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# NONEQUILIBRIUM THERMODYNAMICS OF SUPERCONDUCTING ALLOYS IN HIGH MAGNETIC FIELDS

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# NONEQUILIBRIUM THERMODYNAMICS OF SUPERCONDUCTING ALLOYS IN HIGH MAGNETIC FIELDS

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Неравновесная термодинамика сверхпроводящих сплавов в сильных магнитных полях

В работе исследуется сверхпроводник с немагнитными примесями в предельном случае малой средней длины свободного пробега ($\ell \ll \xi_0$) и сильного магнитного поля ($H \approx H_{C2}$). Используются принципы феноменологической неравновесной термодинамики для вычисления диссипативной функции. Для свободной энергии сверхпроводника применяется функционал, из которого в случае равновесия получается обобщенное уравнение Гинзбурга-Ландау, выведенное Маки. Однако, выражение для плотности тока, которое следует из этого функционала, отличается от выражения Маки порядком операторов. Результаты феноменологического рассмотрения согласуются с зависящим от времени уравнением Гинзбурга-Ландау, полученным недавно Кароли и Маки на основе микроскопической теории.

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Nonequilibrium Thermodynamics of Superconducting Alloys in High Magnetic Fields

A superconductor with nonmagnetic impurities is considered in the limiting case of small mean free path ($\ell \ll \xi_0$) and high magnetic field ($H \approx H_{C2}$). The principles of the phenomenological nonequilibrium thermodynamics are applied to the superconductor and the dissipation function is calculated. For the free energy of the superconductor a functional is used which leads in the equilibrium case to Maki's generalized Ginzburg-Landau equation. However, the current density resulting from this functional differs in the order of the operators from Maki's expression. The results of the phenomenological considerations are in agreement with the time-dependent Ginzburg-Landau equation recently obtained by Caroli and Maki from the microscopic theory.

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## 1. Introduction

We consider a superconductor with nonmagnetic impurities in the limiting case of small mean free path ( $l \ll \xi_o$ ) and high magnetic field ( $H \approx H_{c2}$); the temperature can be arbitrary ( $0<T<T_c$). It is the purpose of this paper to apply the principles of the phenomenological nonequilibrium thermodynamics to this superconductor.

For the free energy of the superconductor we use a functional constructed in such a way that the condition for its stationary value is equivalent to Maki's generalized Ginsburg-Landau equation [1]. This functional leads to a density of the superconducting current which differs from Maki's current density [1] in the order of the operators. ( A recalcula - tion from the microscopic theory has verified our result). By the help of the free energy functional and the conservation laws we calculate the dissipation function.

The applicability of the phenomenological nonequilibrium thermodynamics to the superconductor in the considered limiting case is tested by comparison with results recently obtained by Caroli and Maki [2] from the microscopic theory. We shall see that their time-dependent Ginzburg-Landau equation and their current density satisfy in a simple way the requirement of nonnegative dissipation function.

The considered limiting case is interesting for two reasons.
(i) We have an inhomogeneous equilibrium state and a nonlocal free energy functional containing spatial derivatives of the superconducting order parameter in high order. This leads, for example, to the effect that the kinetic coefficient becomes an operator. (ii) The high magnetic field reduces appreciably the superconducting order parameter. Considering a superconductor containing paramagnetic impurities in a concentration near the critical one, Gor'kov and Eliashberg [3] have recently shown, that such a reduction of the order parameter is necessary for the existence of a time-dependent Ginsburg-Landau equation.

## 2. Nonequlibrium Thermodynamics

We apply the usual scheme of the phenomenological nonequilibrium thermodynamics to our superconductor [x]. The superconductor is assumed to be always in a state of local equilibrium described by the variables $\varrho$ ( charge density of the electrons), $E_{int}$

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[x] For the general methods of nonequilibrium thermodynamics see the monograph by De Groot and Mazur [4]. These methods are first applied to liquid He II for temperatures $T \approx T_\lambda$ by Pitayevsky [5] and to the superconductor for temperatures $T \approx T_c$ by Schmid [6] .

(internal energy density of the superconductor), $\vec{A}$ ( vector potential) and $\Delta$ (complex order parameter of the superconductor). In other words, the elementary excitations of the superconductor are assumed to be always in equilibrium with the prescribed values of the above mentioned variables. We start from the conservation laws for the charge, the entropy and the energy

$$\frac{\partial \rho}{\partial t} + div\, \vec{j} = 0 , \tag{1}$$

$$\frac{\partial S}{\partial t} + div\, \vec{j}^{S} = \frac{R}{T} , \tag{2}$$

$$\frac{\partial E}{\partial t} + div\, \vec{j}^{E} = 0 \tag{3}$$

and the equation of motion for the order parameter, which we write in the form

$$\frac{\partial \Delta}{\partial t} = - 2ie\bar{\varphi}\Delta + h . \tag{4}$$

$\vec{j}$ is the current density; S and E are the densities of the entropy and the total energy ( including the energy of the electromagnetic field)of the system, respectively; $\vec{j}^{S}$ and $\vec{j}^{E}$ are the corresponding current densities; T is the temperature, $e$ the charge of the electron. The dissipation function R and the functions $\bar{\varphi}$ ( real) and h have to be determined. In (4) we have separated the term $-2ie\bar{\varphi}\Delta$ from h for convenience.

The densities of the total and the internal energy are connected by

$$E = E_{int} + \frac{1}{8\pi}\left(\vec{E}^{2} + \vec{H}^{2}\right) + E_{cm} . \tag{5}$$

$\vec{E}$ is the electric, $\vec{H}$ the magnetic field. $E_{cm}$ is the kinetic energy of the centre of mass of the superconductor. $E_{cm}$ can be neglected ( we use the lattice system as reference system), because the ratio of the electron mass and the ion mass is negligibly small ( the term arising from $E_{cm}$ in (3) is for superconducting and normal electrons negligibly small compared with the term $\vec{j}\vec{E}$ arising from the energy of the electromagnetic field).

In the framework of the phenomenological thermodynamics, the internal energy $\mathcal{E}_{int}$ in a nonequilibrium state is assumed to be the same functional of the thermodynamical variables as in equilibrium

$$\mathcal{E}_{int} = \mathcal{E}_{int}\left(S, \rho, \vec{A}, \Delta\right)_{equ} . \tag{6}$$

We begin with the calculation of the time derivative of the energy density.

$$\frac{\partial E}{\partial t} = \frac{\partial E_{int}}{\partial t} - \operatorname{div} \frac{1}{4\pi}(\vec{E} \times \vec{H}) - \vec{j}\vec{E}$$

$$= \frac{\delta \mathcal{E}_{int}}{\delta S}\frac{\partial S}{\partial t} + \frac{\delta \mathcal{E}_{int}}{\delta \varrho}\frac{\partial \varrho}{\partial t} + \frac{\delta \mathcal{E}_{int}}{\delta \vec{A}}\frac{\partial \vec{A}}{\partial t} \tag{7}$$

$$+ \frac{\delta \mathcal{E}_{int}}{\delta \Delta}\frac{\partial \Delta}{\partial t} + \frac{\delta \mathcal{E}_{int}}{\delta \Delta^*}\frac{\partial \Delta^*}{\partial t} - \vec{j}\vec{E} + divergences \; .$$

$\delta/\delta$ means the functional derivative. For the functional derivatives we have the thermodynamical relations

$$\frac{\delta \mathcal{E}_{int}}{\delta S} = T, \tag{8}$$

$$\frac{\delta \mathcal{E}_{int}}{\delta \varrho} = \frac{1}{e}\mu , \tag{9}$$

$$\frac{\delta \mathcal{E}_{int}}{\delta \vec{A}} = -\vec{j}_s \; . \tag{10}$$

$\mu$ is the local chemical potential of the electrons and $\vec{j}_s$ the density of the supercurrent.

The functional derivatives of the internal energy with respect to the order parameter are calculated by the help of the free energy $\mathcal{F}$ of the superconductor ( the derivatives are the same for all thermodynamical potentials, provided for each potential its natural variables are chosen):

$$\left(\frac{\delta \mathcal{E}_{int}}{\delta \Delta}\right)_{S, \varrho, \vec{A}, \Delta^*} = \left(\frac{\delta \mathcal{F}}{\delta \Delta}\right)_{T, \varrho, \vec{A}, \Delta^*} \; . \tag{11}$$

For the free energy we use the functional

$$\mathcal{F} = - \frac{3}{2em v_F^2}\int d^3r \, \varrho \, \Delta^* \left\{ \ln\frac{T_c}{T} + \psi\left(\tfrac{1}{2}\right) - \psi\left(\tfrac{1}{2} + D\vec{Q}^2\right)\right\} \Delta \; , \tag{12}$$

where

$$D = \frac{v_F^2 \tau}{12\pi T} \quad , \qquad \vec{Q} = -i\nabla - 2e\vec{A} \; .$$

m is the mass of the electron, $v_F$ the Fermi velocity, $T_c$ the critical temperature, $\psi(z) = \Gamma'(z)/\Gamma(z)$ the di-gamma function and $\tau$ the electron collision time due to the impurity scattering ( we consider the impurity scattering to be isotropic).

For fields $H \approx H_{c2}$ the order parameter $\Delta$ is small, and the terms of second order in $\Delta$ are sufficient for the thermodynamical considerations. Because we are not discussing the boundary of the system, the functional $\mathcal{F}$ cannot be made unique; one can add to $\mathcal{F}$ a surface integral or a volume integral over a divergence. However, such a surface integral does not influence the functional derivatives. It is also possible to make $\mathcal{F}$ real by adding a divergence. The functional $\mathcal{F}$ is simply chosen in such a way that

$$0 = \frac{\delta \mathcal{F}}{\delta \Delta^*} = -\frac{3\varrho}{2emv_F^2}\left\{\ln\frac{T_c}{T} + \psi\left(\tfrac{1}{2}\right) - \psi\left(\tfrac{1}{2} + D\vec{Q}^2\right)\right\}\Delta \tag{13}$$

coincides ( concerning first order terms in $\Delta$ ) with the generalized Ginzburg-Landau equation derived by Maki [1].

The functional $\mathcal{F}$ leads to the density of the supercurrent ( in the processes of partial integration the charge density $\varrho$ can be considered as constant)

$$\vec{j}_s = -\frac{\delta \mathcal{F}}{\delta \vec{A}}$$

$$= \frac{\tau\varrho}{4\pi T m}\sum_{n=0}^{\infty}\left(\vec{Q}_1^{\,*} + \vec{Q}_2\right)\frac{1}{n+\frac{1}{2}+D\vec{Q}_1^{*2}}\;\frac{1}{n+\frac{1}{2}+D\vec{Q}_2^{2}}\;\Delta_1^*\Delta_2\Big|_{1=2=\vec{r},t} \;. \tag{14}$$

This result for the supercurrent differs from Maki's [1] result in the order of the operators ( in Maki's result the operator $\vec{Q}_1^{\,*} + \vec{Q}_2$ stands at the right). A recalculation of the supercurrent from the microscopic theory has verified our result(14).

We return to the calculation of

$$\frac{\delta \mathcal{E}_{int}}{\delta\Delta}\frac{\partial\Delta}{\partial t} + \frac{\delta \mathcal{E}_{int}}{\delta\Delta^*}\frac{\partial\Delta^*}{\partial t}$$

$$= \overline{\varphi}\,\mathrm{div}\,\vec{j}_s + h\frac{\delta\mathcal{F}}{\delta\Delta} + h^*\frac{\delta\mathcal{F}}{\delta\Delta^*} \;, \tag{15}$$

where we have used equations (4), (11) and the identity

$$2ie\left\{\Delta^*\frac{\delta\mathcal{F}}{\delta\Delta^*} - \Delta\frac{\delta\mathcal{F}}{\delta\Delta}\right\} = \mathrm{div}\,\vec{j}_s \;. \tag{16}$$

We insert equations (1), (2), (8-10) and (15) into (7) and get

$$\frac{\partial E}{\partial t} = R + \vec{j}^{\,s}\nabla T - (\vec{j} - \vec{j}_s)\left(\vec{E} - \tfrac{1}{e}\nabla\mu\right) + \tag{17}$$

$$+(\bar{\varphi}-\varphi-\frac{1}{e}\mu)\,div\,\vec{j_s} + h\frac{\delta \mathcal{F}}{\delta \Delta} + h^*\frac{\delta \mathcal{F}}{\delta \Delta^*} + divergences .$$

Defining the density of the normal current through the relation

$$\vec{j_n} = \vec{j} - \vec{j_s} \tag{18}$$

and comparing (17) with the energy conservation law (3) we get for the dissipation function

$$R = -\vec{j}^{S}\nabla T + \vec{j_n}\left(\vec{E}-\frac{1}{e}\nabla\mu\right) + (\varphi+\frac{1}{e}\mu-\bar{\varphi})\,div\,\vec{j_s} - h\frac{\delta \mathcal{F}}{\delta \Delta} - h^*\frac{\delta \mathcal{F}}{\delta \Delta^*} . \tag{19}$$

The term $(\varphi+\frac{1}{e}\mu)\,div\,\vec{j_s}$ has a nondefinite sign and therefore, has to disappear from R. Accordingly we choose

$$\bar{\varphi} = \varphi + \frac{1}{e}\mu . \tag{20}$$

There are additional terms possible in (20)(for example a term proportional to $div\,\vec{j_s}$ ), but such terms may be included into h.

Thus we arrive at the final equations

$$\frac{\partial \Delta}{\partial t} + 2i(e\varphi+\mu)\Delta = h \tag{21}$$

and

$$R = -\vec{j}^{S'}\nabla T + \vec{j_n}\left(\vec{E}-\frac{1}{e}\nabla\mu\right) - h\frac{\delta \mathcal{F}}{\delta \Delta} - h^*\frac{\delta \mathcal{F}}{\delta \Delta^*} . \tag{22}$$

Equation (21) is the time-dependent Ginzburg-Landau equation. The superconductor is described by the fluxes $\vec{j}^{S}$ , $\vec{j_n}$ , h and $h^*$ and the corresponding thermodynamical forces $-\nabla T$ , $\vec{E}-\frac{1}{e}\nabla\mu$, $-\frac{\delta \mathcal{F}}{\delta \Delta}$ and $-\frac{\delta \mathcal{F}}{\delta \Delta^*}$ . The first and the second term in (22) give the entropy production connected with the heat conductivity and the normal conductivity, respectively. The last two terms describe the entropy production connected with the transformation of superconducting into normal electrons and reversely.

## 3. Comparison with Results from the Microscopic Theory

Recently, Caroli and Maki [2] considering also the limiting case of $1 \ll \xi_0$ and $H \approx H_{c2}$ have derived from the microscopic theory the time-dependent Ginzburg-Landau equation

$$\psi'\left(\tfrac{1}{2}+D\vec{Q}^2\right)\left\{\frac{\partial}{\partial t}+2ie\varphi_{ext}\right\}\Delta = 4\pi T\left\{\ln\frac{T_c}{T}+\psi\left(\tfrac{1}{2}\right)-\psi\left(\tfrac{1}{2}+D\vec{Q}^2\right)\right\}\Delta \,. \qquad (23)$$

We have expanded their result in first order with respect to $\frac{\partial}{\partial t}+2ie\varphi_{ext}$ ; $\psi'$ is the derivative of $\psi$.

Equation (23) describes the reaction of the superconductor to an externally applied potential $\varphi_{ext}$ . As already mentioned, the reduction of the order parameter by the high magnetic field is necessary for the validity of the equation (23). The situation is similar to the case of a superconductor containing paramagnetic impurities with a concentration near the critical one (compare [3]).

The comparison of (23) with (21) shows the following.

(i) h is proportional to $-\frac{\delta\mathcal{F}}{\delta\Delta^*}$ , the role of the kinetic coefficient plays a hermitean positive operator:

$$h = \frac{6\pi T\varrho}{em\, v_F^2}\left[\psi'\left(\tfrac{1}{2}+D\vec{Q}^2\right)\right]^{-1}\left(-\frac{\delta\mathcal{F}}{\delta\Delta^*}\right). \qquad (24)$$

This operator reflects the inhomogeneity of the equilibrium states. Equation (24) satisfies in a simple way the requirement of real and nonnegative R. From the general point of view there would also be possible a complex kinetic coefficient, and the vector force $\vec{E}-\frac{1}{e}\nabla\mu$ could contribute to h ( Curie's principle does not hold, because the equilibrium state is anisotropic).

(ii) On the left hand side of equation (23) we have $e\varphi_{ext}$ instead of $e\varphi+\mu$ in equation (21). Besides the external potential, which does not show the periodicity of the order parameter, $\varphi$ contains also an internal potential $\varphi_{int}$ ( $\varphi = \varphi_{int} + \varphi_{ext}$ ) showing the periodicity of the order parameter. For the case of the reaction of the superconductor to an external potential the comparison of (23) with (21) leads then to

$$e\varphi_{int} + \mu = 0 \,. \qquad (25)$$

(Setting $e\varphi_{int} + \mu$ equal to zero we have fixed the gauge in such a way that $\Delta$ is time-independent in equilibrium). Physically equation (25) means that the behaviour of the system concerning changes in $e\varphi_{int}$ and $\mu$ is the same as in the equilibrium case. This picture can be also verified by microscopic calculations.

For the normal current we have only the force $\vec{E} - \frac{1}{e}\nabla\mu$, if we restrict the considerations to T = const. :

$$\vec{j}_n = \sigma(\vec{H})\left(\vec{E} - \frac{1}{e}\nabla\mu\right), \tag{26}$$

where $\sigma(\vec{H})$ is the conductivity tensor. The current density is $\vec{j} = \vec{j}_n + \vec{j}_s$ with $\vec{j}_s$ given by (14). Using for $\sigma(\vec{H})$ the conductivity of the normal state the resulting $\vec{j}$ coincides with the expression for the current of Caroli and Maki [2].

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