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Interfacial Tension and Interface Delocalization Phase Boundary for Strongly Type-I Superconductors[1]

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We analytically determine the interface delocalization (or wetting) transition phase boundary in the limit of strongly type-I superconductors. In particular, within Ginzburg–Landau theory we derive an analytic expression for the reduced surface tension, $\Gamma_{\mathrm{SC/N}}$, of a type-I superconductor. We find that the truncated expansion $\Gamma_{\mathrm{SC/N}} \approx 2\sqrt{2}/3 - 1.02817\sqrt{\kappa} - 0.13307\kappa\sqrt{\kappa}$ (where κ is the Ginzburg–Landau parameter) is so accurate in the entire type-I regime $0 \leqslant \kappa \leqslant 1/\sqrt{2}$ that derivation of higher-order terms is unnecessary. We further derive an expression for the wall/superconductor interfacial tension which again proves accurate across a broad range of κ values. These expansions allow us to locate the low-κ interface delocalization phase boundary accurately, complementing previous numerical results for the wetting phase diagram.

KEY WORDS: Ginzburg–Landau theory; interfacial tension; superconductivity: wetting transitions.

1. INTRODUCTION

In this paper we present an overview and tutorial summary of some surface tension calculations for type-I superconductors based on Ginzburg–Landau (GL) theory [1, 2]. In particular, in Section 2 we consider the interfacial tension between normal (N) and superconducting (SC) phases in terms of an expansion in the GL parameter κ. This tension is a fundamental quantity in classical superconductivity and, as we discuss, played an important role in the introduction of the GL theory of superconductivity. In Section 3 we determine a similar expansion for an interfacial tension pertinent to the

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case of a semi-infinite geometry with a "wall" corresponding to the surface of the superconducting material. This allows us to derive features of the phase diagram for the interface delocalization transition recently predicted in type-I superconductors [3].

2. SUPERCONDUCTING/NORMAL INTERFACIAL TENSION

In a bulk superconducting material at two-phase coexistence it is natural to consider the interfacial or surface tension between the normal and the superconducting phases, $\gamma_{SC/N}$. This quantity is fundamental in distinguishing type-I superconductors, where the positive surface tension $\gamma_{SC/N} > 0$ stabilizes the subdivision of the sample at a macroscopic scale, and type-II superconductors, with a negative surface tension leading to an array of flux tubes in place of a macroscopic interface. Further, in their groundbreaking paper GL motivated the modeling of superconductivity using the general theory of phase transitions by noting, "The existing phenomenological theory of superconductivity is unsatisfactory since it does not allow us to determine the surface tension at the boundary between the normal and superconducting phases..." [4]. In that original paper Ginzburg and Landau were interested in calculating an expansion for $\gamma_{SC/N}$ in terms of the so-called GL parameter, $\kappa \equiv \lambda/\xi$, which is defined as the ratio of the magnetic penetration depth to the bulk coherence length. Thus, λ and ξ denote the typical length scales over which the magnetic induction and superconducting order-parameter $|\psi|^2$, respectively, vary. In particular, one wants an expansion in the low-κ limit when there is little overlap between the magnetic induction and $|\psi|$. By construction the GL theory is valid only close to the bulk critical temperature T_c. In this region it is convenient to define the "reduced" (temperature independent) surface tension, $\Gamma_{SC/N}(\kappa)$ such that

$$\gamma_{SC/N} \propto \Gamma_{SC/N}(\kappa)\, |T - T_c|^{3/2} \tag{1}$$

where, for concreteness, the constant of proportionality is fixed by choosing $\Gamma_{SC/N}(\kappa = 0) = 2\sqrt{2}/3$. In deriving a low-$\kappa$ expansion for $\Gamma_{SC/N}$ we find it instructive to recall some of the analysis of Ginzburg and Landau. The main ingredient is the introduction of an appropriate free energy functional $\Gamma_{SC/N}$. For our interests it is sufficient to consider the one-dimensional problem in which the x-axis is normal to the boundary separating the SC phase ($x > 0$) and normal phase. For this case Ginzburg and Landau prescribe (for $T < T_c$)

$$\Gamma_{SC/N}[\psi, A] = \kappa \int_{-\infty}^{\infty} dx \{ -\psi^2 + \psi^4/2 + A^2\psi^2 + \dot{\psi}^2/\kappa^2 + [\dot{A} - H_0]^2 \} \tag{2}$$

where A is the vector potential, the applied magnetic field is at the coexistence value $H_0 = 1/\sqrt{2}$, and an overdot denotes differentiation with respect to x. The transition from the SC phase to the N phase takes place in a transition layer in which for $x \to \infty$, we have the SC phase ($\psi \to 1$, $A \to 0$), and for $x \to -\infty$ the N phase ($\psi \to 0$, $\dot{A} \to 1/\sqrt{2}$).

Minimization of Eq. (2) with respect to ψ and A yields the GL equations

$$\ddot{\psi} = \kappa^2[-\psi + \psi^3 + A^2\psi]; \qquad \ddot{A} = \psi^2 A \tag{3}$$

which should be solved subject to the above boundary conditions. These equations can be integrated once, yielding $\dot{A}^2 + \dot{\psi}^2/\kappa^2 = -\psi^2 + \psi^4/2 + A^2\psi^2 + \frac{1}{2}$, although general analytic solutions cannot be found. However, Ginzburg and Landau made progress in the limit $\kappa \to 0$ by noting that the approximation $A = C\exp(-\int \psi\, dx)$ is a valid solution to the second differential equation whenever $|\dot{\psi}/\psi^2| \ll 1$. When κ is small this is satisfied for large x because in this region ψ differs from the bulk value $\psi = 1$ only by exponentially small corrections [4]. Substituting this expression for A into the first integral leads to a solvable equation for ψ appropriate in this region. In particular, within this approximation

$$\psi(x) = \tanh\left(\frac{\kappa x}{\sqrt{2}}\right); \qquad A(x) = C\exp\left[-\frac{\sqrt{2}}{\kappa}\ln\cosh\left(\frac{\kappa x}{\sqrt{2}}\right)\right] \tag{4}$$

valid in the region $1/\sqrt{\kappa} < x < \infty$. Further, from order of magnitude considerations they identify the constant $C \sim 1/\sqrt{\kappa}$. This means that at the boundary of the region of validity of the solutions [Eq. (4)], $A \gg 1$. Hence, from this point on (i.e., $x < 1/\sqrt{\kappa}$) the first GL equation is well approximated by $\ddot{\psi} = \kappa^2 A^2 \psi$. In this case Ginzburg and Landau noted that the scale transformation $\tilde{x} = x\sqrt{\kappa}$, $\tilde{\psi} = \psi/\sqrt{\kappa}$, and $\tilde{A} = A\sqrt{\kappa}$ yields the following "universal equations" for this region, $\tilde{\psi}'' = \tilde{A}^2\tilde{\psi}$ and $\tilde{A}'' = \tilde{\psi}^2\tilde{A}$. Here, primes denote differentiation with respect to $\tilde{x}$. Ginzburg and Landau did not solve these universal equations explicitly but showed that the contribution to $\Gamma_{SC/N}$ from this region is $\mathcal{O}(\sqrt{\kappa})$. Substitution of the results from Eq. (4) into Eq. (2) for $x > 1/\sqrt{\kappa}$ led Ginzburg and Landau to their final result,

$$\Gamma_{SC/N}(\kappa) = 2\sqrt{2}/3 + \mathcal{O}(\sqrt{\kappa}) \tag{5}$$

Surprisingly, the goal of extending this expansion for $\Gamma_{SC/N}(\kappa)$ was not further pursued until recently when Mishonov [5] and Osborn and Dorsey

[6] made predictions for the amplitude of the $\mathcal{O}(\kappa)$ term. Specifically they found

$$\Gamma_{\mathrm{SC/N}}(\kappa)=\begin{cases}2\sqrt{2}/3-1.03\sqrt{\kappa}+\mathcal{O}(\kappa\sqrt{\kappa}), & \text{Mishonov}\\ 2\sqrt{2}/3-0.88\sqrt{\kappa}+\mathcal{O}(\kappa\sqrt{\kappa}), & \text{Osborn/Dorsey}\end{cases} \tag{6}$$

with a clear discrepancy between the two results. Here we demonstrate agreement with the suggestion of Mishonov and further determine the next term in the expansion. We find it convenient to use the rescaled variables described above so that the GL equations take the form

$$\tilde{\psi}''=\tilde{A}^2\tilde{\psi}-\kappa\tilde{\psi}+\kappa^2\tilde{\psi}^3; \qquad \tilde{A}''=\tilde{\psi}^2\tilde{A} \tag{7}$$

We proceed by making perturbation expansions for $\tilde{\psi}(\tilde{x})=\tilde{\psi}_1(\tilde{x})+\kappa\tilde{\psi}_2(\tilde{x})+\cdots$ and $\tilde{A}(\tilde{x})=\tilde{A}_1(\tilde{x})+\kappa\tilde{A}_2(\tilde{x})+\cdots$. Substituting these expansions into Eq. (7) yields the GL universal equations for $\tilde{\psi}_1$ and $\tilde{A}_1$, with similar equations for the higher-order elements. The boundary conditions are such that, for example, the $\tilde{\psi}_i$ are required to recover the term of corresponding order in the expansion of $\tanh(\tilde{x}\sqrt{\kappa}/\sqrt{2})/\sqrt{\kappa}$ for $\tilde{x}\to\infty$. In this way our task is actually to compute the "residual" contributions to the ψ and A, a computation which turns out to lead to an extremely rapidly convergent expansion.

We omit the details of the calculation, which can be found in Ref. 1, restricting ourselves here to the pertinent results. The term of $\mathcal{O}(\sqrt{\kappa})$ in $\Gamma_{\mathrm{SC/N}}$ is given by the formal expression $-4\sqrt{\kappa}\int_{-\infty}^{\infty}d\tilde{x}\,\tilde{A}_1^2\tilde{\psi}_1^2$. This is especially instructive because it explicitly shows that the surface tension correction is negative and that the lowering of the surface tension is due to overlap of $\tilde{\psi}$ and $\tilde{A}$. Our main result is the expansion for $\Gamma_{\mathrm{SC/N}}$,

$$\Gamma_{\mathrm{SC/N}}(\kappa)=2\sqrt{2}/3-1.02817\sqrt{\kappa}-0.13307\kappa\sqrt{\kappa}+\mathcal{O}(\kappa^2\sqrt{\kappa}) \tag{8}$$

where the correction coefficients have been calculated numerically with an accuracy of ± 1 in the fifth decimal. We can continue our scheme to calculate further terms; however, we conclude this section by arguing that this is unnecessary. First, we comment that the expansion [Eq. (8)] truncated after three terms is in excellent agreement with numerical data across the broad range $0\leqslant\kappa\leqslant 1$ [1], not just the region $\kappa\ll 1$, which was our initial goal. This is shown convincingly in Fig. 1, where we plot the truncated expansion as a function of κ. Note that within the thickness of the line the surface tension takes the value of zero at $\kappa=1/\sqrt{2}$. In fact, a measure of the accuracy of the expansion can be seen from noting $\Gamma_{\mathrm{SC/N}}(\kappa=1/\sqrt{2})=-0.00090$, when including the term of order $\kappa\sqrt{\kappa}$. This

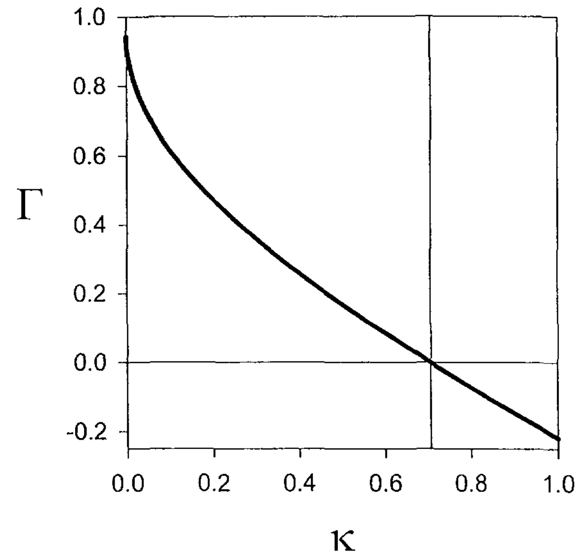

Fig. 1. Plot of the surface tension Γ versus κ taken from the analytic expansion $\Gamma_{SC/N}(\kappa) \approx 2\sqrt{2}/3 - 1.02817\sqrt{\kappa} - 0.13307\kappa\sqrt{\kappa}$. Note the accuracy of this low-κ expansion even at $\kappa = 1/\sqrt{2}$, where the deviation of the surface tension from zero lies within the thickness of the line.

is extremely close to the exact value of zero, and corresponds to the maximum error in the truncated expansion across the entire type-I range.

3. INTERFACE DELOCALIZATION TRANSITION PHASE BOUNDARY

In this section we turn our attention to the interface delocalization transition in type-I superconductors in which a macroscopically thick superconducting layer intrudes from the outer surface or wall (W) of the material into the bulk normal phase [3]. This transition is analogous to the wetting transition in fluids and may be studied using similar techniques, for example, an interface potential approach [7]. The transition may also occur near twinning planes inside bulk superconductors such as Sn and In, although we do not consider that case here [8]. We concentrate specifically on determining the first-order delocalization phase boundary in the low-κ limit not studied in full in Ref. 3.

The interface delocalization transition can be understood in terms of interfacial tensions as follows. Assume that the material is at SC–N coexistence and that the wall favors the SC phase but that the N phase is imposed in the bulk. Now we may ask whether a macroscopic SC layer occurs or if, rather a zero or microscopically thin superconducting sheath is found at the wall. The latter will be the case if the free energy cost of a W/N interface, $\gamma_{W/N}$, is less than that of a W/SC *and* SC/N interface combined, i.e., for $\gamma_{W/N} < \gamma_{W/SC} + \gamma_{SC/N}$. Otherwise, the SC phase "completely wets" the wall and a macroscopic superconducting layer intrudes from the surface into the bulk. For $\kappa < 0.374$ [3] a W/N interface corresponds to the null solution $|\psi|^2 = 0$ everywhere, yielding the surface free energy $\gamma_{W/N} = 0$ [3]. Below we describe the derivation of $\gamma_{W/SC}$ in the limit $\kappa \to 0$ and, using the results of Section 2, derive the phase boundary in the same limit from the condition $\gamma_{W/SC} + \gamma_{SC/N} = 0$.

We again use GL theory to calculate the interfacial tension $\gamma_{W/N}$ and find it convenient to define the reduced tension $\Gamma_{W/N}(\kappa)$ in an analogous manner to Eq. (1). If we assume that the wall lies in the plane, $x = 0$, then the appropriate GL free energy functional is similar to Eq. (2) but with the lower limit of the integral replaced by zero. In addition, a surface term must be included which effectively amounts to the boundary condition $d\psi/dx|_{x=0} = b^{-1}\psi|_{x=0}$. The surface extrapolation length b plays the rôle of a "surface field"—for the case of enhanced superconductivity at the wall, required for the interface delocalization transition, we must take $b < 0$ [9]. The calculation of $\Gamma_{W/SC}$ proceeds along the same lines as that of $\Gamma_{SC/N}$, i.e., making perturbation expansions for ψ and A, solving the GL equations at each order, matching the $\kappa \to 0$ solutions for $x \to \infty$, and substituting into the free energy functional to calculate the interfacial tension. The details of the calculation can be found in Ref. 2. Our final result is

$$\Gamma_{W/SC} = \frac{2\sqrt{2}}{3}(1 - \coth C) + \frac{\tau}{3}\coth^2 C - \frac{\kappa}{2}\tanh C + \frac{\kappa^2}{8\sqrt{2}} \frac{(\tanh^3 C - 2\coth C)}{1 + \coth^2 C} + \mathcal{O}(\kappa^3) \tag{9}$$

where $C \equiv C(\tau)$ is given by $C = \frac{1}{2}\sinh^{-1}(-\sqrt{2}/\tau) > 0$ and we have introduced $\tau = \xi/b$. In contrast to Eq. (8) the expansion is regular in κ, with the coefficients at each order being determined analytically. Comparison of this expansion truncated at (and including) the $\mathcal{O}(\kappa^2)$ term with numerically calculated values of the surface free energy for a range of $b < 0$ and κ values reveals that the expansion is again rapidly convergent and hence valid across a large range of κ values [2].

We conclude by considering the interface delocalization phase boundary in the low-κ limit discussed above. In particular, we consider the phase diagram as a function of the parameters κ and τ. As motivation we comment that the study in Ref. 3 revealed a line of first-order delocalization transitions for $\kappa < 0.374$ showing only slight deviations from linear behavior. Extrapolation to $\kappa = 0$ of the numerical results obtained at higher κ suggests an interception of the phase boundary with the $\kappa = 0$ axis for $\tau \approx -0.55$. Such an extrapolation is not quite consistent with the analytic result $\tau^* = -0.6022$ obtained at $\kappa = 0$, where the GL equations are exactly solvable [3]. Here we study the structure of the phase boundary missed by the crude extrapolation. A simple analytic expression for the phase boundary, $\kappa(\tau)$, can be found using only the leading-order correction in κ in both Eq. (8) and Eq. (9). This yields

$$\kappa(\tau) \approx \left(-\mathscr{D} + \sqrt{\mathscr{D}^2 + \tfrac{2}{3} \coth C [2\sqrt{2}(2 - \coth C) + \tau \coth^2 C]} \right)^2 \qquad (10)$$

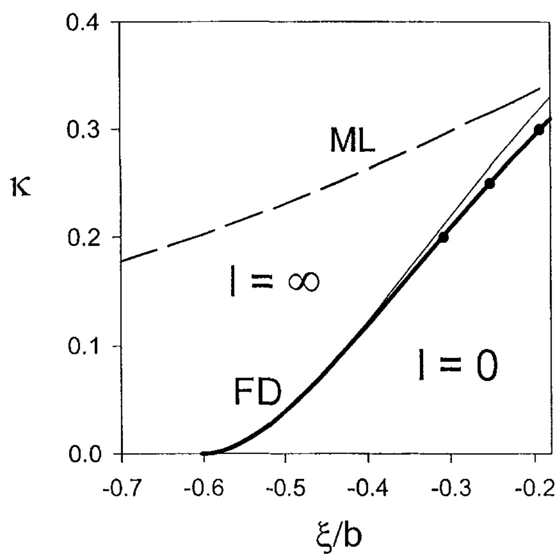

Fig. 2. Local phase diagram showing the first-order delocalization transition phase boundary (FD) accurate to both $\mathcal{O}(\kappa)$ (thin line) and $\mathcal{O}(\kappa^2)$ (thick line). Three data points representative of the numerically calculated phase boundary are also shown. The phases are labeled by the thickness l of the superconducting surface sheath: $l = 0$ (no superconductivity), $l = \infty$ (macroscopic superconducting layer; delocalized SC/N interface). Note that the line FD displays an inflection point at $\kappa \approx 0.1$. This feature is clearly visible in $\mathcal{O}(\kappa^2)$. The metastability limit (ML) explained in the text is shown by the dashed line.

where for brevity we have written $\mathscr{D} \equiv 1.02817 \coth C$. This expression is shown in Fig. 2 by the thin solid line. We can obtain a more accurate result for the phase boundary by including the next-order terms in Eqs. (8) and (9) and solving iteratively. This more accurate result for $\kappa(\tau)$ is shown in Fig. 2 by the thick solid line (FD; first-order delocalization) separating a region in which a macroscopic superconducting layer exists (above the line) and a region in which no superconducting sheath is present. For the range of τ values shown, the delocalization transition is first-order in nature. It has previously been shown [3] that the normal surface state (with $\psi = 0$) can persist as a metastable state up to the dashed line (ML; metastability limit). Also shown in the figure are three data points representative of the numerically calculated phase boundary—we observe that the agreement between our analytic result and these data points is very good, and we are confident that our analysis has determined all the previously missing fine structure of the phase boundary. In particular, expanding Eq. (10) about $\tau^* = -0.6022...$ reveals that the phase boundary approaches the $\kappa = 0$ axis in a parabolic manner $\kappa(\tau) \sim a(\tau - \tau^*)^2$, with $a \approx 4.95$. The origin of this 'parabolic foot" can be traced to the $\mathcal{O}(\sqrt{\kappa})$ correction in Eq. (8)—if we calculate the phase boundary only to $\mathcal{O}(\sqrt{\kappa})$ (so that we use only the $\kappa = 0$ result for $\Gamma_{W/SC}$), the resulting curve still displays the exact parabolic behavior for $\kappa \to 0$, although agreement with the numerical results for $\kappa \geqslant 0.2$ does, not surprisingly, require the addition of the higher-order terms.

4. CONCLUSIONS

Within the framework of GL theory we have described the calculation of expansions for two interface free energies, $\Gamma_{SC/N}$ and $\Gamma_{W/SC}$. These expansions have been derived strictly in the limit $\kappa \to 0$; however, the resulting expressions are observed to be good approximations for a broad range of κ values. Of fundamental interest is the expansion for $\Gamma_{SC/N}(\kappa)$ given by Eq. (8). In that case the expansion truncated after three terms is so accurate for the entire type-I regime that calculation of higher-order terms is unnecessary.

We have used the surface tension expansions to calculate the first-order delocalization transition phase boundary for $\kappa \ll 1$. While numerical results exist for higher $\kappa \geqslant 0.2$ and an analytic result for $\kappa = 0$, solutions at low κ were not explored due to the extra numerical complexity involved with the presence of the small parameter κ. Interestingly, similar techniques to those described above have recently been used to determine an analytic expansion in κ for the location of the critical delocalization transition [10].

This occurs for larger κ and, hence, the rapid convergence of the expansions is of crucial importance in that case.

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