Diamagnetic Susceptibility at the Transition to the Superconducting State

ALBERT SCHMID*†
Department of Physics, Stevens Institute of Technology, Hoboken, New Jersey 07030
(Received 18 November 1968)

Fluctuating Cooper pairs contribute to the diamagnetic susceptibility in a superconductor above the critical temperature. The effect is the greatest in a clean metal where the extra susceptibility is about $10^{-7} \times [T_c/(T-T_c)]^{1/2}$ in a bulk sample.

THE contribution of fluctuations of the Cooper-pair density to the conductivity has been observed by Glover[1] upon a suggestion by Schmidt. At the same time, Aslamasov and Larkin[2] have developed a microscopic theory and given results for the extra conductivity as well as for the specific heat and ultrasonic attenuation in a superconductor. It remains to discuss the diamagnetic properties due to fluctuating Cooper pairs.[3] This will be done here within the framework of the Ginzburg-Landau theory, which not only yields the same results as the microscopic theory[4] but has the advantage of being a direct and more general approach.

A qualitative understanding of the phenomenon can be obtained as follows: Above T_c, droplets of Cooper pairs will grow and decay as a result of thermodynamic fluctuations. Their mean radius will be (approximately) equal to the Ginzburg-Landau coherence length[5] $\xi_{\rm GL}(T)=\hbar(2m|\alpha|)^{-1/2}$. Therefore, the energy[6] $\frac{3}{4}\hbar^2(m\xi_{\rm GL}^2)^{-1}|\Psi|^2 4\pi/3\xi_{\rm GL}^3$ is required to produce a droplet. This energy has to be equal to the thermal energy kT; therefore, $|\Psi|^2=(1/\pi)(m\hbar^{-2})kT\xi_{\rm GL}^{-1}$. Consider now the expression for the diamagnetic susceptibility of atoms[7]

$$\chi=-\tfrac{1}{6}(ne^2/mc^2)\langle r^2\rangle, \qquad (1)$$

where we identify the mean square radius of the atoms with $\xi_{\rm GL}^2$, and the density n of the atoms with $|\Psi|^2$. One obtains

$$\chi=(1/6\pi)(e/\hbar c)^2 kT_c\xi_{\rm GL}, \qquad (2)$$

which increases as $[T_c/(T-T_c)]^{1/2}$ as T approaches T_c.

We now derive relation (2) quantitatively starting with the Ginzburg-Landau free-energy functional

$$F_{\rm GL}=\int d^3r\left[\frac{1}{2m}\left|\left(\hbar\nabla/i+\frac{2e}{c}\mathbf{A}\right)\Psi\right|^2+|\alpha|\cdot|\Psi|^2\right], \qquad (3)$$

where the quartic term has been omitted since $|\Psi|^2$ is small. In the case of a homogeneous magnetic field B, the expression (3) can be written

$$F_{\rm GL}=\sum_{q,k,n}|C(q,k,n)|^2[E(k,n+\tfrac{1}{2})+|\alpha|], \qquad (4)$$

where

$$E(k,\, n+\tfrac{1}{2})=\hbar^2k^2/2m+(n+\tfrac{1}{2})(2e\hbar/mc)B, \quad n=0,1,\cdots \qquad (5)$$

and $C(q,k,n)$ are the expansion coefficients of $\Psi(\mathbf{r})$ with respect to the normalized eigenfunctions of a particle in a magnetic field.[8]

We will proceed according to the following principle, namely, that the Ginzburg-Landau free energy is $(-kT)$ times the logarithm of a *restricted* partition function in which the sum over states is restricted to those states of the whole system in which the order parameter takes on the values of a prescribed function $\Psi(\mathbf{r})$. Therefore, in order to obtain the unrestricted partition function, we have to sum $\exp[-(1/kT)F_{\rm GL}]$ over all possible $\Psi(\mathbf{r})$, i.e.,

$$Z=\int\prod_{q,k,n}d^2C(q,k,n)\exp\left(-\frac{1}{kT}F_{\rm GL}\right)=\prod_{q,k,n}\frac{\pi kT}{E(k,\,n+\frac{1}{2})+|\alpha|}. \qquad (6)$$

Taking into account that the number of (single particle) states of energy $E(k,\, n+\frac{1}{2})$ is $2eB/2\pi\hbar c$ times the cross section of the sample perpendicular to the magnetic field,[8] we obtain the following expression for the

---

* NSF Senior Foreign Scientist Fellow.

† On leave of absence from Institute of Mathematische Physik, Universität Karlsruhe, Karlsruhe, Germany.

[1] R. E. Glover, III, Phys. Letters **25A**, 542 (1967).

[2] L. G. Aslamasov and A. I. Larkin, Phys. Letters **26A**, 238 (1968); Fiz. Tverd. Tela **10**, 1104 (1968) [English transl.: Soviet Phys. Solid State **10**, 875 (1968)].

[3] *Footnote added in manuscript.* The author has learned since this paper was accepted for publication that this susceptibility already has been calculated by H. Schmidt [Z. Physik **216**, 336 (1968)]. The results are the same except for a mistake by which a factor of 4 is missing in the final result of the above reference. In the author's belief there is enough other information contained in this paper in order to justify its publication. The author thanks Dr. H. Schmidt very much for information and conversation on that subject.

[4] E. Abrahams and J. W. F. Woo, Phys. Letters **27A**, 117 (1968); A. Schmid, Z. Physik **215**, 210 (1968); H. Schmidt, Phys. Letters **27A**, 658 (1968).

[5] For a review of the Ginzburg-Landau theory, see P.-G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966), Chap. 6.

[6] The numerical factors should not be taken too seriously. They have been adjusted with respect to the final result.

[7] J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), Chap. IV, para. 123.

[8] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, London, 1964), Chaps. 9.6 and 9.7.

(unrestricted) free energy[9]:

$$F=-kT\ln Z=-VkT\frac{2eB}{2\pi\hbar c}\times\int\frac{dk}{2\pi}\sum_{n=0}^{\infty}\ln\frac{\pi kT}{E(k,n+\frac{1}{2})+|\alpha|}, \quad (7)$$

where V is the volume of the sample. Using Poisson's sum formula,[8] one finds

$$F=F^{(0)}-V\frac{kTeB}{\pi\hbar c}\sum_{s=1}^{\infty}\int\frac{dk}{2\pi}(-1)^s\times\int_0^{\infty}dx\ln\frac{\pi kT}{E(k,x)+|\alpha|}\cos 2\pi xs. \quad (8)$$

Here, $F^{(0)}$ is the free energy in the absence of a magnetic field. The integral over x will be integrated by parts twice, and if

$$(1/2\pi)(2e\hbar B/mc|\alpha|)=(1/\pi)(2e/\hbar c)\xi_{\mathrm{GL}}{}^2B\ll 1, \quad (9)$$

the integral can be approximated by

$$\int_0^{\infty}dx\cdots=\frac{2e\hbar}{mc}B\frac{1}{\hbar^2k^2/2m+|\alpha|}\frac{1}{(2\pi s)^2}. \quad (10)$$

The rest can be done without difficulty; the result is

$$F=F^{(0)}+\tfrac{1}{2}V(1/6\pi)(e/\hbar c)^2kT\xi_{\mathrm{GL}}B^2. \quad (11)$$

Using[10] $-(1/V)\partial^2F/\partial B^2=\chi$, one recovers relation (2). Note the χ is largest in a clean metal. The usual assumption that fluctuations are most important in metals of short mean free path does not hold in this particular case. Inserting for ξ_{GL} its value in a clean metal, we obtain

$$\chi=\left\{-\frac{e^2k_F}{12\pi^2mc^2}\right\}[7\zeta(3)/12]^{1/2}[T_c/(T-T_c)]^{1/2}$$
$$\approx-10^{-7}\times[T_c/(T-T_c)]^{1/2}. \quad (12)$$

The expression in curly brackets is Landau's diamagnetic susceptibility of free electrons. It should be possible to measure the temperature-dependent part of the susceptibility (12); though, according to Eq. (9), the applied magnetic field should be less than, say, 0.1 G.

Consider now a film of thickness d smaller than the coherence length. If the magnetic field is perpendicular to the surface of the film, Eq. (8) is still correct if we replace[2] the integral

$$\int\frac{dk}{2\pi}$$

by $1/d(k=0)$, and the susceptibility is found to be[11]

$$\chi=-(kT/3\pi)(e/\hbar c)^2kT_c(\xi_{\mathrm{GL}}{}^2/d).$$

There is an advantage in that χ exhibits a stronger temperature dependence $\sim T_c/(T-B_c)$. However, it will be difficult to measure a small susceptibility with a sample of very small volume.

It is perhaps worth mentioning that there exists a uniform treatment of susceptibility and conductivity induced by fluctuating Cooper pairs in the framework of the Ginzburg-Landau theory. This is shown in the Appendix. The key point is that one has to supplement the time-dependent Ginzburg-Landau equations[12] by a random force in order to include the changes in $\Psi(\mathbf{r},t)$ because of thermodynamic fluctuations[13]; the resulting equation has to be considered as a generalized Langevin equation of $\Psi(\mathbf{r},t)$.

Finally, we note that the result (2) for the susceptibility can also be obtained by calculating the most singular contribution of the diagrams considered in Ref. 2. The advantage of the method discussed above is that one obtains the estimate (9) of the linear region, and going a step further, a correction factor $[1-(21/5)\times(e/\hbar c)^2\xi_{\mathrm{GL}}{}^4B^2]$ by which the right-hand side of Eq. (2) has to be multiplied.

I wish to thank Dr. E. Abrahams and Dr. M. R. Beaxley for stimulating discussions and valuable comments on this subject. I also would like to thank Dr. H. Meissner for valuable comments and R. Rockefeller for carefully reading the manuscript. Furthermore, I appreciate gratefully the hospitality extended to me by the Physics Department of Stevens Institute of Technology, Hoboken, N. J.

APPENDIX

We propose the following generalized Langevin equation of the order parameter $\Psi(\mathbf{r},t)$:

$$\gamma[\hbar(\partial/\partial t)-2ie\tilde{V}]\Psi$$
$$=-\{1/2m[-i\hbar\nabla+2e/c\mathbf{A}]^2+|\alpha|\}\Psi+f(\mathbf{r},t). \quad (A1)$$

Apart from the random force $f(\mathbf{r},t)$, Eq. (A1) is the linearized form of the time-dependent Ginzburg-Landau equation,[12] which holds in the gapless regime, and particularly, for $T>T_c$. $\mathbf{A}$ is the vector potential and $\tilde{V}$ the electrochemical potential. The random force $f(\mathbf{r},t)$ shall be completely uncorrelated in space and time, i.e.,

$$\langle f^*(\mathbf{r},t)f(\mathbf{r}',t')\rangle=a\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \quad (A2)$$

where $\langle\cdots\rangle$ denotes the ensemble average. The constant a has to be chosen such that in a stationary case,

[9] In order to make this expression definite, one should introduce a cutoff such that $E_{kn}<E_0$.

[10] Actually, $-(1/V)\partial^2F/\partial B^2=\chi(1+4\pi\chi)^{-1}$.

[11] Qualitatively, this result can also be found on the basis of Eq. (1).

[12] A. Schmid, Physik Kondensierten Materie **5**, 302 (1966); E. Abrahams, and T. Tsuneto, Phys. Rev. **152**, 416 (1966).

[13] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press Ltd., London, 1958), p. 118. See also: R. Kubo, in *1965 Tokyo Summer Lectures in Theoretical Physics*, edited by R. Kubo (W. A. Benjamin, Inc., New York, 1965).

$\langle|\Psi|^2\rangle$ assumes the same value which one derives from the probability distribution of $|\Psi|^2$, which is proportional to $\exp[-(1/kT)F_{\mathrm{GL}}]$. This leads to

$$a = V 2\hbar\gamma kT\,. \tag{A3}$$

We consider now the case where a constant homogeneous electric field $\mathbf{E}$ is switched on at time $t=0$. We chose

$$\begin{aligned} \mathbf{A}(t) &= 0, && \text{if} \quad t<0 \\ &= -c\mathbf{E}t, && \text{if} \quad t>0 \end{aligned} \tag{A4}$$

and $\tilde{V}=0$. Introducing the Fourier components

$$\Psi_{\mathbf{q}}(t) = V^{-1}\int d^3r\,\Psi(\mathbf{r},t)\exp(-i\mathbf{qr})\,,$$

we find

$$\hbar\gamma\dot{\Psi}_{\mathbf{q}} = -\{(1/2m)[\hbar\mathbf{q}+(2e/c)\mathbf{A}]^2+|\alpha|\}\Psi_{\mathbf{q}}+f_{\mathbf{q}}(t)\,, \tag{A5}$$

where

$$\langle f^*\mathbf{q}(t) f\mathbf{q}'(t')\rangle = 2\hbar\gamma kT\delta_{\mathbf{q},\mathbf{q}'}\delta(t-t')\,. \tag{A6}$$

In order to find the mean value of the current density

$$\langle \mathbf{j}(t)\rangle = -V^{-1}\sum_{\mathbf{q}}\frac{2e}{m}\left[\hbar\mathbf{q}+\frac{2e}{c}\mathbf{A}\right]\langle|\Psi_{\mathbf{q}}(t)|^2\rangle\,, \tag{A7}$$

we have to determine $\langle|\Psi_{\mathbf{q}}(t)|^2\rangle$ from Eqs. (A5) and (A6). The result is

$$\langle|\Psi_{\mathbf{q}}(t)|^2\rangle = \frac{2kT}{\hbar\gamma}\int_{-\infty}^{t} dt' \exp\left\{-\frac{2}{\hbar\gamma}\int_{t'}^{t} dt''\frac{1}{2m}\times\left[\hbar\mathbf{q}+\frac{2e}{c}\mathbf{A}(t'')\right]^2+|\alpha|\right\}. \tag{A8}$$

Inserting (A8) in (A7) and considering the case where t is very large, one will find it convenient to shift the domain of the $\mathbf{q}$ summation such that $\hbar\mathbf{q}=\mathbf{E}(t+t')$ is the new center. At first, this might seem to be irrelevant since the summation extends over all $\mathbf{q}$. However, the sum is only conditionally convergent,[14] and we will see from the final results[15] that the chosen procedure is the correct one. Introducing simultaneously a new time variable, we substitute altogether as follows:

$$\begin{aligned} \hbar\mathbf{q} &= \hbar\mathbf{p}+e\mathbf{E}(t+t')\,, \\ t' &= u+t, \quad t''=\tfrac{1}{2}(u-u')+t. \end{aligned} \tag{A9}$$

In the limit of a thin film, $d\ll\xi_{\mathrm{GL}}$, and for $t\to\infty$, one obtains

$$\langle\mathbf{j}\rangle = \frac{e^2}{16\hbar d}\frac{T_c}{T-T_c}\mathbf{E}\left\{\int_{-\infty}^{0} dx\,\exp\{x[1+x^2(E/E_0)^2]\}\right\}. \tag{A10}$$

This is the usual result[2] apart from the expression in the curly brackets, which measures the departure from linearity as found and discussed by Smith *et al.*[16] The characteristic field E_0 is given by

$$E_0 = (16\sqrt{3}/\pi)(kT_c/e\xi_{\mathrm{GL}})(T-T_c/T_c)\,, \tag{A11}$$

which varies $\sim[(T-T_c)/T_c]^{3/2}$. Again, the Ginzburg-Landau approach gives additional information on the departure from a linear response.

The general case of arbitrary electromagnetic fields $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{B}(\mathbf{r},t)$ can only be treated in linear approximation. The fields are conveniently represented by a vector potential $\mathbf{A}(\mathbf{r},t)=\mathbf{A}_0\exp(-i\omega t+i\mathbf{kr})$. In the low-frequency, long-wavelength limit one finds[17] an Ohmic current corresponding to the linear form of Eq. (A10), and a diamagnetic current of the form

$$\mathbf{j}_d = -c\chi\mathbf{k}\times(\mathbf{k}\times\mathbf{A})\,, \tag{A12}$$

where χ is given by Eq. (2).

---

[14] See Ref. 9.

[15] For example, the absence of London (accelerated) currents. Looking at this matter from a different point of view, one could say that, in general, a cutoff prescription (Ref. 9) is not gauge-invariant.

[16] R. O. Smith, B. Serin, and E. Abrahams, Phys. Letters **28A**, 224 (1968).

[17] Care has to be taken in the sense of Ref. 15.