Interface Delocalization Transition in Type-I Superconductors

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Within the Ginzburg-Landau theory, which is known to be quantitatively correct for classical superconductors, it is shown that a type-I superconductor with *enhanced* order parameter $|\psi|^2$ at the surface displays an interface delocalization or "wetting" transition. Surprisingly, the order of the transition is controlled by a *bulk* material constant, the Ginzburg-Landau parameter κ. First-order wetting is predicted for $0 \leq \kappa < 0.374$ and critical wetting for $0.374 < \kappa < 1/\sqrt{2}$. Superconductors are likely to be an ideal test case for experimental observation of critical wetting.

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An important advance in the research on superconductivity was the discovery in 1963, by Saint-James and de Gennes, of the nucleation of a thin superconducting sheath at the surface of a superconductor (SC), at a critical field $H_{c3}(T)$ higher than the bulk coexistence field $H_c(T)$ in type-I or bulk critical field $H_{c2}(T)$ in type-II materials [1,2]. The thickness l of this sheath is of the order of the coherence length ξ, and an interesting question is what happens to l when the field is lowered towards the bulk coexistence field. The connection between this question and wetting phenomena was recognized by Speth [3,4]. He concluded that, for type-I SC's with a surface against vacuum or an insulator, l tends to a finite value l_c in the limit that bulk two-phase coexistence between normal and superconducting phases is approached. However, l_c diverges when the borderline between type-I and type-II behavior is reached, that is, when the (temperature-independent) Ginzburg-Landau parameter κ approaches the multicritical value $\kappa_c = 1/\sqrt{2}$. ($\kappa = \lambda/\xi$, with λ the magnetic penetration depth.) This is a noteworthy result, but for any type-I SC (i.e., $\kappa < 1/\sqrt{2}$), vacuum/SC or insulator/SC surfaces do not enhance superconductivity sufficiently to induce an interface delocalization transition in which l_c diverges. In this Letter we show that delocalization does occur for other types of surfaces.

The essential parameter in wetting phenomena is the surface quantity that is responsible for the preferential adsorption of one of the coexisting bulk phases at the surface. For fluids adsorbed at surfaces or interfaces, it is a chemical potential increment $\Delta\mu_1$. For magnets (e.g., Ising models) it is a surface magnetic field H_1. For SC's it is a surface extrapolation length b, which embodies the surface enhancement (for $b < 0$) or suppression (for $b > 0$) of the superconducting order parameter [2]. The Ginzburg-Landau surface free energy functional, including the surface contribution [5], reads

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

Here x is the coordinate perpendicular to the surface, which is at $x = 0$. $\mathbf{A}$ is the vector potential and the applied field $\mathbf{H} = H\mathbf{e}_z$ is parallel to the surface. Furthermore, $\alpha \propto T - T_c$, where T_c is the bulk critical temperature. We choose the gauge so that $\mathbf{A} = (0, A(x), 0)$. Because of the translational invariance along y and z, and by redefining $A(x)$, it is possible to work with real functions $\psi(x)$. A and ψ are determined by the Ginzburg-Landau equations.

The role of b becomes clear when the free energy is minimized with respect to $\psi(0)$. This leads to the familiar boundary condition [2]

$$\dot{\psi}(0) = b^{-1}\psi(0), \quad (2)$$

where the overdot means d/dx. For metal/SC surfaces, $b > 0$, with $b \to 0$ for ferromagnet/SC surfaces [2,5]. For vacuum/SC or insulator/SC surfaces, $b \to \infty$. The case $b < 0$ corresponds to surface enhancement of superconductivity, resulting, for example, when a thin superconducting layer with a higher T_c is present at the surface [6]. It also occurs near twinning planes inside the bulk SC's Sn, In, Nb, Re, and Tl, and at surfaces where grinding-induced twinning planes accumulate [7]. Our study of interface delocalization is restricted to type-I SC's. For type II, different unbinding transitions occur, involving vortex lines [8].

Our main results are concerned with bulk two-phase coexistence between normal (N) and superconducting (SC) states at $H_c(T)$. It is well known that the interfacial tension $\gamma_{\text{SC,N}}$ of the SC/N interface is positive for $\kappa < \kappa_c$. In the presence of a surface (W) we distinguish two surface free energies, $\gamma_{\text{W,N}}$ and $\gamma_{\text{W,SC}}$, depending on

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whether the bulk boundary condition at $x \to \infty$ is the N or the SC phase. The premise of the interface delocalization study is that one of the two bulk phases, N or SC, is preferred by the surface. Our calculations show that the SC phase is preferred for all κ when $b \le 0$ and for sufficiently large κ when $b > 0$. Therefore, we consider $\gamma_{W,SC} < \gamma_{W,N}$. If we now impose the disfavored phase N in the bulk, the question arises whether the material will remain mainly in the N state, with possibly a thin SC sheath at the surface (as anticipated in [1]), or whether a *macroscopic* layer of SC phase will intrude between the surface and the N phase. The thermodynamic equilibrium condition

$$\gamma_{W,N} \le \gamma_{W,SC} + \gamma_{SC,N} \tag{3}$$

is realized as a strict inequality in the former case, and as an equality in the latter. The temperature T_D, if it exists, at which (3) first becomes an equality, marks the transition between an SC/N interface localized (or bound) to the surface, and a delocalized (unbound) SC/N interface. We find that, for $b < 0$, all type-I SC's undergo this interfacial phase transition at some $T_D < T_c$ and a macroscopic SC layer intrudes for $T_D \le T < T_c$. This is, in fact, another realization of Cahn's general concept of critical-point wetting [9].

The determination of the delocalization transition is greatly facilitated by constructing a "phase portrait" in which $\dot{\psi}(0)$ is plotted vs $\psi(0)$, for *arbitrary b.* Figure 1 illustrates this for two representative cases, $\kappa = 0.3$ and $\kappa = 0.5$, for bulk two-phase coexistence ($H = H_c$). The bulk phase is fixed to N. For $\kappa = 0.3$ (solid lines) the concave branch, from O to Y, corresponds to profiles with a superconducting surface sheath. As Y is approached, the sheath thickness l diverges. The convex branch corresponds to W/SC/N profiles, which start from the surface and approach the SC phase for $x \to \infty$. An SC/N interface is added (at $x = \infty$), such that finally the N phase is reached across an infinite SC layer. The straight line represents the boundary condition (2). Intersections of this line with the branches correspond to extrema of the free energy. There is a local minimum at the origin (absence of superconductivity), a local minimum at D (macroscopic SC layer and delocalized SC/N interface), and a maximum at U (thin SC sheath and localized SC/N interface). In order to locate the phase transition, where the two minima exchange stability, we substitute into (1) the A and ψ that satisfy the Ginzburg-Landau equations and the boundary condition $\dot{A}(0) = \mu_0 H$, but with $\psi(0)$ *fixed.* This leads to the surface free energy function $\tilde{\gamma}$, given by

$$\tilde{\gamma}(\psi(0)) = \frac{\hbar^2}{2m}\left[\frac{\psi(0)^2}{b} + \sigma(\psi(0))\right]. \tag{4}$$

By varying σ with $\psi(0)$ we obtain $d\sigma(\psi)/d\psi = -2\dot{\psi}_0(\psi)$, where $\dot{\psi}_0 \equiv \dot{\psi}(0)$. Combined with (4) this leads to

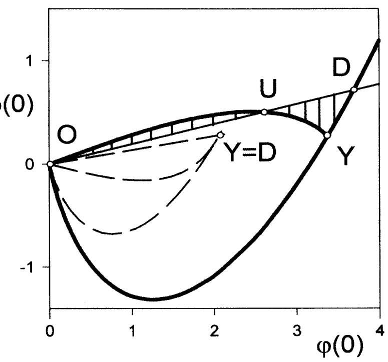

FIG. 1. Phase portraits $-\dot{\varphi}(0)$ vs $\varphi(0)$ for $\kappa = 0.3$ (solid lines) and $\kappa = 0.5$ (dashed lines). Here, $\varphi \equiv \psi\xi/\kappa$ and the dot means $\xi d/dx$. For $\kappa = 0.3$ an equal-areas construction determines the location of the first-order interface delocalization transition. For $\kappa = 0.5$ the meeting point Y determines the location of the critical delocalization.

$$\tilde{\gamma}(\psi(0)) = \tilde{\gamma}(0) + \frac{\hbar^2}{m}\int_0^{\psi(0)} d\psi\left[\frac{\psi}{b} + \dot{\psi}_0(\psi)\right], \tag{5}$$

from which one easily derives an equal-areas rule. Thus, a *first-order* phase transition between a state with $\psi = 0$ and a macroscopic SC layer takes place when b is adjusted so that the hatched areas are equal.

For $\kappa = 0.5$ (dashed lines in Fig. 1) the phase portrait is qualitatively different. Both branches are convex and, depending on b, we have either a stable finite sheath or an infinite sheath. The sheath thickness l diverges continuously approaching Y. *A critical* delocalization transition occurs when the straight line passes through $Y = D$. The precise location of D is obtained by studying the asymptotic behavior of A and ψ, for $x \to \infty$, for W/SC profiles.

Figure 2 presents the global wetting phase diagram in the $(\kappa, \xi/b)$ plane at bulk two-phase coexistence. For a given bulk material, changing T and H, such that $H = H_c(T)$, corresponds to moving horizontally. Increasing T towards T_c means increasing $\xi/|b|$ towards ∞, since $\xi \propto |T - T_c|^{-1/2}$. For $0 \le \kappa < 0.374$ the delocalization transition (line FD) is of first order. In the limit $\kappa \to 0$ we have calculated analytically that it occurs at $\xi/b = -0.603$. For $\kappa > 0.374$, the delocalization transition (line CD) is critical. The sheath thickness diverges as $l \propto \log[1/(T_{CD} - T)]$. The nucleation of the sheath takes place on the critical line CN. The continuation of this line, which is the metastability limit of the normal surface state, is indicated by ML (dashed line).

The lines CD and FD meet in a *critical end point* CEP at $\kappa = 0.374$ [10]. On the other hand, the nucleation transition changes from second to first order at a *tricritical point* TCP at $\kappa = 0.388$. There, the line CN changes (with common tangents) into the first-order nucleation line FN. On the line, between TCP and CEP, nucleation proceeds with

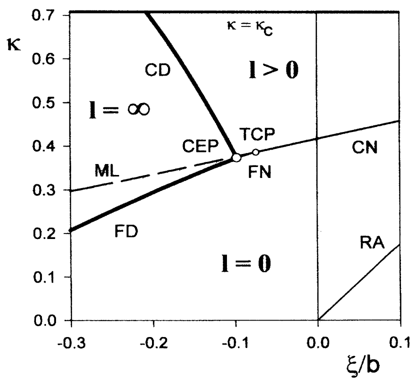

FIG. 2. Global phase diagram of interface delocalization transitions for type-I SC's. The phases are labeled by the thickness l of the superconducting surface sheath: $l = 0$ (no superconductivity), $0 < l < \infty$ (SC/N interface localized at the surface), $l = \infty$ (delocalized SC/N interface). The transitions are explained in the text.

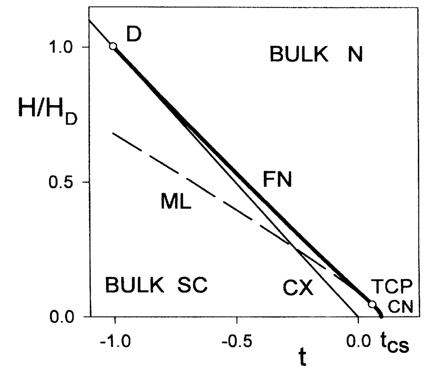

FIG. 3. (H, T) surface phase diagram for $\kappa = 0.2$ and $b < 0$. The line CX denotes bulk two-phase coexistence. The surface superconductivity transitions can be interpreted as first-order (line FN), tricritical (point TCP), and critical (line CN) prewetting transitions, associated with the first-order delocalization transition at D.

a thickness jump, from $l = 0$ to $l = l_{\mathrm{FN}}$, and l_{FN} diverges when CEP is approached. Note that for $b < 0$ all type-I SC's are bound to undergo an interface delocalization transition at some $T_D < T_c$ [11]. For completeness, we draw attention to the line RA, on which $\gamma_{\mathrm{W,N}} - \gamma_{\mathrm{W,SC}}$ passes through zero, corresponding to reversal of preferential adsorption. To the left of this line the SC phase is preferred by the surface.

From the point of view of wetting phenomena as well as that of superconductivity it is important to study what happens as a function of the magnetic field, especially for $H > H_c(T)$. *First-order* wetting transitions have extensions into the bulk one-phase region, called *prewetting lines* [4,9]. In superconductivity, critical nucleation of a SC surface sheath occurs at a field H_{c3} [1], which is a strongly increasing function of $\xi/|b|$ for $b < 0$ [6].

The connection between prewetting and critical nucleation is demonstrated in Fig. 3 for $\kappa = 0.2$ and $b < 0$. In principle, this phase diagram should be directly verifiable experimentally. The temperature variable is $t \equiv (T - T_c)/(T_c - T_D)$, such that the first-order delocalization transition occurs at $t_D = -1$. Similarly, the magnetic field is expressed in units of H_D. The connection with measurable quantities is most easily made by locating the critical point of *surface* superconductivity in zero field at T_{cs}. Indeed, for $b < 0$, $T_{cs} > T_c$ and one easily shows analytically that $\xi(T_{cs})/b = -1$. Since the function $\xi(T)$ is known from the microscopic theory, measuring T_{cs} allows us to estimate b. This in turn allows us to locate T_D, because $t_{cs} = \xi(T_D)^2/b^2$ depends *only* on κ and is obtained directly from our calculations. For $\kappa = 0.2$, $\xi(T_D)/b = -0.308$.

The first-order delocalization transition, at D, has an extension along the first-order nucleation or "prewetting" line FN. This line, which is tangential to the bulk coexistence line CX at D, changes into a critical nucleation line CN at a tricritical point TCP. Note that this is different from prewetting in fluids or magnets, where the prewetting line stops at a simple critical point. At TCP, FN and CN meet with common tangents, and, to the left of TCP, CN continues as the metastability limit ML (dashed line) of the normal surface phase. To the right of TCP, the line CN terminates at the surface critical temperature T_{cs}. An analytic calculation shows that $H_{c3} \propto (T_{cs} - T)^{1/2}$ near T_{cs}. For the thickness l of the surface sheath when bulk two-phase coexistence is approached at fixed T, we find a divergence $l \propto \log[1/(H - H_c)]$ for $T_D < T < T_c$. This is the approach to "complete wetting." In contrast, for $T < T_D$, $l_c = 0$.

The (H, T) surface phase diagram for a type-I SC with $\kappa > 0.374$ and $b < 0$, which displays critical delocalization, is qualitatively different. The line FN is absent, and the line CN continues down to temperatures $T < T_D$. The transition point D, at bulk coexistence, is then isolated. Experimentally D could be detected by monitoring l_c vs T. Also, T_D can be estimated indirectly, as explained above, by measuring the zero-field surface transition temperature T_{cs}.

Our main conclusions and final remarks are the following.

(a) For all type-I SC's with enhanced surface order parameter ($b < 0$), there exists a genuine wetting temperature T_D, which marks an interface delocalization phase transition (Fig. 2). This transition occurs at bulk two-phase coexistence, so that $H_D = H_c(T_D)$. The existence of these transitions demonstrates that, contrary to what is commonly believed, the thickness l of the superconducting surface sheath can be much larger than the bulk coherence length ξ.

(b) The complete phenomenology of wetting is realized in type-I SC's. Surprisingly, unlike in all other wetting systems that we know of, the order of the wetting transition is controlled by a *bulk* material constant, the GL parameter κ. First-order wetting takes place for $0 \leq \kappa < 0.374$ and critical wetting for $0.374 < \kappa < 1/\sqrt{2}$. Consequently, e.g., Al ($\kappa \approx 0.01$) and Sn ($\kappa \approx 0.1$) are predicted to display first-order wetting, whereas Pb ($\kappa \approx 0.6$) is a candidate for critical wetting. Thus there is new physics associated with wetting in SC's because in other systems the order of the transition depends on *surface* parameters which are difficult to determine or control.

(c) The prediction of critical wetting is especially important from an experimental viewpoint. Up to now, detailed experiments on wetting in fluids have provided unambiguous evidence for first-order wetting and prewetting [12]. However, there is to our knowledge no clear experimental verification yet of critical wetting in any system. Thus, type-I SC's with $\kappa > 0.374$ may be the ideal testing ground for observing this phenomenon.

(d) Wetting in SC's is also new in that it provides a realization of systems with exponentially decaying wall-interface interactions (with characteristic length scales λ or ξ), usually referred to as short-range forces. This leads to a *logarithmic* divergence of the sheath thickness when approaching complete wetting ($T > T_D$) and critical wetting. In contrast, in other systems power-law interactions (van der Waals or other) prevail, which are referred to as long-range forces. Especially for critical wetting, theory has long since predicted interesting anomalies in the case of exponentially decaying interactions [13].

(e) We give a new interpretation and make further predictions for twinning-plane superconductivity (TPS). The (H, T) surface phase diagram (Fig. 3) is similar to that of TPS at the same κ [7]. But first-order TPS transitions are now interpreted as prewetting, and we thus predict a first-order wetting transition in which the SC/N interface delocalizes from the twinning plane at the point D at bulk coexistence. Neither this nor the possibility of critical wetting has to our knowledge been predicted yet for TPS.

(f) The case of a (classical) SC is known to be a fairly unique example of a system for which the Ginzburg-Landau theory is quantitatively correct. The experiments on TPS confirm this once more. For other systems (fluids, magnets, etc.) the corresponding mean-field theory is at best qualitative and often a poor approximation. Therefore, the mean-field wetting phase diagram of type-I SC's (Fig. 2) is exceptional in that is provides a quantitative guide for the experimentalist.

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[1] D. Saint-James and P.-G. de Gennes, Phys. Lett. **7**, 306 (1963).
[2] See, e.g., P.-G. de Gennes, *Superconductivity of Metals and Alloys* (Addison-Wesley, Reading, MA, 1966).
[3] W. Speth, Ph. D. thesis, München, 1986.
[4] For a review on wetting, including Speth's contribution, see S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 12, p. 1.
[5] See, e.g., H. Schinz and F. Schwabl, J. Low Temp. Phys. **88**, 347 (1992).
[6] H. J. Fink and W. C. H. Joiner, Phys. Rev. Lett. **23**, 120 (1969).
[7] I. N. Khlyustikov and A. I. Buzdin, Adv. Phys. **36**, 271 (1987); A. A. Abrikosov, A. I. Buzdin, M. L. Kulic, and D. A. Kuptsov, Sov. Phys. JETP **68**, 210 (1989); D. A. Kuptsov and S. V. Polonskii, Sov. J. Low Temp. Phys. **14**, 562 (1989).
[8] See, e.g., L. Balents and M. Kardar, Phys. Rev. B **49**, 13 030 (1994); D. S. Fisher, M. P. A. Fisher, and D. A. Huse, Phys. Rev. B **43**, 130 (1991).
[9] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).
[10] Usually the change from first-order to critical wetting is via a *tricritical point.* See H. Nakanishi and M. E. Fisher, Phys. Rev. Lett. **49**, 1565 (1982). However, critical end point schemes also occur. See, e.g., G. Langie and J. O. Indekeu, J. Phys. Condens. Matter **3**, 9797 (1991).
[11] In the (b^{-1}, T) plane the delocalization phase boundary is described by $b_D^{-1} = A(\kappa)(T_c - T_D)^{1/2}$.
[12] For ordinary fluids, see, e.g., H. Kellay, D. Bonn, and J. Meunier, Phys. Rev. Lett. **71**, 2607 (1993); for quantum fluids, see, e.g., K. S. Ketola, S. Wang, and R. B. Hallock, Phys. Rev. Lett. **68**, 201 (1992); J. E. Rutledge and P. Taborek, Phys. Rev. Lett. **69**, 937 (1992).
[13] R. Lipowski, D. M. Kroll, and R. K. P. Zia, Phys. Rev. B **27**, 4499 (1983); E. Brézin, B. I. Halperin, and S. Leibler, Phys. Rev. Lett. **50**, 1387 (1983).