Fluctuations of the Order Parameter in Small Superconducting Samples

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We study the effect of the time-dependent fluctuations of the order parameter in superconducting samples in which the dimensions are smaller than the coherence length. We find that within the mean field theory, the static properties (specific heat, spin susceptibility), as well as the transport properties, nuclear-spin relaxation time, and the tunneling density of states, diverge as T approaches T_c. Therefore, the fluctuation corrections are much more important in those "zero-dimensional" superconductors than in the one-, two-, and three-dimensional ones. In particular, the width of the critical region is very large and increases when the size of the samples decreases. These effects should be observable if the problems of sample preparation can be solved.

I. INTRODUCTION

It is well known that the effect of the fluctuations of the order parameter can be enhanced by reducing the size of a superconducting sample.[1-3] Although fluctuation effects have been recently detected on bulk samples, they were first observed in thin films.[1-5] A thin film can be viewed as a two-dimensional sample with respect to the spatial variations of the order parameter Φ.

In this work, we will systematically study the effects of fluctuations in zero-dimensional samples. Such samples are obtained when one considers an aggregate of small grains, the average radius R of which is smaller than the coherence length ξ. We call such samples zero-dimensional samples because the spatial variations of the order parameter require too much energy to be thermally excited. Let us point out that we do not consider here so-called granular samples which are obtained by special evaporation procedures. We assume in the following that the thickness of insulating material between adjacent grains is large enough for the grains to be perfectly insulated electrically. Typically, for aluminium grains, a zero-dimensional sample is obtained with grain sizes smaller than 1000 Å. Since we do not take into account here the possible modifications of the electronic structure in the normal state due to the size effect, the diameter of the grains should exceed a few tens of Å.

Consequently, these systems are of particular interest in two respects: first, only the time-dependent fluctuations of the order parameter need to be considered and second, we expect large fluctuation effects. In particular, we expect a large width (i.e., experimentally accessible) of the critical region, i.e., the region around the critical temperature where the mean field theory is no longer valid.[6,7]

On the other hand, the preparation of such samples and a precise size control might be experimentally difficult. We repeat that the sizes we are interested in are smaller than 1000 Å. Nevertheless, we shall present here our theoretical investigations, with the hope that these difficulties will be circumvented in the near future.

Although we have stated that the deviations from the mean field theory will be remarkable in small grains, we calculate various thermodynamical as well as dynamical properties by making use of the mean field approach. Thus, in Sec. II we shall be interested in the thermodynamical properties in the classical region, such as the specific heat and the diamagnetic susceptibility. In Sec. III we shall study some dynamical response functions such as the density of states and the nuclear spin relaxation time. We defer the discussion of the possible deviation from the mean field theory to Sec. IV.

II. THERMODYNAMICAL PROPERTIES

As our introduction to the general problem of the fluctuations in zero-dimensional systems, we start by considering the thermodynamical properties associated with the time-dependant fluctuations of the order parameter. As we have already shown,[7,8] one can discuss the *equilibrium* properties in terms of the Ginzburg-Landau functional of the order parameter. In the zero-dimensional case, the Ginzburg-Landau free-energy functional to be used will be the time-dependent Ginzburg-Landau functional,[9] since, for our purpose, the spatial fluctuations of the order parameter can be considered as being "locked." Thus, the free energy F associated with the fluctuations can be written as

$$F(T,H) = -T \ln Z, \tag{1}$$

$$Z = \int \delta\Phi(\tau) \exp\{-\Omega \int_0^\beta \mathcal{L}[\Phi(\tau')]\, d\tau'\}. \quad (2)$$

In (1), Z is the partition function and H is an applied magnetic field. In (2), Ω is the volume of the grain ($\Omega = \frac{4}{3}\pi R^3$) and $\Phi(\tau)$ is the fluctuation field with an "imaginary" time ($0 < \tau < \beta = T^{-1}$).[10] Formula (2) means that the partition function, in the present case, is obtained by a summation over all the possible time-dependent variations of the order parameter, each variation being associated with a value of the time-dependent Ginzburg-Landau energy functional. This functional, in the presence of H, is given by[11]

$$\mathcal{L}[\Phi(\tau)] = N(0)\Phi^\dagger(\tau)\left[\ln\frac{T}{T_{c0}} + \psi\left(\tfrac{1}{2} + \frac{-i\omega + \alpha(H)}{4\pi T}\right) - \psi(\tfrac{1}{2})\right]\Phi(\tau). \quad (3)$$

In (3), $N(0)$ is the electron density at the Fermi level, T_{c0} is the transition temperature of the bulk system, ω is the operator $d/d\tau$, $\psi(z)$ is the digamma function, and $\alpha(H)$ is the pair-breaking energy. In the absence of any magnetic impurity inside the grains, we will write $\alpha(H)$ as a sum of two terms

$$\alpha(H) = \alpha_0 + \alpha_1(H). \quad (4)$$

$\alpha_1(H)$ is the usual contribution to the pair-breaking energy due to the applied magnetic field. We have

$$\alpha_1(H) = \frac{4De^2}{c^2}\langle \vec{A}^2 \rangle, \quad (5)$$

where D is the electronic diffusion constant (limited by the mean free path or the size of the sample, for sufficiently small specimens) and $\langle \vec{A}^2 \rangle$ is the value of the square of the vector potential averaged over the sample. For a spherical grain of radius R, we have

$$\alpha_1(H) = \frac{2}{5}\frac{De^2}{c^2} H^2 R^2. \quad (6)$$

α_0 is the contribution to $\alpha(H)$ due to the proximity effect.[7,10] Indeed, the order parameter is not strictly constant in the specimen but is slightly lowered in the vicinity of the surface. The proximity of the dielectric imposes boundary conditions on the order parameter resulting in the lowering of the transition temperature. The value of α_0 is, in turn, of the order of the shift in the critical temperature. Consequently, we will assume

$$\alpha_0 \simeq \frac{T_{c0}}{p_0 R} \quad (7)$$

for a spherical grain of radius R, p_0 being the Fermi momentum of the material considered.

Note that, in (3), we have completely neglected the nonlinear term of the Ginzburg-Landau functional. This amounts to treating the fluctuation effects within the mean field approximation.

Now, we introduce the Fourier decomposition

$$\Phi(\tau) = \sum_{n=-\infty}^{+\infty} e^{i\omega_n \tau}\Phi_n, \quad \omega_n = 2n\pi T \quad (8)$$

with the usual Matsubara boundary conditions. The evaluation of Z is then straightforward. Indeed

$$Z = \int_{-\infty}^{+\infty} d\Phi_n \exp\left(-\frac{\Omega N(0)}{T}\sum_n |\Phi_n|^2 K_n\right) = \prod_{n=0}^{\infty}\left(\frac{\pi T}{N(0)\Omega K_n}\right), \quad (9)$$

K_n being such that

$$K_n = \ln\frac{T}{T_{c0}} + \psi\left(\frac{1}{2} + \frac{|\omega_n| + \alpha(H)}{4\pi T}\right) - \psi(\tfrac{1}{2}). \quad (10)$$

Thus, from (1) and (7), the free energy is such that

$$F(T, H) = T\sum_{n=0}^{\infty} \ln K_n + C. \quad (11)$$

As we are close to the transition temperature, it is sufficient, for our subsequent investigations to retain only the $n = 0$ term in the summation (11), so that

$$F(T, H) \simeq T\ln K_0 \simeq T\ln\left[\ln\frac{T}{T_{c0}} + \psi\left(\frac{1}{2} + \frac{\alpha(H)}{4\pi T}\right) - \psi(\tfrac{1}{2})\right] \simeq T\ln\left(\ln\frac{T}{T_c}\right) \simeq T\ln\eta, \quad (12)$$

with

$$\eta = \ln\frac{T}{T_c} \simeq \frac{\Delta T}{T_c}$$

for

$$T \simeq T_c,$$

where T_c is defined by

$$\ln\frac{T_c}{T_{c0}} + \psi\left(\frac{1}{2} + \frac{\alpha(H)}{4\pi T_c}\right) - \psi(\tfrac{1}{2}) = 0 \quad (13)$$

and ΔT by

$$\Delta T = T - T_c. \quad (14)$$

Of course T_c is the transition temperature of the grain in the applied magnetic field H in the absence of any fluctuation effect.

The expressions of the thermodynamical quantities such as the specific heat and the diamagnetic susceptibility come out easily.

A. Specific Heat

The specific heat per grain $C(T)$ is given by

$$C(T) = -T\frac{\partial^2 F}{\partial T^2} \simeq \frac{1}{[\ln(T/T_c)]^2} = \frac{1}{\eta^2}. \quad (15)$$

Thus in the classical region, the specific heat will exhibit a $[T_c/(T-T_c)]^2$ divergence. Note that for the experimental system in which the grains are imbedded in a dielectric, the total value $C_t(T)$ of the specific heat per unit volume will be

$$C_t(T) = N/\eta^2 , \tag{16}$$

where N is the number of spheres per unit volume.

B. Magnetization M

For M, we have

$$M = -\frac{\partial F}{\partial H} \simeq \frac{1}{\ln(T/T_c)} \frac{\partial T_c}{\partial H} , \tag{17}$$

$$M = -\frac{\alpha(H)}{2\pi H} \times \left[\frac{\psi^{(1)}\{\frac{1}{2} + [\alpha(H)/4\pi T_c]\}}{1 - [\alpha(H)/4\pi T_c]\psi^{(1)}\{\frac{1}{2} + [\alpha(H)/4\pi T_c]\}} \right] \frac{1}{\eta^2} , \tag{18}$$

where $\psi^{(1)}(z)$ is the trigamma function.

Consequently we have for the diamagnetic susceptibility per spherical grain

$$\chi(T,H) = -\frac{De^2R^2}{5\pi c^2} \times \left[\frac{\psi^{(1)}\{\frac{1}{2} + \alpha(H)/4\pi T_c\}}{1 - [\alpha(H)/4\pi T_c]\psi^{(1)}\{\frac{1}{2} + [\alpha(H)/4\pi T_c]\}} \right] \frac{1}{\eta} . \tag{19}$$

Thus in the classical region, the diamagnetic susceptibility will exhibit a $[T_c/(T-T_c)]$ divergence. We can also rewrite Eq. (19) as

$$\chi(T,H) = \tfrac{4}{5}(e^2/c^2) R^2 \xi^2(T,H) T_c \tag{20}$$

provided that $\xi(T,H)$ is defined by

$$\xi(T,H) = \left[\frac{D}{4\pi T \ln(T/T_c)} \times \frac{\psi^{(1)}\{\frac{1}{2} + [\alpha(H)/4\pi T_c]\}}{1 - [\alpha(H)/4\pi T_c]\psi^{(1)}\{\frac{1}{2} + [\alpha(H)/4\pi T_c]\}} \right]^{1/2} . \tag{21}$$

It is easily checked that, in the limit $\alpha(H)/4\pi T_c \to 0$, $\xi(T,H)$ reduces to the ordinary coherence length.

III. DYNAMICAL PROPERTIES

We will consider essentially three quantities that might be accessible to experiment: first, the tunneling density of states (this quanitity could be measured through the method developed by Zeller and Giaever[12]); second, the electromagnetic response for finite frequencies; third, and perhaps the most directly accessible, the nuclear spin relaxation time.

Before studying each of these quantities, we shall first outline how the method of calculation of the dynamical properties is different from the previous ones. Indeed it has been shown in (7) that, as far as thermodynamical properties were concerned, the diagrammatic-perturbational method was equivalent to the functional-integral method where the Ginzburg-Landau functional is used as the effective Lagrangian. However, we have not been able to prove so far that a similar equivalence holds for dynamical properties. Moreover, it seems that this is not true in the case of the electric conductivity in a two-dimensional system for example. The analysis by Schmidt[13] using the time-dependent Ginzburg-Landau equation (TDGL) only takes care of the Aslamazov-Larkin term. However, from the microscopic calculation there is another term as important as this one. In most experiments done in the two-dimensional systems, on the other hand, this additional term is of little importance, possibly because its logarithmic divergence can be suppressed[14] by the introduction of a pair-breaking parameter at the surface of the film.[15]

However, in the zero-dimensional system, there is no contribution due to the so-called Aslamazov-Larkin term, since the order parameter cannot carry the electric current. On the other hand, the other term often referred to as Maki's is the only diverging one even in the presence of the pair-breaking interaction.

Consequently, for present purposes, we shall perform our calculations using the standard perturbation procedure.[13,14,16,17] We represent on Figs. 1 and 2 the diagrams which have to be considered for the evaluation of the density of states and of the electromagnetic response respectively. Calculations of the density of states have been done in Refs. 7 and 17 and we can adapt them straightforwardly to our case. For the calculation of the electromagnetic response it is easily seen, from the Aslamazov-Larkin expression[16] that diagrams δ and ϵ yield a zero contribution when the order parameter has no spatial variation. Thus the only contribution to the electromagnetic response comes from diagrams α, β, and γ of Fig. 2, since diagrams δ and ϵ are negligible in front of α, β, and γ. Simi-

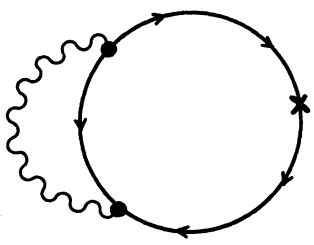

FIG. 1. Diagram giving rise to the lowest-order correction to the density of states.

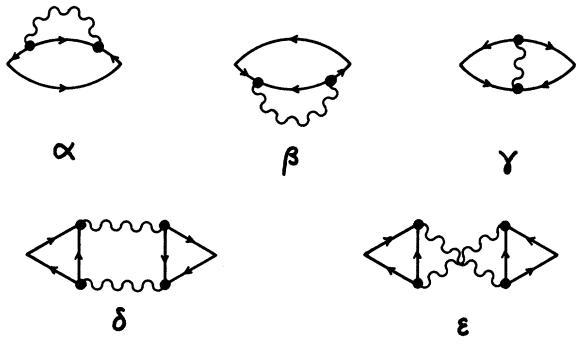

FIG. 2. Lowest-order diagrams contributing to the electromagnetic response function.

larly, for the calculation of the nuclear-spin relaxation time T_1, it will be also sufficient to consider diagrams α, β, and γ. In the present case diagrams δ and ϵ vanish identically owing to the spin conservation. Thus it turns out that the calculations of Refs. 18 and 19 can be used in this particular problem.

A. Tunneling Density of States

The calculations are the same as in Refs. 7 and 17. If ω is the energy to the Fermi level, we consider $\nu(\omega)$,

$$\nu(\omega)=N(\omega)/N_n(\omega)-1\ , \tag{22}$$

where $N(\omega)$ is the actual density of states and $N_n(\omega)$ is the density of states in the normal situation where the effect of fluctuations has been ignored. We have for $\nu(\omega)$,

$$\nu(\omega)=\frac{4T}{N(0)\,\Omega\eta}\,\mathrm{Re}\left(\frac{1}{[2i\omega+(8T/\pi)\eta]^2}\right). \tag{23}$$

Expression (23) is obtained for a particle of volume Ω in the absence of any applied magnetic field. If a magnetic field is applied, it is sufficient to change T_{c0} in Eq. (23) to T_c, as defined by (13), to obtain the corresponding density of states.

The problem is now to measure such a quantity. The experiment we think of is the experiment by Zeller and Giaever.[12] In this experiment, the metallic grains are imbedded in the oxide of the tunneling barrier. The tunneling takes place preferentially *through* the grains. If the grains had the same volume Ω, the barrier was symmetrical, and the grains were sufficiently large so that quantum charge effects (yielding giant zero-bias anomalies) could be avoided, then the conductance $G(eV)$ of the function could be written as

$$G(eV)=\frac{dI}{d(eV)}=C\left(1-\frac{4T}{N(0)\Omega\ln(T/T_c)}\right.$$

$$\left.\times\ \mathrm{Re}\ \frac{1}{[2ieV+(8T/\pi)\ln(T/T_c)]^2}\right), \tag{24}$$

where C is a constant and V is the applied voltage at the insulating barrier. In order to give a precise account of the effects of the fluctuations in an actual experimental situation, the theory should consider the quantum charge effects,[19] the asymmetry of the barrier, and the fact that the grains do not feel the same potential. We will not go into these details but we will only point out that our expression (24) might be relevant to an experiment of the Zeller-Giaever type.

B. Complex Conductivity

The electromagnetic response, i.e., the current $j(\vec{r},\omega)$ induced by a time varying potential vector $A(\vec{r},\omega)$, is given by the relation (18),

$$\vec{j}\,(\vec{r},\omega)=Q(-i\omega)\vec{A}(\vec{r},\omega)\ . \tag{25}$$

The quantity $Q(-i\omega)$ is yielded considering diagrams α, β, γ of Fig. 2. As already explained in the zero-dimensional superconductor, diagrams δ and ϵ do not contribute to $Q(-i\omega)$, since the order parameter cannot have any spatial dependence or cannot carry any current. As pointed out in Ref. 20, an analogy can be drawn between the present case and the gapless regime.[11] This follows from the fact that each of diagrams α, β, γ contains a single fluctuation propagator. Since there is no possibility of confluence of two poles in the two propagators, we can evaluate the contribution from the fluctuation propagator in these diagrams by only taking the component with $\omega_\nu=0$. In the notations used in Ref. 11, the gapless expressions depend essentially on Δ^2 and α. Δ^2 is the square of the order parameter and α the pair-breaking parameter. The expression for Q in the present case can be deduced from the gapless expression if we make the substitutions (26) and (27),

$$\Delta^2\to(T/\Omega)\mathfrak{D}(\omega_\nu=0), \tag{26}$$

$$\alpha\to\alpha(H)\ . \tag{27}$$

In (26), $\mathfrak{D}(\omega_\nu)$ is the correlation function for the order parameter and ω_ν the boson Matsubara frequency. We have for $\mathfrak{D}(\omega_\nu)$,

$$\mathfrak{D}(\omega_\nu)=\frac{1}{N(0)}\left[\ln\frac{T}{T_{c0}}\right.$$

$$\left.+\psi\left(\frac{1}{2}+\frac{|\omega_\nu|+\alpha(H)}{4\pi T}\right)-\psi\left(\tfrac{1}{2}\right)\right]^{-1}. \tag{28}$$

Consequently, using the result of (18) and (11) we can write $Q(-i\omega)$ as

$$Q(-i\omega)=\sigma_n\left\{i\omega-\frac{\mathfrak{D}(\omega_\nu=0)}{2\pi N(0)}\left[\psi^{(1)}\left(\frac{1}{2}+\rho-\frac{i\omega}{2\pi T}\right)\right.\right.$$

$$- \left(\frac{2\pi T}{i\omega} + \frac{2\pi T}{i\omega - 2\alpha(H)}\right)$$

$$\times \left(\psi\left(\frac{1}{2}+\rho-\frac{i\omega}{2\pi T}\right) - \psi\left(\tfrac{1}{2}+\rho\right)\right)\Bigg]\Bigg\} \ , \qquad (29)$$

where $\rho = \alpha(H)/(2\pi T)$ and σ_n is the conductivity of the normal state.

Substituting Eq. (28) into (29), the conductivity $\sigma(\omega)$ can be written in the low-frequency limit $(\omega/T_c \ll 1)$ as

$$\sigma(\omega) = \sigma_n \left\{1 + \frac{T}{2\pi N(0)\Omega \ln(T/T_c)}\right.$$

$$\times \left.\left(\frac{1}{2\alpha(H) - i\omega}\ \psi^{(1)}\left(\tfrac{1}{2}+\rho\right) + \frac{3}{4\pi T}\ \psi^{(2)}\left(\tfrac{1}{2}+\rho\right)\right)\right\} . \qquad (30)$$

Such an anomalous behavior of the conductivity could be detected through standard microwave experiments. We note here that in opposition to the case with higher dimensions we have a diamagnetic term at all temperatures. This diamagnetic part coincides exactly with what we obtained in Sec. II using the Ginzburg-Landau functional in the presence of a magnetic field H.

C. Nuclear Relaxation Time T_1

Here too, the analogy can be drawn with the gapless regime. Thus we can write for the ratio T_1/T_{1n} (T_{1n} being the value of T_1 in the normal state and in the absence of fluctuation effects)

$$\frac{T_1}{T_{1n}} = \left[1 + \frac{1}{2\pi N(0)\Omega \ln(T/T_c)}\left(\frac{1}{2\alpha(H)}\ \psi^{(1)}\left(\tfrac{1}{2}+\rho\right)\right.\right.$$

$$\left.\left. + \frac{3}{2}\ \frac{1}{2\pi T}\ \psi^{(2)}\left(\tfrac{1}{2}+\rho\right)\right)\right]^{-1} \qquad (31)$$

or

$$\frac{T_1}{T_{1n}} = \left(1 + \frac{\pi}{8N(0)\Omega}\ \frac{1}{\alpha(H)\eta}\right)^{-1} . \qquad (32)$$

As pointed out in Ref. 21, expression (32) predicts quite observable effects for grains smaller than, or of the order of, 1000 Å.

So far, we have performed our calculations using the mean field approximation. We shall now investigate the validity of such an approximation.

IV. BREAKDOWN OF MEAN FIELD APPROXIMATION

In the above calculations we have estimated various response functions assuming that, in the Hamiltonian, the BCS interaction could be considered as a perturbation. The expansion in powers of this interaction has led us to consider the order parameter correlation function $\mathfrak{D}(\omega_\nu)$. In zeroth-order perturbation, $\mathfrak{D}(\omega_\nu)$ is yielded by the bare bubble [diagram (a) of Fig. 3] $\Pi_0(\omega_\nu)$. A better approximation for $\mathfrak{D}(\omega_\nu)$ is provided by the mean field theory, where, for the evaluation of $\mathfrak{D}$, we treat the BCS interaction within the RPA. Thus we have for $\mathfrak{D}(\omega_\nu)$

$$\mathfrak{D}(\omega_\nu) = \langle T\{\Phi^\dagger(t)\Phi(0)\}\rangle_{\omega_\nu} = \frac{|g|^2\Pi_0(\omega_\nu)}{1 - |g|\Pi_0(\omega_\nu)} \ , \qquad (33)$$

where g is the BCS coupling constant, T is the time ordering operator, and $\Phi^\dagger(t)$ is the operator,

$$\Phi^\dagger(t) = |g| \sum_p a^\dagger_{p\uparrow}(t)\, a^\dagger_{-p\downarrow}(t) \ . \qquad (34)$$

From (33), it is a readily seen that we obtain expression (28) for $\mathfrak{D}(\omega_\nu)$. The form (28) is also yielded by the functional-integral method when one uses the Ginzburg-Landau expression (3) as the effective Lagrangian. When $T \to T_c$, $\mathfrak{D}(\omega_\nu = 0)$ diverges as $T_c/(T - T_c)$.

It is of interest to note here that the problem of the fluctuations of the order parameter in a small superconducting sample close to its critical temperature is quite analogous to the problem of spin fluctuations in dilute nearly magnetic alloys. The diverging correlation function is then the localized spin-spin correlation function when the impurity is close to being magnetic.[8]

The general expression for $\mathfrak{D}(\omega_\nu)$ in the present case can be written as

$$\mathfrak{D}(\omega_\nu) = \frac{|g|^2\Pi(\omega_\nu)}{1 - |g|\Pi(\omega_\nu)} \ , \qquad (35)$$

where $\Pi(\omega_\nu)$ is the full renormalized particle-particle or hole-hole bubble. Consequently, it will be possible to use form (33) for $\mathfrak{D}$ if the renormalization effects[7] on $\Pi(\omega_\nu)$ can be neglected. In order to check this last point, we will consider again a perturbation expansion of $\Pi(\omega_\nu)$ in powers of the BCS interaction. This calculation has been done in Ref. 7 for the case of three-, two-, and one-dimensional superconductors. Thus we shall consider the diagrammatic expansion represented on Fig. 3. On Fig. 3, the diagram (a) is the zeroth-order approximation for Π, i.e., Π_0. The diagram (b) is the first-order corrections to Π, the diagram (c) one of the second-order corrections.

In the RPA, $\mathfrak{D}(\omega_\nu)$ can be written as (33) or (28), or since we are close to T_c, as

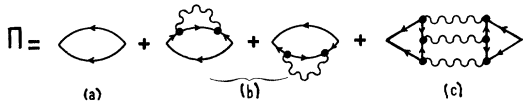

FIG. 3. Self-energy corrections to the order-parameter correlation function (i.e., the fluctuation propagator).

$$\mathfrak{D}(\omega_\nu)=\left[N(0)\left(\eta+\frac{\pi|\omega_\nu|}{8T_c}\right)\right]^{-1}. \tag{36}$$

Once the perturbation effects on $\Pi(\omega_\nu)$ are taken into account, $\mathfrak{D}(\omega_\nu=0)$ can be written as

$$\mathfrak{D}(\omega_\nu=0)=[N(0)\tilde{\eta}]^{-1}. \tag{37}$$

The mean field theory will then be applicable as long as $[(\tilde{\eta}-\eta)/\eta]\ll 1$. We notice that the calculation of Ref. 7 can be adapted quite straightforwardly to our case. As a result, we find that $\tilde{\eta}$ can be expanded as

$$\tilde{\eta}=\eta\left[1+\frac{a_0}{\eta^2}+\frac{a_0^2}{\eta^4}+O\left(\frac{a_0^3}{\eta^6}\right)+\cdots\right], \tag{38}$$

where a_0 is given by

$$a_0=7\zeta(3)/8\pi^2\Omega N(0)T_c. \tag{39}$$

Thus, the mean field approach is found to break down when $\eta=\eta_c$, where

$$\eta_c\sim\left(\frac{7\zeta(3)}{8\pi^2\Omega N(0)T_c}\right)^{1/2}. \tag{40}$$

Relation (40) ($\eta=\eta_c$) defines the onset of the critical region and the calculations in Secs. II and III are thus valid when $\eta>\eta_c$. Noting that, from (39),

$$a_0=\xi_0/p_0R^3, \tag{41}$$

the width of the transition region ΔT_c is for aluminum typically

$$\Delta T_c=10^2/R^{3/2}, \tag{42}$$

with R in Å. Thus if $R\sim 100$ Å, $\Delta T_c\sim 0.1$ °K, which is quite a large value for a superconducting sample.

The problem arises now to evaluate the fluctuation propagator that we have considered inside the critical region. One could be tempted to handle the renormalization problems by selecting certain classes of diagrams. For example, one might think of summing up "self-energy" diagrams such as diagram (b) of Fig. 3. However, it has been shown in Ref. 8 that such a renormalization procedure is not valid (this result has been obtained for the problem of renormalization of the localized spin fluctuation propagator but this is also true for the present problem) because it ignored corrections which were as or more important. More generally, a series such as the series (38) seems difficult to be summed up into a simple analytic expression.

On the other hand, it has been shown in (8) that the renormalized fluctuation propagator $\mathfrak{D}(\omega_\nu=0)$ could be expressed in a closed form through the functional integral formalism. Indeed, we have for $\mathfrak{D}(\omega_\nu=0)$

$$\mathfrak{D}(\omega_\nu=0)=\int_0^{1/\beta}d\tau\int\delta\Phi\,\Phi^\dagger(\tau)\Phi(0)\times\exp\left[-\int_0^{1/\beta}d\tau'\,F(\tau')\right], \tag{43}$$

where $F(\tau')$ is the Ginzburg-Landau functional where the only nonlinear term present is the lowest-order one. Thus

$$F(\tau')=N(0)\left\{\Phi^\dagger(\tau')\left[\ln\frac{T}{T_c}+\frac{\pi}{8T_c}\left(-i\frac{d}{d\tau'}\right)+\frac{\Gamma_3}{2}\left|\Phi(\tau')\right|^2\right]\Phi(\tau')\right\}, \tag{44}$$

where Γ_3 is such that

$$\Gamma_3=7\zeta(3)/8\pi^2T_c^2. \tag{45}$$

However, it seems difficult to perform the functional integral (43) without the help of some approximation. For example, the calculation can be carried out within Schrieffer's "static" or "RPA" approximations.[22] Unfortunately, we have recently realized (see the second article of Ref. 8) that such approximations were equivalent to selecting a certain class of diagrams and that, consequently, they were no longer valid when the mean field theory was breaking down too. So that finally, the problem of the renormalization of the fluctuation propagator seems to remain quite open.

V. CONCLUSION

We have studied the effect of time-dependent fluctuations of the order parameter in small superconducting samples on thermodynamic properties and dynamical response functions. These fluctuations have been analyzed within the mean field approximation and have been shown to give rise to rather large effects. In order to substantiate this point, let us estimate explicitly some quantities for aluminum spherical grains of radius R.

A. Width of Critical Region

The width of the critical region is yielded by relation (42). For $R=100$ Å, $\Delta T_c\simeq 10^{-1}$ °K, and for $R=500$ Å, $\Delta T_c\simeq 10^{-2}$ °K. We emphasize again that such widths are extremely large for a superconducting sample. For a very dirty two-dimensional sample, we recall that $\Delta T_c\simeq 10^{-4}$ °K. And ΔT_c is still smaller for a very dirty three-dimensional sample. Thus, the zero-dimensional samples seem to be the only superconducting samples in which the critical behavior could be conveniently investigated. Moreover, we have outlined the analogy between the fluctuation effects in such samples and the problem of localized paramagnons. Thus experiments on zero-dimensional superconducing samples could be fruitfully compared to experiments in dilute nearly magnetic alloys.

B. Nuclear-Spin Relaxation Time

If $\alpha_0\gg\alpha_1(H)$, we have

$$T_1/T_{1n} \simeq \left(1+\frac{10^5}{R^2}\eta\right)^{-1} ,$$

where R is expressed in Å. Thus if $\eta \approx 0.1$, $R \sim 100$ Å,

$$T_1/T_{1n} = 0.5 .$$

C. Specific Heat

If the sample contains N identical spheres of volume Ω such that $N\Omega \sim 10^{-1}$, the specific heat C_t per unit volume of the sample is (R being expressed in Å)

$$C_t = \frac{3\times 10^6}{R^3\eta^2} \text{ erg°K cm}^3 .$$

which can be compared to the value of the electronic specific heat C' of aluminium at $T \sim 1$ °K (neglecting all superconducting effects):

$$C' \simeq 5\times 10^3 \text{ erg °K cm}^3 ,$$

D. Susceptibility $\chi(H=0)$

Assuming always $N\Omega \simeq 10^{-1}$, we can write for the susceptibility

$$\chi \simeq 2\times 10^{-2}\,(e^2/c^2)\,[\xi^2(T)/R]\,T_c ,$$

which can be compared to the similar expression by Schmidt[23] in the corresponding bulk material, χ_B, assuming that the bulk material has the same mean free path as the grains. Thus we find

$$\chi/\chi_B \simeq 0.5\times[\xi(T)/R] .$$

Therefore, we think that the corresponding experiments could be most interesting if the problem of preparing samples containing such small grains could be solved.

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