defined by $\xi^2 \equiv \hbar^2/2m|\alpha|$. Note that $\xi^{-2} \propto |T-T_c|$.

Figure 1 shows the phase portrait for the case of bulk two-phase coexistence between N and SC phases at magnetic field $H_c(T)$ and for $\kappa \to 0$. The thick lines contain the possible trajectories, which follow the arrows as a function of x. The fixed point O corresponds to bulk phase N, and the fixed point Y denotes bulk phase SC. The vertical trajectory at $\psi = 0$ describes the discontinuity in $\dot{\psi}$ that arises as a consequence of the jump in the magnetic induction in the limit $\kappa \to 0$. The straight line OD comes from the boundary condition (2) and is given by $\dot{\psi} = \xi \psi / b$. Intersections of this line with the trajectories give initial conditions $\psi(0)$ and $\dot{\psi}(0)$ corresponding to extrema of the free energy. O and D are (local) minima, and U is a saddle point. In order to discuss wetting by the SC phase, phase N is imposed as the bulk boundary condition (at $x = \infty$). At $\xi/b = -0.602$ a first-order phase transition takes place, in which profile O, with $\psi(x) = 0$, exchanges stability with a macroscopic superconducting layer, from D to Y, followed by a SC/N interface, from Y to O, following the arrows. This is the interface delocalization or wetting transition.[4] An equal-areas rule (see Fig. 1) applies to locate the transition.

The wetting transition has a "prewetting" extension out of bulk two-phase coexistence into phase N. Extending the phase portrait method to off-coexistence states, one obtains the H-T phase diagram for $\kappa = 0$, shown in Fig. 2. The temperature variable is $t \equiv (T-T_c)/(T_c-T_D)$, where T_D is the interface delocalization temperature. The magnetic field is likewise reduced with the interface delocalization field H_D. The thin line CX denotes the bulk two-phase coexistence. The thick line FN, from the interface delocalization transition D to the surface critical point (SCP) is a line of first-order nucleation transitions.[4] On this line the profile with $\psi(x) = 0$ coexists with a superconducting surface sheath of finite thickness l. We remark that this phase diagram is closely similar to the phase diagram of twinning-plane superconductivity (for $\kappa = 0$) obtained by Khlyustikov and Buzdin[8] and (in more detail) by Mishonov.[9]

The wall-interface potential $V(l)$ is defined through application of a constraint on the free energy functional (1). For $\kappa \to 0$ it is natural to define l as the location of the discontinuity in the magnetic induction, so that the latter is zero in the interval $0 \leq x \leq l$ and equals the external field in the remaining regions $x < 0$ (outside the sample) and $x > l$ (in the bulk N phase). $V(l)$ is then the minimum of (1) under the constraint of fixed l. Solutions for $\psi(x)$ in $[0,l]$ must satisfy the boundary condition (2) at $x = 0$ and the continuity requirement $\psi(l) = 0$.

The resulting function $V(l)$ is very different from its counterpart for fluids and magnets. For small l there is a *linear* part, from the minimum at $l = 0$ up to a length scale l_0. The existence of l_0 is a purely quantum-mechanical effect, which can be understood through the following analogy. For small ψ the GL equation reduces to the Schrödinger equation for a particle in a box. The wave number k of the particle is a function of the temperature T of the superconductor, and the box size corresponds to l. At given T and, therefore, fixed k, l must exceed a certain threshold value l_0 in order for a nonzero solution for ψ to exist. The consequence of this for the *nonlinear* GL equation is that, for l

$<l_0$, the free energy (1) is minimized by $\psi(x)=0$. The physical implication of this quantum effect is the existence of a *minimum thickness* $l_0>0$ for uniform superconducting surface sheaths, since it is impossible to impose a nonzero superconducting sheath with a thickness less than l_0. The dependence of l_0 on temperature can be calculated analytically. The ratio l_0/ξ depends only on the ratio $|b|/\xi$. We find

$$l_0/\xi=\begin{cases}\tan^{-1}(|b|/\xi) & \text{for } T\leqslant T_c,\\ \tanh^{-1}(|b|/\xi) & \text{for } T\geqslant T_c.\end{cases} \tag{3}$$

This means that, for example, in the vicinity of the wetting transition (where $|b|/\xi$ is of order unity), the magnitudes of l_0 and ξ are of the same order, i.e., a few thousand Å.

For $l<l_0$ the interface potential takes the simple linear form

$$V(l)=\mu_0 H^2 l/2 \quad \text{for } l<l_0. \tag{4}$$

For $l>l_0$, the optimal profile $\psi(x)$ is nonzero and $V(l)$ is obtained through the auxiliary function $V(\psi_0)$, with $\psi_0\equiv\psi(0)$,

$$V(\psi_0)=(\xi\alpha^2/\beta)\int_0^{\psi_0}d\psi(H_R^2-\psi^4/2)\times[\pm\psi^2+\psi^4/2+H_R^2+E(\psi_0)]^{-1/2}, \tag{5}$$

where the $-$ $(+)$ sign applies for $T<T_c$ $(T>T_c)$. The reduced field H_R is defined through $H_R^2=\mu_0\beta H^2/2\alpha^2$, and the function $E(\psi_0)$ is given by

$$E(\psi_0)=(\xi^2/b^2\mp 1)\psi_0^2-\psi_0^4/2-H_R^2. \tag{6}$$

Likewise, l can also be expressed as a function of ψ_0,

$$l(\psi_0)=\xi\int_0^{\psi_0}d\psi[\pm\psi^2+\psi^4/2+H_R^2+E(\psi_0)]^{-1/2}. \tag{7}$$

$V(l)$ is then found by eliminating ψ_0 between (5) and (7).

Figure 3 shows $V(l)$ (i) for the first-order wetting transition at $\xi/b=-0.602$ and (ii) for a point on the prewetting line, e.g., at $\xi/b=-0.8$. Note the weak singularity at $l=l_0$. We verified analytically that V and dV/dl are continuous at l_0, but d^2V/dl^2 is discontinuous. The mathematical continuation of the linear first part of $V(l)$ is the dashed line. At the first-order wetting transition, $V(l)$ decays exponentially,

$$V(l)\propto\exp(-\sqrt{2}l/\xi) \quad \text{for } l\rightarrow\infty. \tag{8}$$

This is reminiscent of wetting in systems with so-called *short-ranged* forces.[3] The term "short-ranged" is, however, somewhat misleading in the context of superconductivity of type I, because the characteristic length scale ξ is quite large ($\approx 10^3$ Å) compared with other lengths (lattice spacing, Thomas-Fermi screening length, etc.).

At a prewetting transition, $V(l)$ attains a minimum at a finite l value, say, l_1, corresponding to a uniform superconducting surface sheath. Note that always $l_1>l_0$. For large l, $V(l)$ increases linearly as $(\mu_0 H^2-\alpha^2/\beta)l/2$.

Now we can use $V(l)$ to calculate the profile of an inclined SC/N interface near the surface W at bulk two-phase coexistence. In thermodynamic equilibrium the contact angle θ between the interface and W is determined by the temperature, so that $\theta>0$ for $T<T_D$ (partial wetting) and $\theta=0$ for $T>T_D$ (complete wetting). In a partial wetting state, the minimum of $V(l)$ is at $l=0$, with $V(0)=0$, and $V(l)$ approaches the value $\gamma_{\mathrm{SC},N}(1-\cos\theta)$ for $l\rightarrow\infty$, with $\gamma_{\mathrm{SC},N}=4\xi\alpha^2/(3\sqrt{2}\beta)$. The contact line, where interface and surface meet, is parallel to the z axis, since the magnetic field orients the normal domain.[1] We now define the interface profile as the location $l(y)$ of the jump in the magnetic induction, which marks the boundary between the N and SC phases. Note that this boundary is sharp, since its width λ is negligible for $\kappa\rightarrow 0$. (We recall that y is a coordinate parallel to the surface and that l is measured along the direction x perpendicular to the surface.)

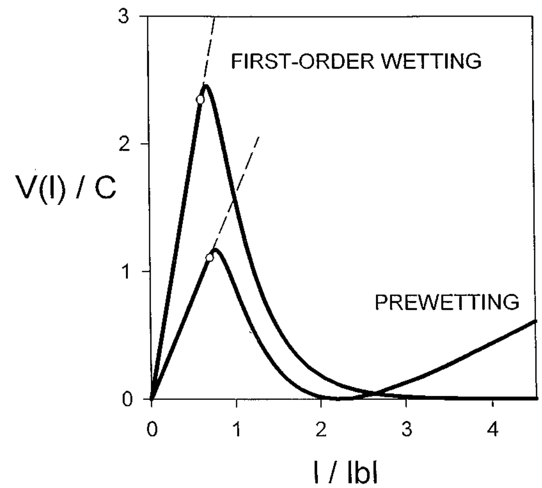

FIG. 3. Interface potential $V(l)/C$ vs $l/|b|$. The constant C equals $\hbar^4/(4\beta m^2|b|^3)$. The two potentials shown are for the first-order interface delocalization or wetting transition D (at $\xi/b=-0.602$) and for a point on the first-order nucleation or prewetting line FN (e.g., for $\xi/b=-0.8$). The open circle locates the weak singularity at $l=l_0$, as explained in the text.

For calculating $l(y)$ we introduce an interface displacement model for type-I superconductors, following what was done previously for fluids by several authors.[5,12] The model is defined through the excess free energy functional $\tau[l]$, in which a gradient-squared deformation energy is added to the interface potential for uniform sheaths,

$$\tau[l]=\int_{-\infty}^{\infty}dy\left\{\frac{\gamma_{\mathrm{SC},N}}{2}\left(\frac{dl}{dy}\right)^2+V(l(y))+c(y)\right\}. \tag{9}$$

The function $c(y)$ is piecewise constant and is given, e.g., in Eq. (4.10) in Ref. 12. Its role is twofold. It ensures that the integrand vanishes in the limiting surface states for $|y|\rightarrow\infty$. Also, it guarantees that the excess free energy is independent of the mathematical dividing line (cf. Gibbs dividing surface) between the limiting surface states.

For nonuniform states, $\tau[l]$ gives the *line tension* of the contact line where the SC/N interface meets the surface. The gradient-squared approximation is reasonable as long as dl/dy is not too large. We therefore assume a small contact angle θ, that is, T close to T_D. Minimization of $\tau[l]$ leads to the Euler-Lagrange equation

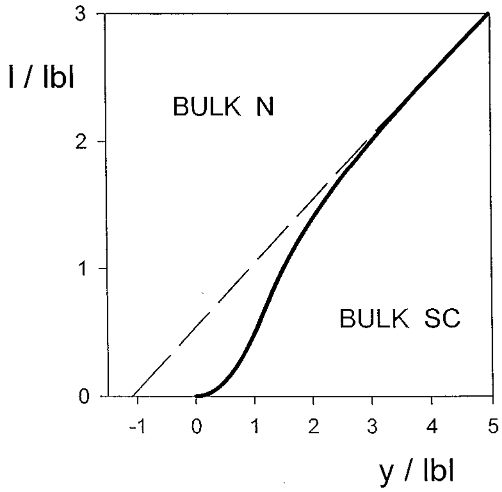

FIG. 4. Application of the interface potential method to an inhomogeneous surface state consisting of an inclined SC/N interface meeting the surface. Shown is the projection of the interface onto the xy plane. The surface is in the yz plane at $l=0$. The structure is translationally invariant along z, the direction of the applied field. The interface profile $l(y)$ marks the discontinuity in magnetic induction, where N and SC phases meet. For large l the interface becomes tangent to the dividing surface (dashed line), which makes a contact angle θ (determined by $dl/dy \rightarrow \tan\theta$) with the surface.

$$\gamma_{\mathrm{SC},N} \frac{d^2 l}{dy^2} = \frac{dV(l)}{dl}, \tag{10}$$

which, together with the boundary conditions

$$l(y) \rightarrow \begin{cases} y \ \tan\theta + \mathrm{const} & \text{for} \ \ y \rightarrow \infty, \\ 0 \quad \text{for} \ \ y \rightarrow -\infty, \end{cases} \tag{11}$$

determines the equilibrium profile $l(y)$.

The resulting location $l(y)$ of the jump in the magnetic induction is shown in Fig. 4, for $\xi/b = -0.55$, which is not far below the wetting temperature. We find an S-shaped deformation of the profile near the surface. This S shape is due to the presence of a *barrier* in the interface potential (Fig. 3), which in turn is due to the vicinity of a *first-order* wetting transition (for analogous situations in fluids, see Ref. 12). At small l, $l(y)$ is determined by the linear part of $V(l)$. This leads to a *parabolic* "foot," with $l(y)=0$ for $y<0$ and

$$l(y) = 3\sqrt{2} y^2/(16\xi) \quad \text{for} \ \ y>0, \tag{17}$$

so that ξ is the length scale relevant to the *curvature* of the profile near the surface. This parabola extends to $l=l_0$, where it smoothly joins (with a discontinuity in d^3l/dy^3) the form determined by the second part of $V(l)$. As in the context of fluids, the extrapolation of the far interface to the surface (dashed line) defines a so-called "dividing surface." We thus distinguish a contact region where the interface is tangent to the surface, an intermediate convex region for $l \approx l_0$ (with $l_0/b = -0.587$), and an asymptotic concave region $l \gg l_0$ with exponentially rapid approach toward the dividing surface. If all lengths are scaled with $|b|$, the ratio ξ/b controls both the macroscopic contact angle and the deformation of $l(y)$ near W. We stress that only the jump in the magnetic induction is shown in the figure. The wave function $\psi(x,y)$ *smoothly* increases from zero to its bulk value 1 over a distance ξ, to the right of the line $l(y)$.

Finally, we discuss to what extent these results remain valid for $\kappa>0$, in which case the magnetic penetration depth λ is no longer negligible compared to ξ. The sharp step in the phase portrait (Fig. 1) at $\psi=0$ becomes rounded for $\kappa>0$, and, moreover, the fields ψ and A become coupled.[4] The consequences for $V(l)$ (Fig. 3) are that (i) the definition of l is no longer unique (since the jump in dA/dx becomes rounded), (ii) the calculation of $V(l)$ will involve also the profile $A(x)$, (iii) the linear character of $V(l)$ at small l will soften to $dV/dl=0$ at $l=0$, so that one may then expand $V(l)$ around $l=0$ to study small fluctuations, and (iv) the quantum effect leading to the existence of a minimum sheath thickness l_0 will, however, persist at small $\kappa>0$, since the spectrum of the particle-in-a-box problem is only quantitatively changed when the steps in the confining potential become rounded. Therefore we expect that the low-κ approximation remains *qualitatively* correct up to $\kappa=0.374$, where the first-order wetting transition changes to critical wetting.[4] The consequence of $\kappa>0$ for the interface profile (Fig. 4) is that its representation by a sharp boundary $l(y)$ becomes less precise, since the jump in magnetic induction is smeared out over the length λ.

It should be possible in principle to verify the predicted S-shaped distortion of the interface experimentally. Any technique that can detect a rapid spatial variation of magnetic induction and that can scan from the surface into the sample to a depth of several times the coherence length ξ would be adequate.

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[10] It is understood here that the thickness of the deposited film is small compared with the coherence length ξ of the bulk superconductor. The effect of this film, or of another surface treatment (e.g., cold working), is then to a good approximation taken into account by a change in the extrapolation length b.

[11] We remark that the well-known concern that strain energies can play an important role in wetting problems does not apply here. This concerns applies when the two adsorbed phases differ in structure, such as in adsorption of solid layers from a vapor phase, on top of an arbitrary solid substrate. The slow relaxation, as a function of layer thickness l, of the lattice constant in the adsorbed layer towards the lattice constant of the same solid in bulk then causes a long-ranged elastic contribution to the interface potential $V(l)$ [see, e.g., T. Gittes and M. Schick, Phys. Rev. B **30**, 209 (1984); D. Huse, *ibid*. **29**, 6985 (1984)]. In the case of a type-I superconductor, even in the presence of a thin deposited film at the surface, the ‘‘adsorbate’’ is the (semi-infinite) bulk superconductor itself, which consists of a *single* solid. The two phases (SC and *N*) do not differ in lattice structure, but in conductivity, so that there is no strain contribution to the free energy of interaction $V(l)$ between the surface and the SC/*N* interface.

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