PHYSICAL REVIEW B VOLUME 10, NUMBER 3 1 AUGUST 1974

Order-parameter fluctuations in small superconducting particles

B. Mühlschlegel
Institut für Theoretische Physik, Universität zu Köln, Köln, Germany
(Received 9 November 1973)

The generalized Ginzburg-Landau approximation for small metal particles is reconsidered with respect to its applicability to the specific heat and the diamagnetic susceptibility.

The thermodynamic properties of small superconducting particles have been extensively studied in a previous paper[1] by the use of a static approximation for the BCS-functional integral and by allowing for finite level spacings.[2] Also included in the paper was a generalized Ginzburg-Landau (GGL) formulation as a simple approximative description of order-parameter-fluctuation contributions. This GGL treatment has been subsequently criticized by Gunther, Deutscher, and Imry,[3] and was reformulated in a—in the opinion of these authors—consistent calculation. It is the purpose of this addendum to Ref. 1 and Ref. 3 to clarify the discrepancies by some simple general remarks.

(i) In the static approximation, the partition function for a small specimen is given by

$$Z \propto \int d|\psi|^2 e^{-\beta F(|\psi|^2,\beta)} . \tag{1}$$

Here, F is the BCS free-energy functional and $\beta = 1/k_B T$. The integration over the spatially uniform order parameter ψ must be performed numerically (as was done in Sec. III of Ref. 1). However, as a first approximation one can use a Ginzburg-Landau truncation for F:

$$F_{\mathrm{GL}} = \Omega N(0)[\ln t|\psi|^2 + 0.526(\beta^2/\pi^2)|\psi|^4] . \tag{2}$$

Here, $t = T/T_c$, and $\Omega N(0)$ is the single-spin density of states in the small particle of volume Ω. The integral in Eq. (1) then becomes a quadrature, as has been noted[1] repeatedly:

$$Z \propto e^{\Delta \bar{t}^2}[1 - \mathrm{erf}(\Delta \bar{t})] , \tag{3}$$

with

$$\Delta \bar{t} = (\mathrm{const}) t^{1/2} \ln t . \tag{4}$$

Equation (3) and the free energy $f(t)$ following it may be used to calculate any quantity of interest, like, for instance, $\langle |\psi|^2 \rangle$ or the specific heat $c(t) = -t f''(t)$. Clearly, such a calculation is meaningful only for $T/T_c = t \approx 1$, where

$$\Delta \bar{t} \to (\mathrm{const})(t-1) , \tag{5}$$

since otherwise the Ginzburg-Landau approximation (2) becomes insufficient.

(ii) It must be emphasized that *all* results presented in Sec. II of Ref. 1 follow from the steps contained in Eqs. (2)–(5) above and are therefore fully consistent within the frame of the GGL treatment, in contrast to the statement made in Ref. 3. It should be conceded, however, that the formulation used in the beginning of Sec. II of Ref. 1 may not, perhaps, be considered optimal, since the above steps were performed simultaneously, which then made it look as if some β were put equal to β_c and some were not. Any possible misunderstanding due to this formulation is removed by replacing Eq. (2.6) of Ref. 1 with Eq. (2) above.

(iii) Gunther, Deutscher, and Imry concentrate on the specific heat and find for $t < 1$ for this quantity a smaller slope than the one obtained in the above GGL treatment. This discrepancy is easily traced back to the fact that they use for F_{GL} the phenomenological expression in which $\ln t$ is replaced by $t-1$ and β by β_c in Eq. (2). Accordingly, $\Delta \bar{t}$ of Eq. (4) is changed into

$$\Delta \tilde{t} = (\mathrm{const}) t^{-1/2}(t-1) . \tag{6}$$

Due to the second derivative in the specific heat, $c(t) = -f''(t)$, $\Delta \bar{t}$ and $\Delta \tilde{t}$ *must* lead to different $c(t)$ curves, even in the temperature region near $t \approx 1$, where both expressions are equal to $(\mathrm{const})(t-1)$. For the same reasons, none of these Ginzburg-Landau approaches is actually correct concerning the slope and the curvature of the specific heat below T_c, since contributions from terms higher than $|\psi|^4$ in $F(|\psi|^2, \beta)$ enter. All that goes beyond $|\psi|^4$ was called "quasiparticle contributions" in Ref. 1, and has been calculated there for all interesting physical quantities within the framework of the static approximation. Clearly, as was noted by Gunther, Imry, and Deutscher, for the special case of a very small critical region, it is sufficient to incorporate the $|\psi|^6$ term in addition to the appropriate temperature dependences of the $|\psi|^2$ and $|\psi|^4$ terms in order to obtain the right (BCS) slope of $c(t)$ just below T_c, and this is no small-size effect at all. It should be borne in mind, however, that Sec. III of Ref. 1 was devoted to the general case, which needs much more effort since, for the study of the small-size effect within the chosen model, it is necessary to calculate the integral of Eq. (1).

(iv) The validity of the static approximation, i.e., the unimportance of dynamical fluctuations, has been recently justified by Hassing and Wilkins,[4] at least in the critical region. This, together with the experimental results for the diamagnetic transition in small aluminum particles,[5] puts the GGL treatment on a sound basis, as long as one is dealing with magnetic properties of small superconducting particles. On the other hand, a precise measurement of the specific heat, though difficult, would be very interesting, since it could show that besides order-parameter fluctuations there might be quasiparticle contributions that are not contained in the simple GGL approximation.

I would like to thank Dr. R. Denton for some useful discussions.

[1]B. Mühlschlegel, D. J. Scalapino, and R. Denton, Phys. Rev. B 6, 1767 (1972), and references therein.

[2]It should be noted here that the numerical calculations performed for the different values of the parameters $\bar{\delta}$ given in Ref. 1 indicate that replacing the continuum limit by finite level spacings has comparatively little influence on the calculated values of the static functional integral.

[3]L. Gunther, G. Deutscher, and Y. Imry, Phys. Rev. B 7, 3393 (1973).

[4]R. F. Hassing and J. W. Wilkins, Phys. Rev. B 7 1890 (1973).

[5]R. A. Buhrman and W. P. Halperin, Phys. Rev. Lett. 30, 692 (1973).