Theory of Dissipative Current-Carrying States in Superconducting Filaments

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A simple generalized time-dependent Ginzburg-Landau equation valid for dirty superconductors in the vicinity of T_c is derived. For thin homogeneous filaments it exhibits oscillatory phase-slip solutions below and above the critical depairing current. The results are compared with I-V curves observed in whiskers and microbridges.

Up to now there has been no satisfactory theory of the current-induced transitions observed in superconducting filaments near T_c. Except very close to T_c, where fluctuation effects dominate, the normal state is approached through successive voltage jumps and hysteresis appears a few millidgrees Kelvin below T_c. The succession of critical currents and intervening states have been investigated thoroughly on "one-dimensional" samples [transverse dimension of the sample small compared to the coherence length $\xi(T)$ and penetration depth $\lambda(T)$]: on tin whiskers by Meyer and others[1,2] and on tin microbridges by Skocpol, Beasley, and Tinkham.[3] The jumps are now generally related to the appearance of localized "phase-slip centers."[3] The (dissipative) superconducting states with phase-slip centers appear to exist above the "critical depairing current" j_{max} at which the lossless superconducting state becomes unstable.[1,2] In fact, recent experiments show that the occurrence of a phase-slip center at a neighboring location.[2,4]

It was shown recently that the simple time-dependent Ginzburg-Landau (TDGL) theory exhibits oscillatory phase-slip solutions for long thin filaments in a very narrow range of currents below the "reversible critical current" j_c (which is lower than j_{max}).[5] The present Letter represents a generalization of this work for dirty superconductors in the vicinity of T_c. We derive generalized TDGL equations from microscopic theory and discuss solutions relevant for long, thin current-carrying filaments. The existence of periodic phase-slip solutions above j_{max} which can carry an average supercurrent larger than j_{max} is established rigorously for the first time. This provides a theoretical justification of the phase-slip–center concept and shows that a step structure appears even in a completely homogeneous filament.[6]

We start from a set of equations describing dirty superconductors near T_c in the presence of time-dependent electromagnetic fields $(\vec{A}, \varphi)$ which may be derived along the lines of Larkin and Ovchinnikov (LO)[7] and Schmid and Schön (SS).[8] The gap function Δ, current density $\vec{j}$, and charge density ρ are determined from (with $\hbar = k_B = c = 1$)

$$\left[\frac{\pi}{8T_c\epsilon}\frac{\partial}{\partial t} - \frac{1}{|\Delta|\epsilon}\int_0^\infty dE(R_2\delta f + iN_2 f_1)\right]\Delta = \xi^2(\nabla - 2ie\vec{A})^2\Delta + \left(1 - \frac{|\Delta|^2}{\Delta_0^2}\right)\Delta, \tag{1}$$

$$\vec{j} = \frac{\sigma_0}{e}\left\{\frac{\pi}{4T_c}|\Delta|^2\vec{Q} + \int_0^\infty dE\left[(N_1^2 + N_2^2)\left(\nabla f_1 - e\frac{\partial f_0}{\partial E}\frac{\partial \vec{A}}{\partial t}\right) + 2N_2R_2\vec{Q}\delta f\right]\right\}, \tag{2}$$

$$\rho = -2eN(0)\left(e\varphi + \int_0^\infty dE\, N_1 f_1\right), \tag{3}$$

where $\epsilon = (T_c - T)/T_c$, $\xi^2 = \pi D/8T_c\epsilon$, diffusion constant $D = v_F l/3$, $\Delta_0^2 = 8\pi^2 T_c^2\epsilon/7\zeta(3)$, $N(0)$ is the normal density of states, normal conductivity $\sigma_0 = 2e^2DN(0)$, superfluid velocity $\vec{Q} = -(\nabla\theta + 2e\vec{A})$, and $\Delta = |\Delta|\exp(-i\theta)$. One may set $\rho = 0$ in Eq. (3) as will be shown later on.

The real functions $N_1(E)$ and $R_1(E)$ are defined by

$$N_1(E) + iR_1(E) = \alpha(E), \quad N_2(E) + iR_2(E) = \beta(E). \tag{4}$$

Here α and β are the (retarded) normal and anomalous Green's functions defined by Usadel[9] in the no-

tation of SS.[8] For small deviations from equilibrium the static equations of motion[7-9]

$$\tfrac{1}{2}D[\alpha(\nabla - 2ie\vec{A})^2\beta - \beta\nabla^2\alpha] = (1/2\tau_E - iE)\beta - \Delta\alpha, \tag{5}$$

together with $\alpha^2+\beta^2=1$ may be used. In Eq. (5) inelastic electron-phonon scattering (τ_E is the inelastic collision time) is included in the usual approximation where it leads to lifetime broadening of the excitations.

Finally, we write down the kinetic equations for the odd and even distribution functions $f=f_0+\delta f$ [$f_0=\tanh(E/2T)$] and f_1 valid for small deviations from equilibrium and slow time variations ($\Omega \ll \Delta_0$):

$$D\nabla\cdot[(N_1^2-R_2^2)\nabla\delta f] + 2DN_2R_2\vec{Q}\cdot\left(\nabla f_1 - e\frac{\partial f_0}{\partial E}\frac{\partial\vec{A}}{\partial t}\right) - N_1\left(\frac{\partial}{\partial t}+\frac{1}{\tau_E}\right)\delta f = R_2\frac{\partial f_0}{\partial E}\frac{\partial|\Delta|}{\partial t}, \tag{6}$$

$$D\nabla\cdot\left[(N_1^2+N_2^2)\left(\nabla f_1 - e\frac{\partial f_0}{\partial E}\frac{\partial\vec{A}}{\partial t}\right)\right] + 2DN_2R_2\vec{Q}\cdot\nabla\delta f - N_1\left(\frac{\partial}{\partial t}+\frac{1}{\tau_E}\right)\left(f_1+e\varphi\frac{\partial f_0}{\partial E}\right) - N_2|\Delta|\left(2f_1+\frac{\partial f_0}{\partial E}\frac{\partial\theta}{\partial t}\right)=0. \tag{7}$$

The inelastic collision integrals in Eqs. (6) and (7) have been replaced by the "mutilated collision operator" with energy-independent collision time[10] τ_E; Eq. (3) with $\rho=0$ has been used to eliminate the scattering-in term in Eq. (7).

We now introduce a local equilibrium approximation for Eqs. (5)–(7) by omitting the gauge-invariant space and time derivatives. This is valid as long as the various quantities vary in space slowly over the inelastic diffusion length $L_E=(D\tau_E)^{1/2}$ and in time slowly over τ_E. The condition $L_E \ll \xi$, i.e.,

$$8T_c\tau_E\epsilon/\pi\ (=0.271\tau_E\Delta_0^2/T_c) \ll 1 \tag{8}$$

seems sufficient to ensure the validity of all the approximations made.

Equations (5)–(7) now lead to

$$\alpha = \frac{E+i/2\tau_E}{[(E+i/2\tau_E)^2-|\Delta|^2]^{1/2}}, \qquad \beta = \frac{i|\Delta|}{[(E+i/2\tau_E)^2-|\Delta|^2]^{1/2}}, \tag{9}$$

$$\delta f = -\frac{R_2}{N_1}\tau_E\frac{\partial f_0}{\partial E}\frac{\partial|\Delta|}{\partial t}, \tag{10}$$

$$f_1 = -\frac{N_1e\varphi + N_2\tau_E|\Delta|\dot{\theta}}{N_1+2N_2\tau_E|\Delta|}\frac{\partial f_0}{\partial E}. \tag{11}$$

This type of approximation was introduced for stationary problems by SS.[8]

When inserting these results into Eqs. (1)–(3) the following exact relations are useful:

$$\int_0^\infty \frac{N_2^2}{N_1+2\tau_E|\Delta|N_2}dE = \frac{\pi}{4\tau_E}\{1-[1+(2\tau_E|\Delta|)^2]^{-1/2}\}, \tag{12}$$

$$\int_0^\infty \frac{R_2^2}{N_1}dE = \frac{\pi}{4\tau_E}\{[1+(2\tau_E|\Delta|)^2]^{1/2}-1\}. \tag{13}$$

Equation (3) now leads to

$$\rho = -eN(0)\frac{\pi|\Delta|}{2T_c}\frac{\tau_E|\Delta|}{[1+(2\tau_E|\Delta|)^2]^{1/2}}(2e\varphi-\dot{\theta}) \tag{14}$$

which is negligible for $\epsilon \ll 1$. Also, Eqs. (1) and (2) go over into

$$\frac{u}{[1+\gamma^2|\psi|^2]^{1/2}}\left[\frac{\partial}{\partial t}+i\mu+\tfrac{1}{2}\gamma^2\frac{\partial|\psi|^2}{\partial t}\right]\psi = \xi^2(\nabla-2ie\vec{A})^2\psi + (1-|\psi|^2)\psi, \tag{15}$$

$$\vec{j} = \xi\,\mathrm{Im}[\psi^*(\nabla-2ie\vec{A})\psi] - \xi\nabla\mu, \tag{16}$$

where $u=\pi^4/14\zeta(3)=5.79$, $\gamma=2\tau_E\Delta_0$, $\psi=\Delta/\Delta_0$, $\mu=2e\varphi t_0$, and $t_0=\xi^2/Du$. Time and current density are now measured in units of t_0 and $j_0=\sigma_0/2et_0\xi$. An equation of the same structure as (15) but with different coefficients was introduced recently by Golub for short filaments.[11]

For $\gamma \ll 1$, i.e., $(T_c\tau_E)^2\epsilon \ll 0.0266$, Eq. (15) goes over into the simple TDGL equation. We consider solutions of (15) and (16) for long, thin current-carrying filaments where $\vec{A}$ can be neglected and all quantities depend on x only. As in the case $\gamma=0$ there exist two simple stationary solutions[5]: the fully superconducting (S) state $\psi=f_\infty\exp(iqx)$, $\mu\equiv 0$, which exists and is locally stable for all $j<j_{max}=0.385$, and the normal (N) state $\psi\equiv 0$, $\mu'=-j/\xi$ which is locally stable for all $j\neq 0$. The stability of the N state, however, becomes "weaker" with increasing γ: The amplitudes of the stationary threshold solutions which separate decreasing from increasing solutions (and which for the case $\gamma\ll 1$ exist in the range[5] $j<j_c=0.335$) decrease and j_c itself increases with increasing γ. In fact, we find that for $\gamma>\gamma_c\approx 5.5$ the threshold solutions exist above j_{max} and for $\gamma\to\infty$ it is easy to show that they exist for all values of j. This means that no truly reversible S-N transition can take place (see Ref. 5) and

that there exists a stable solution besides the N and S states.

Consequently we looked for oscillatory phase-slip solutions which for $\gamma \ll 1$ exist in a very narrow range of currents $j_{\min} < j < j_c$ ($j_{\min} = 0.326$; numerical methods similar to those of Ref. 5 were used). As γ increases this range actually increases to higher as well as to lower currents. Clearly "isolated phase-slip solutions" where the S state is approached asymptotically on both sides can exist only below $j_{\max}$. For these solutions the electric field decays asymptotically over the "quasiparticle diffusion length"

$$\lambda_Q = \xi(1+\gamma^2 f_\infty^{\,2})^{1/4}\sqrt{u}\, f_\infty$$

$$[\to (4T_c\tau_E D/\pi\Delta_0 f_\infty)^{1/2} \text{ for } \gamma \gg 1] \qquad (17)$$

which may become much larger than the coherence length. We find that solutions with a periodic array of phase-slip centers exist above $j_{\max}$. Figure 1 shows I-$\bar{V}$ curves for such solutions for $\gamma = 10$ and 20 and various values of the periodic length d ($\bar{V} = \Delta\bar{\mu}$ = time-averaged voltage drop per period). At low currents the curves join the S state in the same way as for $\gamma \ll 1$ (see Ref. 5). Above a fairly well-defined current the solutions cease to be stable. Whereas the minimum current is fairly insensitive to d, the maximum current first increases with decreasing d and then decreases again.

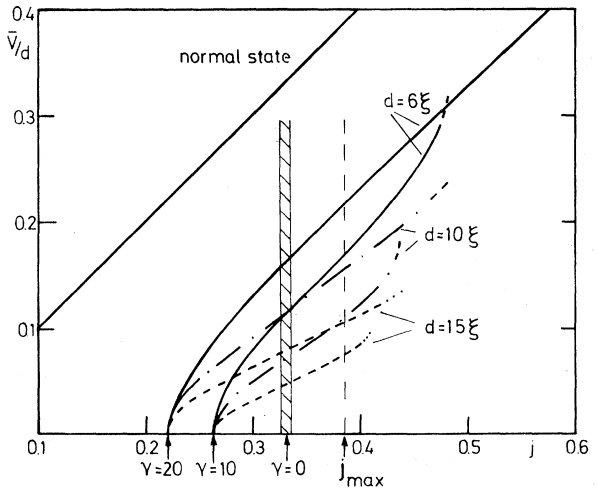

FIG. 1. Time-averaged voltage drop per period $\bar{V}$ divided by the periodic length d is plotted as a function of current density j for a periodic array of phase-slip centers for $d = 6$, 10, 15, and ξ and $\gamma = 10$ and 20. The curve for $\gamma = 20$, $d = 6\xi$ persists up to $j = 0.76$. Within simple TDGL theory ($\gamma = 0$) phase-slip solutions exist only in the narrow shaded region.

The I-$\bar{V}$ curves exhibit significant almost-linear portions which may be parametrized approximately by $\bar{V} = (j - \beta j_{\max})\Lambda/\xi$ with $\Lambda \simeq 7.5\xi(T)$ (independent of d and γ) and $\beta = 0.6$ and 0.46 for $\gamma = 10$ and 20 (independent of d). Thus each phase-slip center acts like a piece of filament of length Λ through which a time-averaged normal current of magnitude $j - \beta j_{\max}$ flows. The maximum current up to which the solutions exist appears to increase until d becomes approximately equal to Λ. Thus solutions with an I-$\bar{V}$ curve steeper than in the N state should not be observable. Note that Λ and λ_Q have different temperature dependence.

These results agree in many respects with experiments on Sn,[1-3] where, however, approximately temperature-*independent* values of Λ and β are found. Very recent measurements by Dolan and Jackel[12] have revealed the local structure of a phase-slip center. Their measurements of λ_Q on Sn agree with Eq. (17) when taking $\tau_E = 2\times10^{-10}$ sec which is obtained from a theoretical estimate[3] ($f_\infty \simeq 1$). This restricts the validity of our theory to $\epsilon \lesssim 0.4\times10^{-2}$ [see Eq. (8)] and here the temperature dependence of the measured differential resistance is indeed consistent with our results whereas for $\epsilon \gtrsim 0.7\times10^{-2}$ the temperature dependence becomes weaker. The agreement should be looked upon with some caution for the following reason: According to Dolan and Jackel[12] the high-temperature data tend to overestimate Λ because these data sample $d\bar{V}/dI$ only for low values of I where I-$\bar{V}$ curve is nonlinear.

An extension of the calculations to lower temperatures seems highly desirable. Unfortunately one then probably has to solve the full set of Eqs. (1)-(7) which is a rather cumbersome task. Note, however, that the local equilibrium approximation can be expected to hold for the asymptotic region of a phase-slip center, as described by Eq. (17), in the larger range $L_E \ll \lambda_Q$, which is equivalent to $\epsilon \ll u^{-1}$.

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[1]J. Meyer and G. v. Minnigerode, Phys. Lett. 38A, 529 (1972); J. D. Meyer, Appl. Phys. 2, 303 (1973); J. D. Meyer and R. Tidecks, Solid State Commun. 18, 305 (1976).

[2]J. Meyer and R. Tidecks, Solid State Commun. 24, 639, 643 (1977).

[3]W. J. Skocpol, M. R. Beasley, and M. Tinkham, J. Low Temp. Phys. 16, 145 (1974).

[4]A similar effect is observed for two closely spaced short microbridges: J. E. Mooij, private communication.

[5]L. Kramer and A. Baratoff, Phys. Rev. Lett. 38, 518 (1977), and to be published.

[6]Recent experiments on extremely thin and homogeneous tin wires drawn out of a jet pipe support this result: R. Doll and R. Meier-Hirmer, private communication.

[7]A. I. Larkin and Yu N. Ovchinnikov, Zh. Eksp. Teor. Fiz. 73, 299 (1977) [Sov. Phys. JETP (to be published)]; Yu N. Ovchinnikov, J. Low Temp. Phys. 28, 43 (1977).

[8]A. Schmid and G. Schön, J. Low Temp. Phys. 20, 207 (1975).

[9]K.-D. Usadel, Phys. Rev. Lett. 25, 507 (1970).

[10]U. Eckern and G. Schön, to be published.

[11]A. A. Golub, Zh. Eksp. Teor. Fiz. 71, 341 (1976) [Sov. Phys. JETP 44, 178 (1976)].

[12]G. J. Dolan and L. D. Jackel, Phys. Rev. Lett. 39, 1628 (1977).

CH Vibration Softening and the Dehydrogenation of Hydrocarbon Molecules on Ni(111) and Pt(111)

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High-resolution electron energy-loss measurements of ethylene on Ni(111) and cyclohexane on Ni(111) and Pt(111) show an extra CH stretching vibration—not found in free molecules or organometallic compounds—which is strongly broadened and shifted to lower frequencies relative to another, more typical CH stretching vibration. This softened and broadened CH frequency is attributed to a new electronic interaction with the surface which we relate to the mechanism of hydrocarbon dehydrogenation.

Despite many recent advances in understanding the bonding of atoms and molecules to surfaces[1-3] and experimentally determining reaction products on surfaces,[2,3] little information exists regarding the physical mechanisms for surface reactions. Of the only detailed studies to investigate molecular reaction mechanisms, namely the dissociative adsorption of methane on W[4] and Rh,[5] the mechanism is disputed.

Here, we report new results which provide evidence that vibrational spectroscopy permits the detection of changes in vibrational potentials which are important to the chemical transformation of molecules on surfaces, and that suggest a specific interaction mechanism for dehydrogenation reactions. Namely, using high-resolution electron energy-loss spectroscopy, we observe that adsorbed ethylene on Ni(111) and cyclohexane on either Ni(111) or Pt(111) show two sets of CH stretching frequencies. One frequency (2900–3000 cm^{-1}) is reasonable for CH stretching vibrations as found in free molecules,[6] adsorbed hydrocarbons,[3,7] or organometallic compounds,[8] while the second CH frequency (2590–2720 cm^{-1}) is unusually low and broadened by 200–300 cm^{-1}. This latter CH stretching frequency and frequency broadening have not been observed previously[3,6-8] and appear to be directly related to the ability of these particular molecules to dehydrogenate on the surface at higher temperature tures.

We present evidence that this CH vibration softening and broadening arise from an electronic interaction between some of the molecule's hydrogen atoms and the surface, similar to that occurring in hydrogen bonding. We postulate that this interaction not only modifies the shape of the CH vibrational potential but also lowers the activation barrier to CH bond rupture so as to make dehydrogenation the preferred reaction path at higher temperatures. Such a surface interaction has not been detected by other techniques and may provide a physical basis for understanding other chemical reactions on surfaces.

Electron energy-loss spectroscopy (ELS) was performed with a two-stage analyzer/monochromator which typically allows 65–80-cm^{-1} (8–10 meV) energy resolution and provides a low, uniform background as described elsewhere.[3] The choice of primary beam energy and (total) scat-