Soc. Japan 17, 1740 (1962).
[6]M. Shimizu and T. Takahashi, J. Phys. Soc. Japan 15, 2236 (1960).
[7]M. Shimizu, T. Takahashi, and A. Katsuki, J. Phys. Soc. Japan 18, 240 (1963).
[8]M. Shimizu, H. Kimura, and A. Katsuki, J. Phys. Soc. Japan 21, 307 (1966).
[9]A. P. Miiller and B. N. Brockhouse, Can. J. Phys. 49, 704 (1971).
[10]G. T. Furukawa, W. G. Saba, and M. L. Reilly, National Standard Reference Data System–Natl. Bur. Std.–18, 1968 (unpublished).
[11]V. E. Lyusternik, Pribory i Tekhn. Eksperim. 4, 127 (1959).
[12]V. Piesbergen, Z. Naturforsch. 18A, 141 (1963).
[13]P. Sommelet and R. L. Orr, J. Chem. Eng. Data 11, 64 (1966).
[14]G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnigs, J. Res. Natl. Bur. Std. (U.S.) 57, 67 (1956).
[15]D. A. Ditmars and T. B. Douglas, National Bureau of Standards Certificate, Reference Material 720 (unpublished).
[16]K. F. Sterret, D. H. Blackburn, A. B. Bestul, S. S. Chang, and J. Horman, J. Res. Natl. Bur. Std. (U.S.) 69δ, 19 (1965).
[17]W. W. Weller and K. K. Kelley, U. S. Bur. Mines Rept. Invest. No. 5984, 1 (1962).
[18]D. H. Dennison, K. A. Gschneidner, and A. H. Daane, J. Chem. Phys. 44, 4273 (1966).
[19]L. D. Jennings, R. E. Miller, and F. H. Spedding, J. Chem. Phys. 33, 1849 (1960).
[20]J. R. Berg, F. H. Spedding, and A. H. Daane, U.S. AEC Report No. IS-327, 1961, p. 1 (unpublished).
[21]Z. Bieganski and B. Stalinski, Bull. Acad. Polon. Sci. Ser. Sci. Chim. 9, 367 (1961).
[22]F. M. Jaeger and W. A. Veenstra, Rec. Trav. Chim. 53, 677 (1934).
[23]P. Mitacek and J. G. Aston, J. Am. Chem. Soc. 85, 137 (1963).
[24]F. M. Jaeger and T. J. Poppema, Rec. Trav. Chim. 55, 492 (1936).
[25]K. Clusius, C. G. Losa, and P. Franzosini, Z. Naturforsch. 12a, 34 (1947).
[26]J. A. Kok and W. H. Keesom, Physica 3, 1035 (1936).
[27]K. Clusius, C. G. Losa, and P. Franzosini, Z. Naturforsch. 2a, 90 (1947).
[28]W. B. Kendall, R. L. Orr, and R. J. Hultgren, J. Chem. Eng. Data 7, 516 (1962).
[29]J. E. Rowe and J. C. Tracey, Phys. Rev. Letters 27, 799 (1971).
[30]G. S. Flemming and T. L. Loucks, Phys. Rev. 173, 685 (1968).
[31]D. Koelling and A. J. Freeman (private communication).
[32]D. A. Papaconstantopoulos, J. R. Anderson, and J. W. McCaffrey, Phys. Rev. B 5, 1214 (1972).
[33]O. K. Anderson and A. R. Mackintosh, Solid State Commun. 6, 285 (1968).
[34]F. M. Mueller, A. J. Freeman, J. O. Dimmoch, and A. M. Furdyna, Phys. Rev. B 1, 4617 (1970).
[35]G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in *Superconductivity VII*, edited by R. D. Parks (Marcel Dekker, New York, 1969).
[36]J. Wittig, Phys. Rev. Letters 24, 812 (1970).
[37]J. W. Ross, F. Y. Fradin, L. L. Isaacs, and D. J. Lam, Phys. Rev. 183, 645 (1969).

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Thermodynamic Properties of Small Superconducting Particles*

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In bulk superconducting systems the large intrinsic range of the pair coherence length implies an extremely narrow critical region. However, as is well known, the size of the critical region becomes larger as the dimensions of the system decrease below the coherence length. An interesting limiting case corresponds to particles with all dimensions less than a coherence length which form essentially zero-dimensional systems. Here we calculate the thermodynamic properties of small superconducting particles using a static approximation. Within this approximation, both the order parameter and the quasiparticle contribution are explicitely studied.

I. INTRODUCTION

In bulk superconducting systems the large intrinsic range of the pair coherence length implies an extremely narrow critical region so that, for example, the observed specific heat follows the classic mean-field behavior. However, this large coherence length ξ also means that systems with dimensions less than ξ can conveniently be studied experimentally. For such small particles the deviations from the results of mean-field theory become important, and furthermore, they are simpler to treat theoretically because of the resulting suppression of spatial variations. Hurault, Maki, and Béal-Monod have examined the effects of these fluctuations to lowest order and found a large critical region.[1] Here we calculate the thermodynamic properties of small superconducting particles within the static approximation and compare our results with those obtained by Hurault *et al.* as well as with the mean-field limit. We explicitly consider the thermodynamic contribution of the quasiparticles and the effects of finite level spacing.

When the dimensions of the small particle are much less than the coherence length ξ, spatially uniform fluctuations of the order parameter dominate the thermodynamics. In Sec. II we integrate the Ginzburg-Landau free-energy functional over all such static uniform order parameters. This provides a simple approximate description of the thermodynamics of small particles. However, it not only treats the order parameter statically, but in addition it fails to treat the effect of quasiparticles and the structure of the one-electron spectrum in small particles.

The important parameter characterizing the shift from the mean-field results is the ratio of the average single-electron level spacing δ to kT_c

$$\bar{\delta} = \delta/kT_c = 1/N(0)\Omega kT_c \ . \qquad (1.1)$$

Here $N(0)$ is the single-spin energy density of states per unit volume and Ω is the small-particle volume. The width of the region $\Delta T/T_c$ in which deviations from the mean-field BCS results occur is proportional to $\bar{\delta}$. For particles of order 100 Å in size $\bar{\delta}$ is of order 0.1–1.0. The resulting broadening of the thermodynamic transition becomes sufficiently wide so that the quasiparticle contribution must be included on the same footing as the order-parameter-fluctuation contributions. In Sec. III we use a functional method, introduced previously for the bulk superconducting problem,[2] to carry this out within a static approximation.

In addition to explicitly considering the thermodynamic contribution of the quasiparticles, the effects of the finite level spacing can also be examined. As $\bar{\delta}$ increases from the bulk limit of 0, the effects of the discrete level spacings can become important. From our analysis[3] of small normal-metal particles, we expect that the actual distribution of energy levels must be considered for values of δ/kT such that $\delta/kT > 10$. However, for small superconducting particles, important deviations from the mean-field theory already enter for $\bar{\delta} \ll 1$. Therefore, in the range of temperatures which we will study here, the actual details of the level distributions can be neglected. In Sec. III we have considered the simple case of equal level spacings to determine if the discrete effects are important for $\bar{\delta} < 1$. Any effects due to the finite level spacing should be indicated by a variation in the thermodynamic properties as the chemical potential μ is varied. We have calculated the specific heat and spin susceptibility for the cases in which μ is fixed to coincide with a single electron level and when it occurs halfway between the levels. For values of $\bar{\delta} < 1$, the variations were found to be negligible.

It should be pointed out here that in calculating discrete effects we retain the influence of static fluctuations by performing the full functional integration. This differs from a treatment of size quantization in small particles by Strongin *et al.*,[4] which ignores the influence of fluctuations on thermodynamical properties by using only the zeroth-order saddle-point approximation for the partition function.

Perhaps the most important small-particle effect is the restriction to fixed electron number. In our work on normal-metal particles this, rather than the discrete levels, caused the dominant effect for $\delta/kT \lesssim 1.0$. In the superconducting case in which pairing plays a major role, the restriction to fixed electron number is surely even more important. The calculations of Sec. III are based on a grand canonical ensemble, with the electron level spacings taken to be equal. In an attempt to determine the importance of fixed particle number, we have considered in Sec. IV the projection of the canonical ensemble from the grand canonical representation by means of a saddle-point integration. This is known[3] to be a satisfactory approximation for small normal-metal particles when $\delta/kT \lesssim 1.0$, but it could simply be fortuitous. Further work on developing a canonical description for small superconducting particles is needed.

Finally some comments on the static approximation used in these calculations are appropriate. Practically, it allows results to be obtained over the entire temperature region. It therefore leads to definite predictions which can be checked against experiment. Second, we believe it provides a useful initial approximation at T_c and at small temperatures compared to T_c. Further work, in which the fluctuations about this static approximation are treated, would be extremely useful.

II. GENERALIZED GINZBURG-LANDAU APPROXIMATION

In their original treatment of the thermal equilibrium properties of the superconducting state near T_c, Ginzburg and Landau[5] (GL) introduced a free-energy functional which depended upon a complex order parameter $\psi(x)$:

$$F\{\psi\} = \int d^3x \left(a\,|\psi|^2 + \tfrac{1}{2} b\,|\psi|^4 + c\,|\nabla\psi|^2\right) \ . \qquad (2.1)$$

The parameters b and c were positive while a vanished linearly as T approached T_c:

$$a=a'(T-T_c) \quad (a'>0) . \tag{2.2}$$

The equilibrium properties were determined by evaluating F for the order parameter which made it stationary,

$$0=\delta F/\delta\psi^*=(a+b\,|\,\psi\,|^2-c\nabla^2)\psi . \tag{2.3}$$

More generally, one can view Eq. (2.1) as a reduced energy in which all degrees of freedom have been taken into account except those associated with the order parameter ψ. Then the partition function becomes a functional integral of $e^{-\beta F\{\psi\}}$ over all order parameter fields $\psi(x)$:

$$Z=\int \delta\psi\, e^{-\beta F\{\psi\}} , \tag{2.4}$$

where β is $(kT)^{-1}$. This is in fact just the static limit of a functional form for Z, near the transition temperature, derived from the microscopic theory by Hurault and Maki.[6] The GL treatment corresponds to a saddle-point evaluation of Eq. (2.4).

While for a large system the generalized GL expression (2.4) for Z has eluded evaluation, it greatly simplifies for the small system of interest here.[7–9] For particles whose dimensions are less than the coherence length $(c/a)^{1/2}$, the uniform spatial mode dominates and (2.4) reduces to the quadrature

$$Z=2\pi\int_0^\infty d\,|\,\psi|\;|\,\psi\,|\,\exp[-\beta\Omega(a\,|\,\psi\,|^2+\tfrac{1}{2}b\,|\,\psi|^4)] , \tag{2.5}$$

where Ω is the volume of the particle. Near the transition temperature, where (2.5) applies, we can replace β by β_c. With a normalization in which ψ has dimensions of the energy gap, the parameters a and b are given by

$$a=N(0)\,(T-T_c)/T_c , \quad b=7\zeta(3)N(0)/8\pi^2(kT_c)^2 , \tag{2.6}$$

where $\zeta(n)$ is the ζ function. Changing variables to $\lambda^{1/2}=\beta_c\,|\,\psi|/\pi$, the expression (2.5) for Z becomes

$$Z=\frac{\pi^3}{\beta_c^2}\int_0^\infty d\lambda\exp\left(-\frac{\pi^2}{\delta}\,[(t-1)\lambda+\bar{b}\,\lambda^2]\right), \tag{2.7}$$

with

$$\bar{\delta}=\beta_c/N(0)\Omega=\delta/kT_c ,$$
$$\bar{b}=7\zeta(3)/16=0.526 , \qquad t=T/T_c . \tag{2.8}$$

The integral over λ can be expressed in terms of the error function, and we find to within an unimportant multiplicative factor

$$Z=e^{\Delta\bar{t}^{\,2}}[1\pm\operatorname{erf}(|\,\Delta\bar{t}\;|\,)] , \tag{2.9}$$

where the upper sign applies for $\Delta\bar{t}<0$ and the lower when $\Delta\bar{t}>0$, with

$$\Delta\bar{t}=\tfrac{1}{2}\pi(t-1)/(\bar{\delta}\,\bar{b})^{1/2} . \tag{2.10}$$

The free energy associated with the superconducting part of the system is then

$$f=\frac{F}{C_N(T_c)T_c}=-\frac{3}{2\pi^2}\,t\,\bar{\delta}\,[\ln Z(t)+\text{const}] , \tag{2.11}$$

where f is measured in units of T_c times the normal-state specific heat at T_c.

The contribution to the specific heat obtained from (2.11) is

$$\frac{C}{C_N}=\frac{3t}{2\pi\bar{b}}\left(\frac{[\pi^{1/2}t\Delta\bar{t}-2(\bar{\delta}\,\bar{b}/\pi)^{1/2}]\,e^{-(\Delta\bar{t})^2}}{1\pm\operatorname{erf}(|\,\Delta\bar{t}\;|\,)}-\frac{t\,e^{-2(\Delta\bar{t})^2}}{[1\pm\operatorname{erf}(|\,\Delta\bar{t}\,|\,)]^2}+\pi(\tfrac{3}{2}t-1)\right) , \tag{2.12}$$

where, as before, the upper signs apply for $\Delta\bar{t}<0$ and the lower are appropriate when $\Delta\bar{t}>0$. If $\bar{\delta}$ is small, then there is a region near the transition temperature, where $|\,1-t\,|\ll 1$, but with the condition $|\,\Delta\bar{t}\,|\gg 1$ also satisfied. In this temperature region C/C_N has the asymptotic behavior

$$\frac{C}{C_N}\cong\begin{cases}\dfrac{3}{8\bar{b}}\,\dfrac{1}{\Delta\bar{t}^{\,2}} , & \Delta\bar{t}>0\\[2ex] \dfrac{3}{4\bar{b}}\left(1+4(t-1)+\dfrac{\Delta\bar{t}}{\pi^{1/2}}\,e^{-\Delta\bar{t}^2}\right) , & \Delta\bar{t}<0 .\end{cases} \tag{2.13}$$

In the limit of a bulk system $\bar{\delta}$ vanishes and there is a jump in the normalized specific heat of $3/4\bar{b}=1.43$ at T_c. The asymptotic form for $\Delta\bar{t}>0$ given in Eq. (2.13) agrees with the mean-field treatment of the fluctuations obtained by Hurault *et al.*[1] However, as noted by these authors, this limiting form fails when $\Delta\bar{t}\lesssim 1$. This is just the criterion $\eta\lesssim\eta_c$ in their paper. The present calculation gives results within the static approximation for $\Delta\bar{t}$ inside this so-called critical region.

In Fig. 1, results for the superconducting part of the specific heat obtained from Eq. (2.9) are plotted for the value $\bar{\delta}=0.01$. To facilitate comparison with the bulk answer[10] we have added a linear term t to Eq. (2.12). This is the specific heat of a normal metal normalized to $C_N(T_c)$. Clearly, at temperatures where the gap becomes significant this procedure is artificial. However, near T_c it allows a more meaningful comparison in the spirit of the two-fluid model. The perturbation-theory result obtained by Hurault *et al.*, but with the added term linear in t, is given by

$$C/C_N\cong t+3/8\bar{b}(\Delta\bar{t})^2 . \tag{2.14}$$

This is plotted as the dashed line in Fig. 1 for $\bar{\delta}=0.01$. Although perturbation theory breaks down

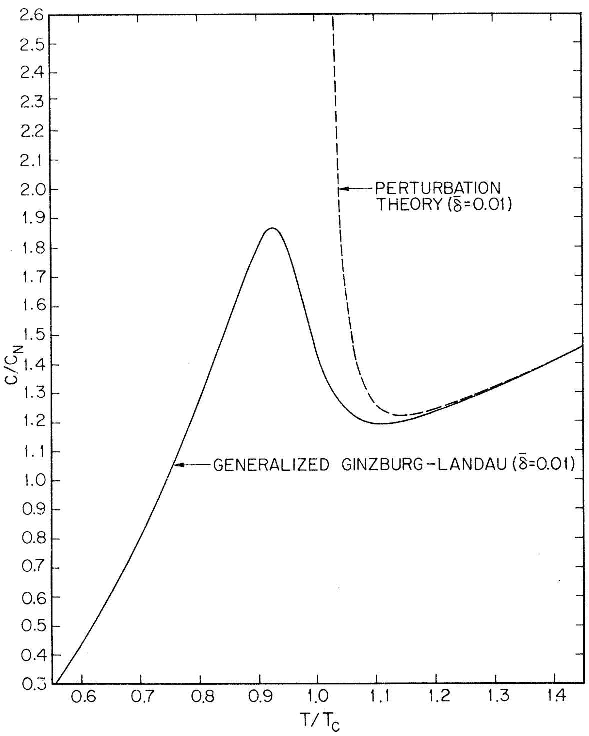

FIG. 1. Comparison of the normalized specific heat calculated using perturbation theory with the results from the generalized GL approach near $T=T_c$. Here the parameter $\bar{\delta}=\delta/kT_c$ has the value 0.01.

as t approaches 1, the generalized GL treatment leads to a specific heat which remains finite at $t=1$. The finite-size effects are clearly evident, giving rise to both a shift and broadening of the peak in the specific heat.

As $\bar{\delta}$ goes to zero, the results approach those for the bulk near $t=1$. Typically a particle of size ~ 1000 Å has $\delta \sim 10^{-3}$ K, so that if T_c is of order 1 K it would correspond to $\bar{\delta}\sim 10^{-3}$. Since δ varies inversely as the volume, if the particle size were reduced to ~ 100 Å then $\bar{\delta}$ would approach unity. Thus it should be possible to study this behavior over a wide range of $\bar{\delta}$ if the size distribution can be adequately controlled.[11] In Fig. 2 the specific heat given in Eq. (2.12) is plotted for several values of $\bar{\delta}$. Here also the term linear in t has been added. It is seen that $\bar{\delta}$ must become quite small before the bulk limit at $t=1$ is approached. On the other hand, as $\bar{\delta}$ approaches 1, the specific-heat anomaly is washed out. The discrete nature of the one-electron spectrum can also become important for $\bar{\delta}$ of order unity, and this is discussed in Sec. III.

To complete this section we now consider the diamagnetic susceptibility within the framework of the generalized GL scheme. Here we consider the weak-magnetic-field limit and take the particles to be spheres of radius R less than the penetration depth. Under these conditions, the rate of change of the transition temperature with magnetic field is given by

$$\frac{dT_c}{dH} = -\frac{\pi}{10}\frac{De^2}{c^2} R^2 H , \tag{2.15}$$

where D is the electronic diffusion constant appropriate for the small particle. Since the free energy depends upon H through T_c only, the magnetization becomes

$$M = -\frac{\partial F}{\partial H} = -\frac{\partial T_c}{\partial H}\frac{\partial F}{\partial T_c} . \tag{2.16}$$

Then, from Eq. (2.15) it follows that the linear field dependence of the magnetization is

$$M = \left(\frac{\pi}{10}\frac{De^2}{c^2} R^2\right)\frac{\partial F}{\partial T_c} H , \tag{2.17}$$

with F evaluated in the zero-field limit.[12] For temperatures near T_c, only the variation in the parameter a is significant, so that using Eq. (2.5) we can write

$$\frac{\partial F}{\partial T_c} = -\frac{N(0)\Omega}{T_c}\langle|\psi|^2\rangle . \tag{2.18}$$

Then combining Eqs. (2.17) and (2.18) we find that the zero-field diamagnetic susceptibility per unit volume for small spherical particles can be ex-

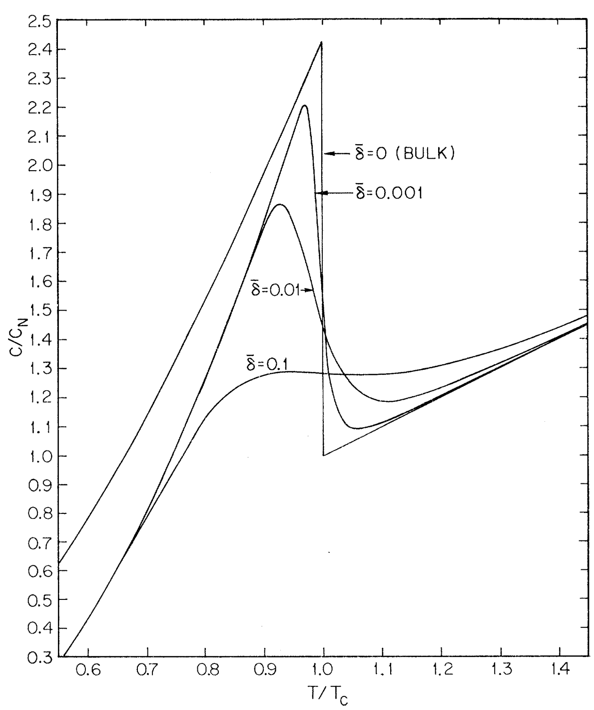

FIG. 2. Normalized specific heat near $T=T_c$ calculated in the GL approach for several values of the parameter $\bar{\delta}=\delta/kT_c$. For reference the bulk BCS limit is also shown.

pressed in the form

$$\chi = -\frac{\pi}{10}\,\frac{De^2R^2}{c^2}\,\frac{N(0)}{T_c}\,\langle|\psi|^2\rangle\ . \qquad (2.19)$$

In order to compare this with experiment, it is convenient to write χ in a form given by London,[13]

$$\chi = -(1/4\pi)\,R^2/10\lambda^2(T)\ . \qquad (2.20)$$

Here, we find for T near T_c an effective temperature-dependent penetration depth

$$[\lambda_0/\lambda(T)]^2 = 2\langle|\psi|^2\rangle/(\pi k T_c)^2\ , \qquad (2.21)$$

with

$$\lambda_0^2 = mc^2/4\pi n e^2\chi_G\ . \qquad (2.22)$$

χ_G is Gorkov's impurity function, which is equal to $1.33 l/\xi_0$ when the electron mean free path l is small compared to the BCS coherence length. For the small particles under consideration here l varies as the particle radius R.

Within the generalized GL formulation, it is straightforward to calculate $\langle|\psi|^2\rangle$:

$$\langle|\psi|^2\rangle = (\pi k T_c)^2\,\frac{1}{2\pi}\left(\frac{\bar\delta}{\bar b}\right)^{1/2} \times\left(\frac{2}{\pi^{1/2}}\,\frac{e^{-\Delta\bar t^2}}{1\pm\operatorname{erf}(|\Delta\bar t|)} - 2\Delta\bar t\right)\ , \qquad (2.23)$$

where as before the upper sign applies for $\Delta\bar t<0$ and the lower when $\Delta\bar t>0$. For $\Delta\bar t$ negative and $|\Delta\bar t|\gg 1$, $\langle|\psi|^2\rangle$ approaches the usual mean-field result with an exponentially small correction:

$$\frac{\langle|\psi|^2\rangle}{(\pi k T_c)^2} \approx \frac{1}{2\bar b}(1-t) + \frac{1}{2\pi}\left(\frac{\bar\delta}{\pi\bar b}\right)^{1/2} e^{-\Delta\bar t^2} \qquad (\Delta\bar t \ll -1)\ . \qquad (2.24)$$

while for $\Delta\bar t$ positive and large compared with 1, we obtain the lowest-order perturbation-theory limit

$$\frac{\langle|\psi|^2\rangle}{(\pi k T_c)^2} \approx \frac{\bar\delta}{\pi^2}\,\frac{1}{t-1} \qquad (\Delta\bar t \gg 1)\ . \qquad (2.25)$$

In Fig. 3, these two asymptotic forms are plotted as dashed lines while the full expression (2.23) is shown as a solid line. As one expects, $\langle|\psi|^2\rangle$ shows a continuous onset, remaining finite at T_c and approaching the mean-field result at low temperatures.

Returning to the diamagnetic susceptibility, the expression for $\langle|\psi|^2\rangle$ given by Eq. (2.23) has been used to determine $\chi(T)$ for various $\bar\delta$ values. These results are plotted vs $t-1$ in Fig. 4. Here it is clear that deviations from the bulk limit are important over a substantial range of reduced temperatures even for relatively small $\bar\delta$ values. In fact, as this region extends below reduced temperatures of order 0.9, deviations arising from the inadequacy of the phenomenological GL theory should be taken into account.

Finally, before leaving this case in which exact results for the generalized GL theory can be obtained, it seems worthwhile to compare it with an approximate scheme often used in higher dimension. In dealing with the $|\psi|^4$ term at high temperatures, a simple approximation is to replace it by the Hartree-Fock approximation $2\langle|\psi|^2\rangle|\psi|^2$. Here the factor of 2 arises from the two ways in which the four-field term can be reduced. We anticipate that this should be a reasonable approxi-

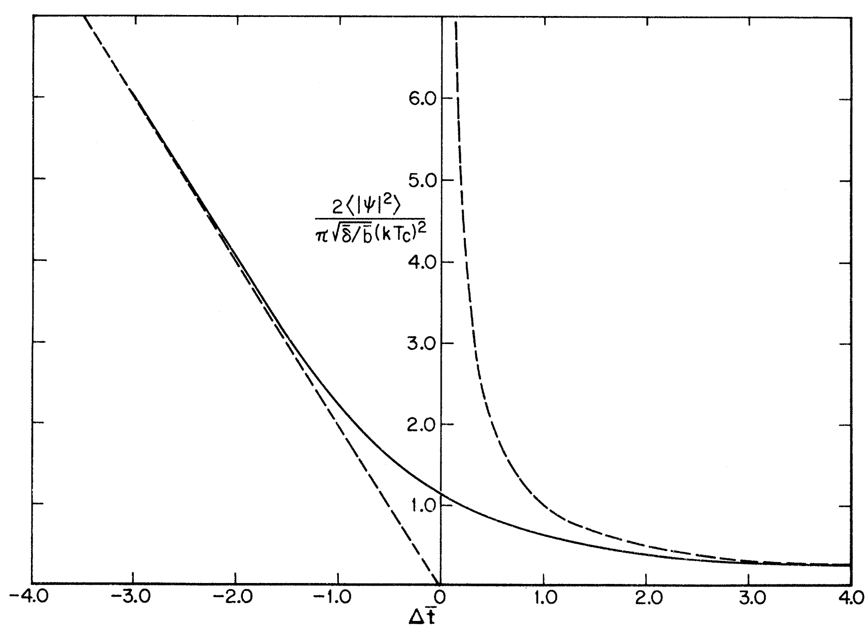

FIG. 3. Mean-square order parameter in reduced units is plotted as the solid curve vs $\Delta\bar t$. The dashed curve for $\Delta\bar t<0$ is the mean-field result and for $\Delta t>0$ represents the first-order fluctuation correction to the mean-field result.

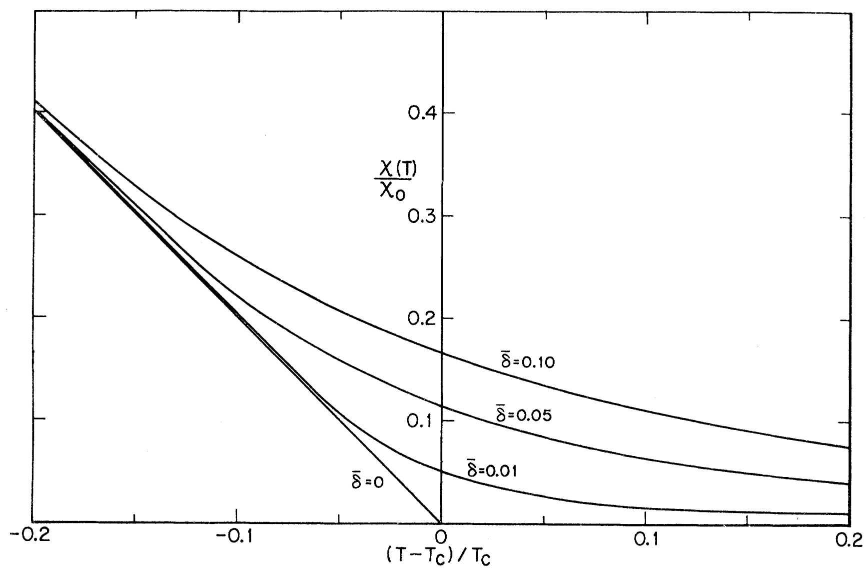

FIG. 4. Zero-field diamagnetic susceptibility per unit volume of a small superconducting particle vs reduced temperature. The normalization factor χ_0 is equal to $-R^2/40\pi\lambda_0^2$, where λ_0 is the low-temperature penetration depth $(mc^2/4\pi n e^2 \chi_G)^{1/2}$.

mation for $\Delta\bar{t} \gg 1$. However, at temperatures less than T_c, where $\Delta\bar{t} \ll -1$, one would guess that $\langle|\psi|^4\rangle$ should in fact approach simply the Hartree term $\langle|\psi|^2\rangle^2$. In order to see how this happens in the special case of small particles, we have evaluated $(\langle|\psi|^4\rangle - \langle|\psi|^2\rangle^2)^{1/2}/\langle|\psi|^2\rangle$ and plotted it vs $\Delta\bar{t}$ in Fig. 5. It can be seen that $\langle|\psi|^4\rangle$ follows a smooth variation from the high-temperature form $2\langle|\psi|^2\rangle^2$ to the low-temperature form $\langle|\psi|^2\rangle^2$. It is also clear that theories in which the Hartree-Fock (Hartree) replacement is made fail in the critical region, as well as at low (high) temperatures. Note: we have just learned that, interestingly enough, a similar GL approach has been applied by Grossman and Richter to describe the photon fluctuations at the laser threshold.[14]

III. SMALL-SIZE EFFECTS WITH STATIC APPROXIMATIONS

As discussed in Sec. I, when the particle size becomes sufficiently small that the discrete nature of the one-electron spectrum becomes important, it is no longer sufficient to use the results of Sec. II. In addition, the quasiparticle behavior is not adequately treated within the GL framework. As $\bar{\delta}$ increases toward unity, the width of the temperature region of interest broadens so that it becomes essential to account for the quasiparticle contributions to the thermodynamic properties. Finally, in order to treat specific quasiparticle effects such as the spin susceptibility, one must

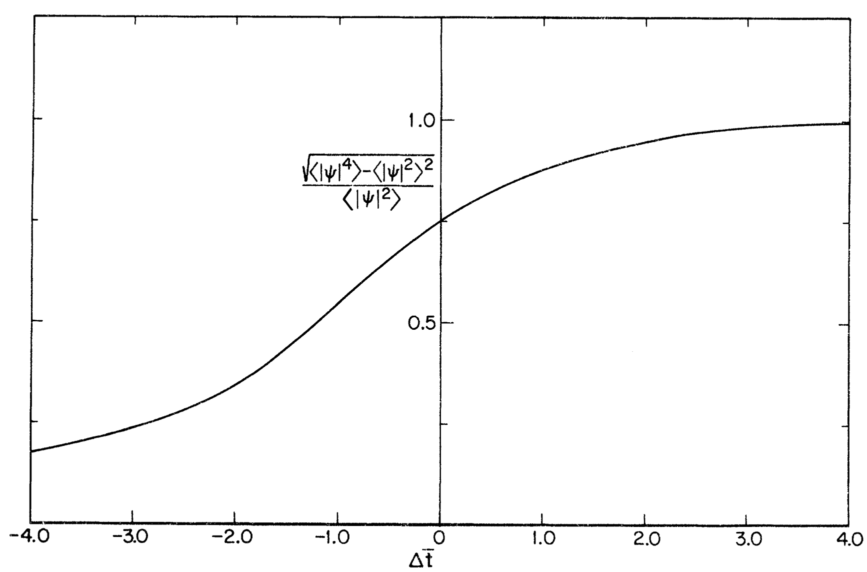

FIG. 5. rms deviation of $\langle|\psi|^4\rangle$ from $\langle|\psi|^2\rangle^2$ vs $\Delta\bar{t}$.

also develop a more complete description.

Here we extend the functional-averaging method of treating the BCS Hamiltonian to the problem of a discrete level system. A pairing interaction is taken between the time-reversed states of the small particle and treated in the reduced BCS form

$$H=\sum_\alpha \epsilon_\alpha(n_\alpha+n_{\tilde\alpha})-g\delta\sum_{\alpha\alpha'}{}' b^\dagger_\alpha b_{\alpha'}\,, \qquad (3.1)$$

where $n_\alpha=c^\dagger_\alpha c_\alpha$ and $b^\dagger_\alpha=c^\dagger_\alpha c^\dagger_{\tilde\alpha}$. The time-reversed single-electron states have been labeled by α and $\tilde\alpha$, and g is the usual dimensionless phonon-exchange coupling constant which is of order $\frac14$ to $\frac12$ and $\delta=[N(0)\Omega]^{-1}$ with Ω the particle volume. The prime on the $\alpha\alpha'$ summation implies a cutoff for states outside an energy shell $\pm\omega_D$ about the Fermi energy.

Introducing a time-dependent complex random field $\xi(\tau)$, the grand canonical partition function can be represented by[2]

$$Z=\int\delta\xi(\tau)\exp\left[-\pi\int_0^1 d\tau\,|\xi(\tau)|^2\right]\prod_\alpha \mathrm{Tr}\exp\left[-\int_0^1 d\tau\left\{\beta(\epsilon_\alpha-\mu)(n_{\alpha\tau}+n_{\tilde\alpha\tau})-(\pi g\beta\delta)^{1/2}[\xi(\tau)b^\dagger_{\alpha\tau}+\xi^*(\tau)b_{\alpha\tau}]\right\}\right]. \qquad (3.2)$$

Proceeding in the same spirit as Sec. II we investigate the static limit of (3.2) in which $\xi(\tau)$ is replaced by a complex number ξ. The trace appearing in (3.2) can now be performed giving

$$e^{-\beta[(\epsilon_\alpha-\mu)-E_\alpha]}(1+e^{-\beta E_\alpha})^2\,, \qquad (3.3)$$

with

$$\beta E_\alpha=[\beta^2(\epsilon_\alpha-\mu)^2+\pi g\beta\delta|\xi|^2]^{1/2}\,. \qquad (3.4)$$

Changing the integration variable to $s=\pi g|\xi|^2$, the static approximation for (3.2) becomes

$$Z=\frac1g\int_0^\infty ds\exp\left(-\frac sg-\sum_\alpha[\beta(\epsilon_\alpha-\mu)-\beta E_\alpha-2\ln(1+e^{-\beta E_\alpha})]\right), \qquad (3.5)$$

with

$$\beta E_\alpha=[\beta^2(\epsilon_\alpha-\mu)^2+\beta\delta s]^{1/2}\,. \qquad (3.6)$$

Actually, the interaction cutoff is not yet properly included in (3.6). This can be easily remedied by dividing by the free-fermion partition function

$$Z_0=\prod_\alpha\exp\{-\beta[(\epsilon_\alpha-\mu)-|\epsilon_\alpha-\mu|]\}\times(1+e^{-\beta|\epsilon_\alpha-\mu|})^2 \qquad (3.7)$$

to obtain

$$\frac{Z}{Z_0}=\frac1g\int_0^\infty ds\,e^{-A(s)}\,, \qquad (3.8)$$

with

$$A(s)=\frac sg+\sum_\alpha{}'\,[\beta|\epsilon_\alpha-\mu|-\beta E_\alpha+2\ln(1+e^{-\beta|\epsilon_\alpha-\mu|})-2\ln(1+e^{-\beta E_\alpha})]\,, \qquad (3.9)$$

where the prime implies a cutoff at $|\epsilon_\alpha-\mu|=\omega_D$.

In order to understand the relationship between this static functional expression and the generalized GL theory discussed in Sec. II, we examine the continuum limit of (3.9). Replacing the α sums by integrals

$$A(s)=\frac sg+\frac{2\beta}{\delta}\int_0^{\omega_D}d\epsilon\left[\epsilon-\left(\epsilon^2+\frac{\delta}{\beta}s\right)^{1/2}\right]+\frac4\delta\int_0^\infty d\epsilon\left[\ln(1+e^{-\beta\epsilon})-\ln\left\{1+\exp\left[-\beta\left(\epsilon^2+\frac\delta\beta s\right)^{1/2}\right]\right\}\right], \qquad (3.10)$$

where the cutoff can be neglected in the second integral as long as $e^{-\beta\omega_D}$ is negligible. Setting $\lambda=\beta\delta s/\pi^2$ and carrying out the first integral in Eq. (3.10), one finds, neglecting terms of order $(\lambda\pi/\beta\omega_D)^2$,

$$A(\lambda)=(\pi^2t/\delta)[\lambda\ln(T/T_c)+a(\lambda)]\,, \qquad (3.11)$$

with

$$a(\lambda)=\tfrac13+\lambda[\ln(\gamma\lambda^{1/2})-\tfrac12]-(4/\pi)\times\int_0^\infty dx\ln(1+e^{-\pi[x^2+\lambda]^{1/2}})\,, \qquad (3.12)$$

where $\ln\gamma$ is Euler's constant 0.5772. Here, as in Sec. II, $\bar\delta$ is the ratio of the average level spacing δ to kT_c with

$$kT_c=1.14\omega_D e^{-1/g}\,. \qquad (3.13)$$

This equation is the defining equation for the transition temperature T_c in terms of the BCS parameters ω_D and g. Certainly for small particles the values of ω_D and g would be expected to deviate from their bulk values. For the purpose of calculating the effects on the superconductivity as $\bar\delta$ varies, however, they are treated here as phenomenological constants. Near the transition temperature small values of λ dominate, and it is appropriate to expand $a(\lambda)$ in a power series[5]:

$$a(\lambda)=-4\sum_{\nu=2}^\infty\binom{\frac12}{\nu}(1-2^{-(2\nu-1)})\zeta(2\nu-1)\lambda^\nu=\tfrac{7}{16}\zeta(3)\lambda^2-\cdots\,. \qquad (3.14)$$

Thus in this limit

$$A(\lambda)\approx(\pi^2/\bar\delta)[\lambda(t-1)+\tfrac{7}{16}\zeta(3)\lambda^2] \qquad (3.15)$$

and Eq. (3.8) for Z/Z_0 reduces to

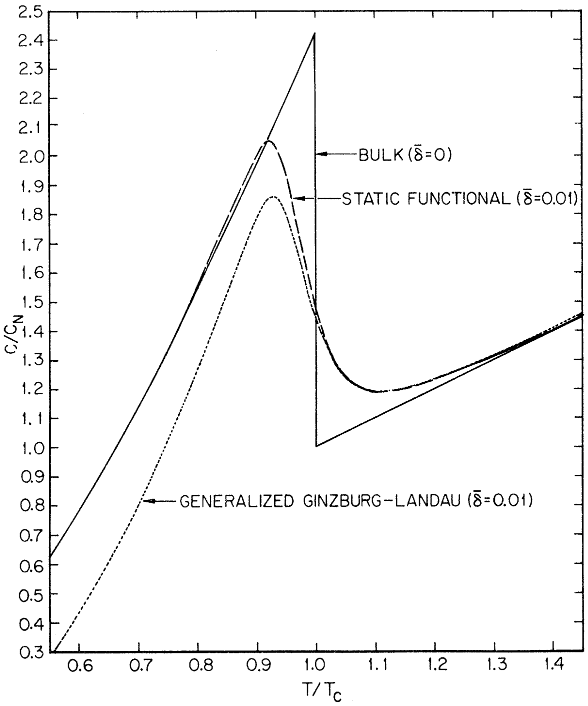

FIG. 6. Comparison of the normalized specific heat from the static functional calculation with that from the GL calculation, for the special value of $\bar{\delta}=0.01$. For reference the bulk BCS limit is also included.

$$\frac{Z}{Z_0} \approx \frac{\pi^2}{\bar{\delta} g} \int_0^\infty d\lambda \exp\left(-\frac{\pi^2}{\bar{\delta}} \left[\lambda(t-1) + \tfrac{7}{16}\zeta(3)\lambda^2\right]\right). \quad (3.16)$$

In these two equations the variable $t=T/T_c$ has been replaced by unity except in the critical term $(t-1)$ arising from the logarithm in the equation (3.11) for $A(\lambda)$. The resulting expression for Z/Z_0 differs only by a multiplicative constant from the generalized GL expression (2.7) studied in Sec. II.

Returning to the general result (3.8) for the static approximation of a discrete level system, we express the total free energy normalized to $C_N(T_c)T_c$ as

$$f = \frac{F}{C_N(T_c)T_c} = -\frac{3}{2\pi^2}\bar{\delta} t \ln(Z)$$
$$= -\frac{3}{2\pi^2}\bar{\delta} t \left[\ln(Z_0) + \ln\left(\frac{Z}{Z_0}\right)\right]. \quad (3.17)$$

The normalized specific heat is given as before by

$$\frac{C}{C_N(T_c)} = -t\frac{\partial^2}{\partial t^2} f. \quad (3.18)$$

Although one could choose to consider first the exact expression for the continuum limit (3.11), passing to this limit immediately might appear inconsistent for values $\bar{\delta}=\delta/kT_c$ of order unity. In addition, δ/kT can become large compared to unity as the temperature is lowered, and effects from the discrete sums can enter. Since we are interested in a range of values for $\bar{\delta}$ including values approaching unity, we have just gone directly to a calculation of the special case of equal level spacings, with the discrete sums being done numerically. In these calculations g was set equal to $\frac{1}{2}$ and two μ values corresponding to setting μ at a level and halfway between two levels were used. The sensitivity of the results for these two different values of the chemical potential provides a measure of the importance of the discrete effects. The differentiation (3.18) is first performed. This results in several integrals over s, in which the integrands contain either the discrete level expression (3.9) for $A(s)$ or derivatives of $A(s)$ with respect to t. The discrete sums have been evaluated numerically as a function of s, and then, of course, the integrals over s were computed numerically.

In Fig. 6, the results for the specific heat obtained in this way for $\bar{\delta}=0.01$ and μ at a level are compared with the bulk specific heat and the result obtained in Sec. II. Near T_c, there is good agreement with the generalized GL result for this relatively small value of the level spacing. However, away from T_c the generalized GL result fails to adequately describe the quasiparticle contribution, while the equal level result approaches the bulk behavior as expected. Continuing with the numerical results obtained from the static approximations (3.8) and (3.9) in the equal level case, Fig. 7 shows how the specific-heat anomaly is washed out as $\bar{\delta}$ increases. Also for these curves, μ was taken to coincide with a level, and $g=\frac{1}{2}$ was used. By the time the level spacing is equal to kT_c, only a very broad remnant of the specific-heat anomaly remains. Furthermore, the numerical results indicate only an $\approx 3\%$ variation of the specific heat for μ between two levels with $\bar{\delta}$ as large as unity, and this variation decreases as $\bar{\delta}$ becomes smaller. Since for these values of $\bar{\delta}$ the specific-heat anomaly is already washed out, the effects are relatively uninteresting in considering the specific heat.

From a formal point of view it is also of interest to investigate small-particle effects on a purely quasiparticle property such as the spin susceptibility χ_s. In order to explore this behavior without competing effects, spin-orbit coupling will be neglected although it can produce important modifications in χ_s. Since for our present considerations the spin is a good quantum number, the term $\epsilon(n_\alpha + n_{\tilde{\alpha}})$ is replaced by

$$(\epsilon+h)n_\alpha + (\epsilon-h)n_{\tilde{\alpha}}, \quad (3.19)$$

with $h=\frac{1}{2}g\mu_B H$. With this modification the trace given by Eq. (3.3) becomes

$$e^{-\beta[(\epsilon_\alpha-\mu)-E_\alpha]}(1+e^{-\beta(E_\alpha+h)})(1+e^{-\beta(E_\alpha-h)}) . \quad (3.20)$$

Expanding the sum of the logarithms of the field-dependent terms to the second order in βh yields

$$\ln(1+e^{-\beta(E_\alpha+h)})+\ln(1+e^{-\beta(E_\alpha-h)})=2\ln(1+e^{-\beta E_\alpha}) + (\beta h)^2 f(\beta E_\alpha)[1-f(\beta E_\alpha)] , \quad (3.21)$$

where f is the Fermi function. Then the generalization of Eq. (3.9) for the case in which a magnetic field couples to the spins is

$$A_{\rm spin}(s)=A(s)-(\beta h)^2\textstyle\sum_\alpha f(\beta E_\alpha)[1-f(\beta E_\alpha)] . \quad (3.22)$$

Using (3.22) the partition function to order $(\beta h)^2$ can be written

$$\frac{Z(h)}{Z_0}=\frac{Z}{Z_0}\left(1+\int_0^\infty ds\, e^{-A(s)}(\beta h)^2\sum_\alpha f(\beta E_\alpha)[1-f(\beta E_\alpha)]\Big/\int_0^\infty ds\, e^{-A(s)}\right), \quad (3.23)$$

where Z/Z_0 is the zero-field partition function, Eq. (3.8). Computing the free energy and susceptibility from (3.23) in the usual way, one finds the ratio of the spin susceptibility to the normal-state Pauli susceptibility:

$$\frac{\chi_s}{\chi_N}=\beta\delta\int_0^\infty ds\, e^{-A(s)}\sum_\alpha f(\beta E_\alpha)[1-f(\beta E_\alpha)]\Big/\int_0^\infty ds\, e^{-A(s)} . \quad (3.24)$$

Before evaluating this, it is interesting to observe how it reduces to the bulk result as $\bar{\delta}$ goes to zero. First the discrete sum over α is converted to an integral, and the integration variable s is again changed to $\lambda=\beta\delta s/\pi^2$. The integrand can be simplified by using an identity which follows from the form of $a(\lambda)$, Eq. (3.12):

$$2\beta\int_0^\infty d\epsilon\, f(\beta E)[1-f(\beta E)]=1-2\lambda a''(\lambda) . \quad (3.25)$$

We then obtain the simple form

$$\frac{\chi_s}{\chi_N}=\int_0^\infty d\lambda\, e^{-A(\lambda)}[1-2\lambda a''(\lambda)]\Big/\int_0^\infty d\lambda\, e^{-A(\lambda)} . \quad (3.26)$$

In the bulk limit where $\bar{\delta}$ vanishes the above integral can be evaluated by steepest descent, and we obtain

$$\chi_s/\chi_N=1-2\lambda_0 a''(\lambda_0) , \quad (3.27)$$

with

$$E=[\epsilon^2+(\pi/\beta)^2\lambda_0]^{1/2} .$$

Here λ_0 is determined from the saddle-point condition

$$\ln t + a'(\lambda_0)=0 . \quad (3.28)$$

This is just the BCS gap equation with $\Delta=(\pi/\beta)\lambda_0^{1/2}$, so that (3.27) is the well-known bulk result for χ_s/χ_N.[10] This is shown in Fig. 8 along with the numerical results obtained from (3.24) for several values of $\bar{\delta}$. For the numerical results the special case of equal spacings was again calculated with $g=\frac{1}{2}$ and μ coinciding with a level.

With reference to the specific-heat curves, it is interesting that when $\bar{\delta}$ approaches unity, there is hardly a remnant of the superconducting phase transition at $T=T_c$. One might then be inclined to assume the superconducting effects are essentially washed out by this time. On the other hand, the spin-susceptibility curves give clear evidence of the superconducting effects, even for $\bar{\delta}$ as large as unity.

IV. CANONICAL PROJECTION FOR $\beta\delta \lesssim 1$

We consider briefly the canonical projection of the partition function onto N particles. For the

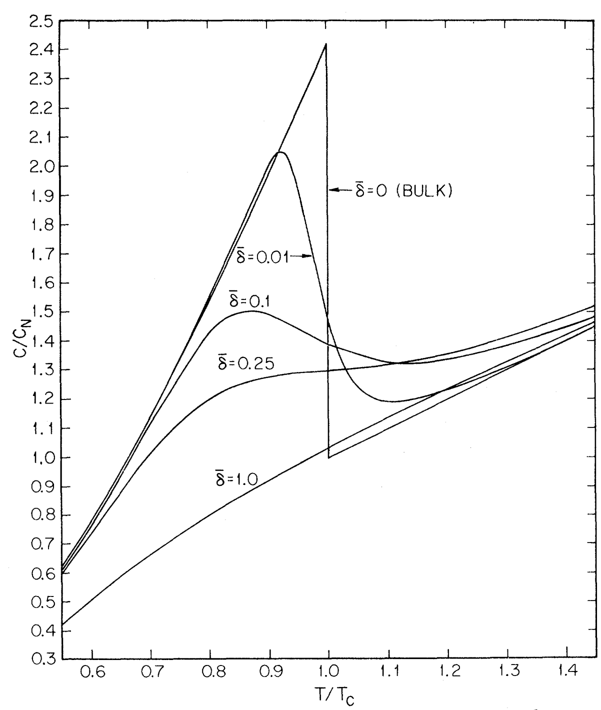

FIG. 7. Normalized specific heat calculated in the static functional approximation for several values of $\bar{\delta}=\delta/kT_c$. For reference the bulk BCS limit is also shown.

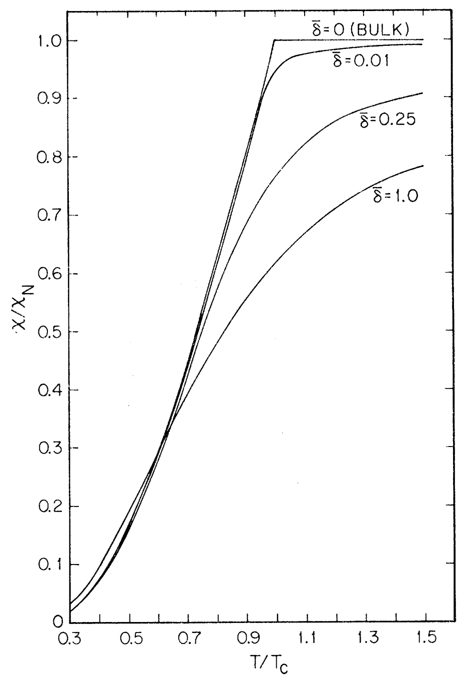

FIG. 8. Spin susceptibility normalized to the Pauli value $2|\frac{1}{2}g\mu_B|^2/\delta$. The results for several values of $\bar{\delta} = \delta/kT_c$ are shown together with the BCS limiting value.

case of small normal-metal particles at temperatures with $kT \ll \delta$, the exact projection leads to thermodynamic behavior which varies depending on odd or even conduction-electron number. At higher temperatures, however, such that $kT > \delta$, a saddle-point integration of the canonical projection yields the most important consequence of the fixed electron number. In the case of the specific heat, this results in its being lowered by $\frac{1}{2}k_B$ per particle. Also for superconducting small particles, we expect to find a variation in the thermodynamic behavior at low temperatures, depending on odd or even electron number. Corresponding to the normal case, for $kT > \delta$, one might expect a saddle-point integration to yield the first effect due to fixed particle number. It will be shown below that the saddle-point integration for the superconducting case also leads to a lowering of the specific heat, similar to the normal case.

Formally the canonical projection on N particles is given by a contour integration around the origin of the grand canonical partition function,

$$Z(N) = (1/2\pi i)\oint (d\psi/\psi^{N+1})\, Z(\mu)\ , \tag{4.1}$$

where $\psi = e^{\beta\mu}$. Here $Z(\mu)$ is given in Eq. (3.5) with the cutoff being handled appropriately. The reason for the difficulty in an exact calculation, such as can be carried out for normal metals, lies in the appearance of μ in the expression for E_α:

$$\begin{aligned}\beta E_\alpha &= [\beta^2(\epsilon_\alpha-\mu)^2+\beta\delta s]^{1/2}\\ &= [\beta^2\epsilon_\alpha^2 - 2\beta\epsilon_\alpha\ln\psi + (\ln\psi)^2 + \beta\delta s]^{1/2}\ .\end{aligned} \tag{4.2}$$

$Z(N)$ can be rewritten in a form which lends itself to the saddle-point integration over ψ:

$$Z(N) = \frac{1}{g}\int_0^\infty ds\, e^{-s/g}\oint \frac{d\psi}{2\pi i}\, e^{\varphi(\psi, s)}\ , \tag{4.3}$$

where

$$\varphi(\psi, s) = -(N+1)\ln\psi - \textstyle\sum_\alpha [\beta\epsilon_\alpha - \ln\psi - \beta E_\alpha - 2\ln(1+e^{-\beta E_\alpha})]\ . \tag{4.4}$$

In the case of normal metals there is an analogous $\varphi(\psi)$ given by setting $E_\alpha = \epsilon_\alpha - \mu$, and so φ does not depend on s. The integration over s is then trivial. We review this case, since the superconducting case involves a simple generalization. It is found that provided $\beta\delta \ll 1$ a saddle-point integration is justified. One has

$$Z_{\rm normal}(N) = e^{\varphi(\psi_0)}\oint \frac{d\psi}{2\pi i}\, e^{\varphi''(\psi_0)(\psi-\psi_0)^2/2}\ , \tag{4.5}$$

where ψ_0 is determined by

$$\left.\frac{\partial\varphi(\psi)}{\partial\psi}\right]_{\psi_0} = 0\ . \tag{4.6}$$

This last condition is just an implicit equation for the chemical potential in terms of the particle number N. One finds that the contour integration must be taken parallel to the imaginary axis, with the contour passing through ψ_0. The integration gives

$$Z_{\rm normal}(N) = e^{\varphi(\psi_0)}/[2\pi\varphi''(\psi_0)]^{1/2}\ , \tag{4.7}$$

with

$$\varphi''(\psi_0) = (2/\psi_0^2)\,(1/\beta\delta)\ . \tag{4.8}$$

For this last result, Eq. (4.6), which defines ψ_0 in terms of N, was used to eliminate the particle number N which appears in $\varphi''(\psi_0)$, and the α sum was converted to an integral. The $\varphi(\psi_0)$ term is responsible for the usual linear law for the specific heat, while the $\varphi''(\psi_0)$ term leads to a correction of $-\frac{1}{2}k_B$ in the specific heat of normal-metal small particles.

The superconducting case is analogous although somewhat more tedious. Because of the s dependence in $\varphi(\psi, s)$, Eq. (4.6) determines the critical value ψ_0 as a function of s: $\psi_0 = \psi_0(s)$. The ψ integration passing through $\psi_0(s)$ then gives

$$Z = \frac{1}{g}\int_0^\infty ds\, e^{-s/g}\, \frac{e^{\varphi(\psi_0(s), s)}}{[2\pi\varphi''(\psi_0(s), s)]^{1/2}}\ , \tag{4.9}$$

where $\varphi(\psi, s)$ was given in Eq. (4.4). The $\varphi''(\psi_0(s), s)$ term in the above equation reduces to a simple form after again using Eq. (4.6) and converting the α sums to integrals:

$$\varphi''(\psi_0(s), s) = \frac{2}{\psi_0^2(s)} \frac{1}{\beta\delta}$$

$$\times\left(\frac{x_0}{(x_0^2+\beta\delta s)^{1/2}} \frac{e^{(x_0^2+\beta\delta s)^{1/2}}-1}{e^{(x_0^2+\beta\delta s)^{1/2}}+1} + \frac{2}{e^{x_0}+1}\right), \quad (4.10)$$

where

$$x_0 = (1/t)\, e^{1/g}/1.14 . \quad (4.11)$$

Note this expression for $\varphi''(\psi_0(s), s)$ just reduces to the normal result, when the variable s is set equal to zero.

Because of the s dependence in ψ_0 this integral is difficult to do. However, if we assume particle-hole symmetry exists, it is found that ψ_0 does not depend on s. It then has the same constant value as for the normal system. In this case, we have calculated the specific heat numerically from the partition function [Eq. (4.9)], similar to the previous numerical calculations. It is found that the principal added effect arises from $1/\beta\delta$ appearing in $\varphi''(\psi_0)$. The terms in brackets are not important, since the value of x_0 is always large compared to $\beta\delta s$, at least over those values of s for which the integrand gives the largest contribution to the integral. The bracketed terms can then just be set equal to unity. The $1/\beta\delta$ dependence in $\varphi''(\psi_0)$ leads to the specific heat being lowered by $-\frac{1}{2}k_B$. If the normalization of the specific heat is to $C_N(T_c)$ as before, then the change is

$$-k_B/2C_N(kT_c/\delta) . \quad (4.12)$$

This simple correction to the specific heat may be the most important result of the canonical projection, at least as long as $\delta/kT = \bar{\delta}/t$ remains small. Similar to the case of normal metals, however, when the ratio $\bar{\delta}/t$ is greater than unity, more dramatic results probably depend on a better approximation to the canonical projection.

Note added in proof. After this work was carried out, we learned gradually that this approach has a venerable history. At LT-X, V. V. Shmidt gave a paper[7] in which he treated this problem and evaluated $\langle|\psi|^2\rangle$ and the magnetization. In 1969, in unpublished lectures at Orsay, R. Ferrell[8] discussed zero-dimensional systems from this point of view. More recently, we have learned from the Abstract of the First European Conference on the Physics of Condensed Matter, Florence (1971) that J. B. Parkinson[9] has also treated this problem. We have included our treatment, Sec. II of this paper, because it provides a useful introduction and a basis for comparison of the more complete theory of Sec. III, which includes quasiparticles.

ACKNOWLEDGMENTS

We would like to thank Dr. J. Crow for pointing out Shmidt's paper (Ref. 7) and Dr. G. Thomas for the reference to the talk by Parkinson (Ref. 9). One of the authors (D. J. S.) acknowledges with pleasure a discussion with Professor John Wilkins which led to the investigation of the deviation $\langle|\psi|^4\rangle - \langle|\psi|^2\rangle^2$ discussed in Sec. II.

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[1]J. P. Hurault, K. Maki, and M. T. Béal-Monod, Phys. Rev. B 3, 762 (1971).

[2]B. Mühlschlegel, J. Math. Phys. 3, 522 (1962).

[3]R. Denton, B. Mühlschlegel, and D. J. Scalapino, Phys. Rev. Letters 26, 707 (1971).

[4]M. Strongin, R. S. Thompson, O. F. Kannerer, and J. E. Crow, Phys. Rev. B 1, 1078 (1970).

[5]V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. 20, 1064 (1950).

[6]J. P. Hurault and K. Maki, Phys. Rev. B 2, 2560 (1970); see also T. M. Rice, Phys. Rev. 140, A1889 (1965).

[7]V. V. Shmidt, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow*, 1966, edited by M. P. Malkov (Proizvodstrenne-Izdatel'skii Kombinat, VINITI, Moscow, 1967), Vol. 2B, p. 205.

[8]R. Ferrell (private communication).

[9]J. B. Parkinson, in Proceedings of the First European Conference on the Physics of Condensed Matter, Florence, 1971 (unpublished), abstract B4.2.

[10]B. Mühlschlegel, Z. Physik 155, 313 (1959).

[11]Since the parameter T_c is known to vary with the physical properties of the particle, sample preparation (size, shape, surface, etc.) forms the heart of any experiment on small particles.

[12]Actually the pair breaking will modify the coefficient b in (2.6); compare, for instance, K. Maki, in *Treatise on Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 2, Chap. 18. However, we expect this to be a higher-order effect.

[13]F. London, *Superfluids* (Dover, New York, 1961), Vol. 1, p. 41.

[14]S. Grossmann and P. H. Richter, Z. Physik 242, 458 (1971).