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Finite-size effects and polycrystalline high-T_c materials

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We examine the effect of thermal and quantal fluctuations on small superconducting grains using a BCS-like Hamiltonian. A comparison between the static path approximation to the Hubbard-Stratonovich representation of the partition function (Z_{HS}) and the order-parameter representation (Z_{OP}) based on the Landau theory of phase transitions shows that one should use the expectation value of the pairing potential $\mathcal{G}$ instead of the BCS energy gap Δ for the order parameter of a superconducting system. Unlike Z_{HS}, Z_{OP} is not restricted to positive-definite pairing potentials and can be used for general momentum-dependent pairing potentials. We find that quantal fluctuations are negligible for the crystallites of the polycrystalline high-T_c materials and that the results obtained using Z_{OP} are a good approximation to the exact results. Both the sharpening of the peak in the specific heat and the increase in the critical temperature observed during the sintering process of polycrystalline high-T_c materials can be qualitatively understood by taking into account thermal fluctuations. In polycrystalline high-T_c materials there is an anomaly in the specific heat rising above the BCS peak which is not reproduced by including these finite-size effects.

I. INTRODUCTION

Finite-size effects and in particular thermal fluctuations are much more important for high-T_c materials than for conventional superconducting materials for several reasons. First, bulk materials are often sintered polycrystalline materials with the individual crystals being only very weakly linked. This is illustrated by the observation that the critical current in sintered polycrystalline materials is more than an order of magnitude lower than in melt-textured materials where the individual crystallites are aligned[1] and about two orders of magnitude lower than in large single crystals.[2] Secondly, the supercurrent in high-T_c materials seems to be confined to the Cu-O planes[3] and it seems that coupling between Cu-O planes is not essential for high current densities.[4] Furthermore, both the high critical temperatures and the low carrier densities make thermal fluctuations more significant in these materials than in conventional superconductors.

In the light of the weak coupling between the crystallites we treat, as a first approximation, the individual crystallites as isolated superconducting systems. The mean-field treatment neglects thermal and quantal fluctuations, both of which can become important for small systems. The first arises because in finite systems states other than the most probable state (i.e., the state which minimizes the free energy) become accessible at finite temperature. Quantal fluctuations, on the other hand, arise from the approximate nature of the mean-field wave functions. Furthermore, for finite systems one should replace integrals over the density of states by sums over the discrete states. Since the number of states is still very high for the small crystallites, we use instead a simple geometrical modification to the density of states.[5,6]

Using a BCS-like Hamiltonian[7]

$$H = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{k}'} G_{\mathbf{k}\mathbf{k}'} c^{\dagger}_{\mathbf{k}\uparrow} c^{\dagger}_{-\mathbf{k}\downarrow} c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow}, \quad (1.1)$$

we have shown[6] that both the increase in the critical temperature and the sharpening of the peak in the specific heat observed during the sintering process of polycrystalline high-T_c materials can be qualitatively understood by taking into account finite-size effects, and in particular thermal fluctuations and finite-size corrections to the density of states.

However, there is a qualitative difference between the specific heat curves of small conventional superconductors and those of polycrystalline high-T_c superconductors. In conventional superconducting grains the specific heat curve remains below the bulk BCS curve,[8,9] while in polycrystalline high-T_c materials there is an anomaly in the specific heat rising above the BCS curve.[10–12] This is not reproduced in the present work. One can, if one inconsistently uses the gap parameter(s) as an order parameter within the Landau theory of phase transitions, reproduce the anomaly rising above the BCS peak in the specific heat.[12] However, this is an artifact of the inconsistent choice of order parameter, i.e., one should use the expectation value of the pairing potential $\mathcal{G}$ instead of the BCS energy gap Δ for the order parameter.

In a recent paper[13] we considered two approaches to calculate the effect of thermal fluctuations on the system. The first is the static path approximation (SPA) to the Hubbard-Stratonovich representation[14,15] of the partition function (Z_{HS}). The second is based on the Landau theory of phase transitions in which one integrates

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over the accessible states as labeled by a macroscopic order parameter. Both treatments include thermal but not quantal fluctuations. We found that the resulting analytical expressions are very similar for the two formalisms if we choose the expectation value of the pairing potential,

$$\mathcal{G} = \sum_{\mathbf{k}\mathbf{k}'} G_{\mathbf{k}\mathbf{k}'} \langle c^{\dagger}_{\mathbf{k}\uparrow} c^{\dagger}_{-\mathbf{k}\downarrow} c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle, \tag{1.2}$$

for the order parameter of the system instead of, as is traditionally done, the BCS energy gap $\Delta = -G\sum_{\mathbf{k}} \langle c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow}\rangle$ (see, for example, Refs. 16 and 17).

Furthermore, choosing $\mathcal{G}$ for the order parameter resolves some of the conceptual difficulties encountered when using Δ for the order parameter. First, when one uses a momentum-dependent pairing parameter $G_{\mathbf{k}\mathbf{k}'}$, the BCS energy gap

$$\Delta_{\mathbf{k}} = -\sum_{\mathbf{k}'} G_{\mathbf{k}\mathbf{k}'} \langle c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow}\rangle \tag{1.3}$$

is no longer a single parameter characterizing the macroscopic state of the system. $\mathcal{G}$, on the other hand, remains a single macroscopic parameter also for momentum-dependent pairing parameters. Secondly, in an exact calculation the BCS energy gap is exactly zero at both sides of the phase transition. Only within a mean-field calculation do we find that Δ is meaningful as an order parameter in that it is nonzero below the phase transition and zero above. In the thermodynamic limit the expectation value of the pairing potential $\mathcal{G}$ continues to have the expected behavior of an order parameter, even in an exact calculation. In finite systems it remains finite above the phase transition. We feel this indicates that in finite systems both phases coexist at all temperatures.

Z_{OP} has an advantage over Z_{HS} in that it can be used for pairing potentials which are not positive definite. This allows us to evaluate the partition function for Hamiltonians such as the one used in the theory of hole superconductivity proposed by Hirsch and Marsiglio.[18–20] Furthermore, we find that quantal fluctuations are negligible for the small crystallites we are considering. This leads us to believe that the results obtained using $Z_{\mathrm{OP}}(\mathcal{G})$ are a very good approximation to the exact results.

Furthermore, the Hubbard-Stratonovich transformation cannot be used for the general momentum-dependent pairing potential $G_{\mathbf{k}\mathbf{k}'}$. $Z_{\mathrm{OP}}(\mathcal{G})$, on the other hand, does not have this restriction and can be used to give a good approximation to the SPA results and, in cases where quantum fluctuations are negligible, also to the exact results.

We use two BCS-like models. First we use a constant pairing potential of unspecified origin (i.e., not necessarily mediated by phonons), and secondly we use the model of hole superconductivity proposed by Hirsch and Marsiglio.[18–20] In all calculations we include the finite-size corrections to the density of states.[5,6] We find that both the increase in the critical temperature and the sharpening of the peak in the specific heat observed during the sintering process of polycrystalline high-T_c materials[11] can be understood by taking into account finite-size effects, and in particular thermal fluctuations and finite-size corrections to the density of states. For both models we find that the specific heat curve remains below the bulk BCS curve as is experimentally observed for small conventional superconducting particles[8,9] and for Bechgaard salts.[21] Contrary to previous calculations where Δ has been used for the order parameter,[6,12] we do not reproduce the extra rise observed in the specific heat curves of polycrystalline high-T_c materials[11,10] when we use either Z_{HS} or Z_{OP} with $\mathcal{G}$ for the order parameter.

II. THE HUBBARD-STRATONOVICH REPRESENTATION OF THE PARTITION FUNCTION

Consider a system described by a BCS-like Hamiltonian (1.1) with constant attractive pairing potential $G_{\mathbf{k}\mathbf{k}'} = -G$. The grand canonical partition function for such a system is given by

$$Z(\beta, \alpha) = \mathrm{tr}\left[e^{-\beta K}\right], \tag{2.1}$$

where $\beta = \frac{1}{k_B T}$ is the inverse temperature and $\alpha = \beta\mu$ with μ the chemical potential and

$$K = H - \mu N = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} - G\mathcal{P}^{\dagger}\mathcal{P}. \tag{2.2}$$

Here $n_{\mathbf{k}\sigma} = c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}$ counts the number of electrons in the state $|\mathbf{k}\sigma\rangle$ and $\mathcal{P}$ is the pairing operator defined by

$$\mathcal{P}^{\dagger} = \sum_{\mathbf{k}} c^{\dagger}_{\mathbf{k}\uparrow} c^{\dagger}_{-\mathbf{k}\downarrow}. \tag{2.3}$$

The single-particle energies $\epsilon_{\mathbf{k}} = e_{\mathbf{k}} - \mu$ are measured relative to the chemical potential μ. Defining

$$X = \tfrac{1}{2}(\mathcal{P} + \mathcal{P}^{\dagger}), \qquad Y = \frac{i}{2}(\mathcal{P} - \mathcal{P}^{\dagger}), \tag{2.4}$$

we can write the Hamiltonian in a form suitable for the Hubbard-Stratonovich transformation[14,15,22]

$$K = K_0 - G(X^2 + Y^2), \tag{2.5}$$

with

$$K_0 = \sum_{\mathbf{k}} \left[\epsilon_{\mathbf{k}} + \left(\epsilon_{\mathbf{k}} - \frac{G}{2}\right)(n_{\mathbf{k}\uparrow} + n_{-\mathbf{k}\downarrow} - 1)\right]. \tag{2.6}$$

The exact grand canonical partition function can be written in the form of a path integral,

$$Z_{HS}(\beta, \alpha) = \lim_{M\to\infty} \left(\frac{\beta G}{\pi M}\right)^M \int \prod_{n=1}^{M} d\phi_x(t_n) d\phi_y(t_n) \times \left\{ e^{-\frac{\beta G}{M}\sum_{m=1}^{M} \phi_x^2(t_m) + \phi_y^2(t_m)} \times \mathrm{Tr}\left[\mathcal{T} e^{-\frac{\beta}{M}\sum_{m=1}^{M} K_m}\right] \right\}, \tag{2.7}$$

where $\mathcal{T}$ is the imaginary time-ordering operator, M is the number of time slices, and

$$\mathcal{K}_m = K(t_m) = K_0 - 2G[X\phi_x(t_m) + Y\phi_y(t_m)]. \tag{2.8}$$

Note that $\mathcal{K}_m$ is now only quadratic in the fermion operators, while K was quartic. Since the functions $\phi_x(t)$ and $\phi_y(t)$ are periodic with period β they may be expanded as a Fourier series[22,23]

$$\phi_x(t) = \sum_{p=-\frac{M-1}{2}}^{\frac{M-1}{2}} \eta_{xp} e^{-i\frac{2\pi p}{\beta}t}, \tag{2.9}$$

with $\eta^*_{-xp} = \eta_{xp}$, and similarly for $\phi_y(t)$. We can now write the partition function in the following form:

$$\begin{aligned} Z_{\mathrm{HS}} = \lim_{M\to\infty}\left(\frac{\beta G}{\pi}\right)^M \int d\overline{\eta}_x d\overline{\eta}_y \prod_{p=1}^{\frac{M-1}{2}} \int d\eta_{xp} d\eta_{yp} \\ \times \left\{ e^{-\beta G\left(\overline{\eta}_x^2+\overline{\eta}_y^2+\sum_{n=1}^{\frac{M-1}{2}}[\eta_{xn}^2+\eta_{yn}^2]\right)} \right. \\ \left. \times \operatorname{Tr}\left[\mathcal{T}\exp\left(-\beta\int_0^\beta \mathcal{K}(t)dt\right)\right]\right\}. \end{aligned} \tag{2.10}$$

This enables one to define various approximation schemes. In the case of the staticpath approximation (SPA) one approximates $\mathcal{K}(t)$ by its time-averaged value

$$\overline{\mathcal{K}} = K_0 - 2G[X\overline{\eta}_x + Y\overline{\eta}_y] \tag{2.11}$$

with $\overline{\eta}_x \equiv \eta_{x0}$, $\overline{\eta}_y \equiv \eta_{y0}$ and one neglects the term

$$\delta\mathcal{K}(t) = -2G\sum_{p(\neq 0)}(\eta_{xp}X + \eta_{yp}Y)e^{i\frac{2\pi p}{\beta}t}. \tag{2.12}$$

The Gaussian integrals over η_{xp} and η_{yp} can then be performed analytically. Introducing polar coordinates

$$\overline{\eta}_x = \Delta\cos(\theta), \qquad \overline{\eta}_y = \Delta\sin(\theta), \tag{2.13}$$

one obtains

$$Z_{\mathrm{HS}}^{\mathrm{SPA}}(\beta,\alpha) = \beta\int_0^\infty e^{-\beta\Omega(\Delta)}\frac{2\Delta d\Delta}{G} \tag{2.14}$$

with

$$\Omega(\Delta) = \sum_{\mathbf{k}}\left[\epsilon_{\mathbf{k}} - E_{\mathbf{k}}(\Delta) - \frac{2}{\beta}\ln\left(1 + e^{-\beta E_{\mathbf{k}}(\Delta)}\right)\right] + \frac{\Delta^2}{G}, \tag{2.15}$$

with $E_{\mathbf{k}} = \sqrt{\epsilon_{\mathbf{k}}^2 + \Delta^2}$. Note that the extremum of the integrand satisfies the BCS gap equation

$$1 = \frac{G}{2}\sum_{\mathbf{k}}\frac{1 - 2f_{\mathbf{k}}}{E_{\mathbf{k}}} \tag{2.16}$$

with

$$f_{\mathbf{k}} = \frac{1}{1 + e^{\beta E_{\mathbf{k}}}}. \tag{2.17}$$

In order to improve on the SPA one can introduce first order quantum fluctuations by treating $\delta\mathcal{K}(t)$ as a first order perturbation on $\overline{\mathcal{K}}$. The resultant expression for the partition function is

$$Z_{\mathrm{HS}}^{\mathrm{RPA\text{–}SPA}} = Z_{\mathrm{HS}}^{\mathrm{SPA}}\mathcal{Q} \tag{2.18}$$

with

$$\begin{aligned} \mathcal{Q} = \prod_{m(>0)}\left[\left(1 - \frac{\beta G}{2}\sum_k A_{km}\right)\left(1 - \frac{\beta G}{2}\sum_k B_{km}\right) \right. \\ \left. + \left(\frac{\beta G}{2}\sum_k C_{km}\right)^2\right], \end{aligned} \tag{2.19}$$

where

$$\begin{aligned} A_{km} &= \frac{Q_k^2}{S_k}\frac{\tanh(S_k/2)}{S_k^2 + \pi^2 m^2}, \\ B_{km} &= S_k\frac{\tanh(S_k/2)}{S_k^2 + \pi^2 m^2}, \\ C_{km} &= \frac{Q_k}{S_k}\frac{\tanh(S_k/2)}{S_k^2 + \pi^2 m^2 \pi m}, \end{aligned} \tag{2.20}$$

and

$$Q_k = \beta\left(\epsilon_k - \frac{G}{2}\right), \qquad S_k = \beta E_k. \tag{2.21}$$

III. THE ORDER PARAMETER REPRESENTATION OF THE PARTITION FUNCTION AND THE CHOICE OF THE ORDER PARAMETER

In the Landau theory of phase transitions one assumes that the macroscopic state of the system can be characterized by a single macroscopic parameter which is called the order parameter ξ. In the thermodynamic limit both the thermal and the quantal fluctuations approach zero and the mean-field BCS results are exact. In finite systems, however, one should include thermal fluctuations arising due to states other than the most probable state becoming accessible. Furthermore, the mean-field wave functions themselves are no longer exact, causing what are generally called quantum fluctuations. Ignoring quantum fluctuations, the isothermal probability distribution for macroscopic states characterized by the order parameter ξ is given by[17,24]

$$P(\xi) \propto e^{-\beta\Omega(\xi)} = e^{-\frac{V}{k_B T}\Omega'(\xi)}, \tag{3.1}$$

where $\Omega' = \Omega/V$ is the thermodynamic potential per unit volume of the system. Note that in the thermodynamic limit ($N \to \infty, V \to \infty, n = N/V$ finite) only the state which minimizes the thermodynamic potential has a nonzero probability. The partition function in this formalism is given by

$$Z_{\mathrm{OP}}(\beta,\alpha) = N_Z\int_0^\infty e^{-\beta\Omega(\xi)}d\xi, \tag{3.2}$$

where N_Z is the normalization constant and the thermal average of an observable is given by

$$\langle O\rangle = \frac{\int_0^\infty O(\xi)e^{-\beta\Omega(\xi)}d\xi}{\int_0^\infty e^{-\beta\Omega(\xi)}d\xi}. \tag{3.3}$$

Traditionally the order parameter for a superconducting system is chosen to be the gap parameter, defined by $\Delta = -G\sum_{\mathbf{k}}\langle c_{\mathbf{k}\uparrow}c_{-\mathbf{k}\downarrow}\rangle$ (see, for example, Refs. 16 and 17). However, for the case where the pairing potential is momentum dependent the gap parameter itself becomes momentum dependent [see Eq. (1.3)] and it is thus no longer a single parameter which can be used to define the macroscopic state of the system. Furthermore, in an exact calculation the expectation value of the gap parameter is identically zero for all temperatures.

Comparing the static path approximation of the partition function (2.7) with the order parameter representation (3.2), we are led to identify $\xi = \frac{\Delta^2}{G}$ as the order parameter. This quantity can in turn be identified as the expectation value of the pairing potential in the thermodynamic limit.

Let us therefore look at the behavior of the expectation value of the pairing potential $\mathcal{G}$ defined in Eq. (1.2). In the thermodynamic limit ($V, N \to \infty$, N/V finite) $\mathcal{G}$ has a similar behavior to that of the gap parameter Δ, i.e., it remains finite below T_c, and approaches zero at T_c. But unlike the gap parameter $\mathcal{G}$ remains a single macroscopic parameter for a momentum-dependent pairing interaction. Furthermore, it is well defined in an exact calculation. In finite systems $\mathcal{G}$ remains finite above T_c, indicating that both phases coexist at all temperatures.

Now, in order to calculate $Z_{\mathrm{OP}}(\mathcal{G})$ let us transform the Hamiltonian (1.1) into quasiparticle space

$$\begin{aligned} a_{\mathbf{k}\uparrow} &= u_{\mathbf{k}}c_{\mathbf{k}\uparrow} - v_{\mathbf{k}}c^\dagger_{-\mathbf{k}\downarrow}, \\ a_{-\mathbf{k}\downarrow} &= u_{\mathbf{k}}c_{-\mathbf{k}\downarrow} + v_{\mathbf{k}}c^\dagger_{\mathbf{k}\uparrow}. \end{aligned} \tag{3.4}$$

Here $a^\dagger_{\mathbf{k}\sigma}$ and $a_{\mathbf{k}\sigma}$ are the quasiparticle creation and annihilation operators and we have chosen the arbitrary phase factor acquired in the transformation such that $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are real. Choosing the phase factor in this way ensures that Δ is real and Δ is given the physical interpretation of an energy gap. We require further that the quasiparticles obey Fermi statistics so that $u^2_{\mathbf{k}} + v^2_{\mathbf{k}} = 1$. We can thus replace the two parameters $u_{\mathbf{k}}$, $v_{\mathbf{k}}$ by a single transformation parameter $x_{\mathbf{k}}$ defined by

$$\left.\begin{matrix} u^2_{\mathbf{k}} \\ v^2_{\mathbf{k}} \end{matrix}\right\} = \tfrac{1}{2}(1 \pm x_{\mathbf{k}}). \tag{3.5}$$

Taking the expectation value of the transformed Hamiltonian we obtain

$$\mathcal{E} = 2\sum_{\mathbf{k}}\epsilon_{\mathbf{k}}\rho_{\mathbf{k}} + \mathcal{G} \tag{3.6}$$

with

$$\mathcal{G} = \sum_{\mathbf{k}\mathbf{k}'}G_{\mathbf{k}\mathbf{k}'}\tau^*_{\mathbf{k}}\tau_{\mathbf{k}'} + \sum_{\mathbf{k}}G_{\mathbf{k}\mathbf{k}}\rho^2_{\mathbf{k}}, \tag{3.7}$$

where $\rho_{\mathbf{k}}$ is the single-particle density

$$\rho_{\mathbf{k}} = \langle c^\dagger_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}\rangle = \tfrac{1}{2}[1 - x_{\mathbf{k}}(1 - 2f_{\mathbf{k}})] \tag{3.8}$$

with $f_{\mathbf{k}} \equiv \langle a^\dagger_{\mathbf{k}\uparrow}a_{\mathbf{k}\uparrow}\rangle = \langle a^\dagger_{-\mathbf{k}\downarrow}a_{-\mathbf{k}\downarrow}\rangle$, and $\tau_{\mathbf{k}}$ is the pairing tensor defined by

$$\tau_{\mathbf{k}} = \langle c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}\rangle = \tfrac{1}{2}\sqrt{1 - x^2_{\mathbf{k}}}(1 - 2f_{\mathbf{k}}). \tag{3.9}$$

In the thermodynamic limit the second term in Eq. (3.7) is exactly zero and for a constant pairing potential G we have $\mathcal{G} = \frac{\Delta^2}{G}$. Consequently both $\mathcal{G}$ and Δ are in the thermodynamic limit finite below T_c and zero above T_c. For finite systems both terms in Eq. (3.7) have to be considered, resulting in $\mathcal{G}$ being nonzero above the phase transition.

In order to calculate the partition function as a function of $\mathcal{G}$ we minimize the free energy $F = \mathcal{E} - TS$ for each value of $\mathcal{G}$ with respect to the transformation parameters $x_{\mathbf{k}}$, subject to the constraints that the expectation value of the pairing potential is given by (3.7) and that the number of particles is given by $\mathcal{N}$,

$$\mathcal{N} = \langle N\rangle = 2\sum_{\mathbf{k}}\rho_{\mathbf{k}}. \tag{3.10}$$

Let

$$F' = F - \mu\langle N\rangle - \lambda\mathcal{G} \tag{3.11}$$

with λ and μ Lagrange multipliers for the constraints (3.7) and (3.10) respectively. Since $\frac{dF'}{dx_{\mathbf{k}}} = \frac{\partial F'}{\partial x_{\mathbf{k}}} + \frac{\partial F'}{\partial f_{\mathbf{k}}}\frac{df_{\mathbf{k}}}{dx_{\mathbf{k}}}$, F' has a minimum (and we assume in what follows that it is a global minimum) where both $\frac{\partial F'}{\partial x_{\mathbf{k}}} = 0$ and $\frac{\partial F'}{\partial f_{\mathbf{k}}} = 0$. We obtain

$$\begin{aligned} x_{\mathbf{k}} &= \frac{\epsilon'_{\mathbf{k}}}{\sqrt{\epsilon'^2_{\mathbf{k}} + \Delta'^2}}, \\ \epsilon'_{\mathbf{k}} &= \epsilon_{\mathbf{k}} - \frac{G_{\mathbf{k}\mathbf{k}'}}{2}(1 + \lambda)\rho_{\mathbf{k}}, \\ \Delta'_{\mathbf{k}} &= (1 + \lambda)\sum_{\mathbf{k}'}G_{\mathbf{k}\mathbf{k}'}\tau_{\mathbf{k}'}, \end{aligned} \tag{3.12}$$

and

$$f_{\mathbf{k}} = \frac{1}{1 + \exp(\beta\sqrt{\epsilon'^2_{\mathbf{k}} + \Delta'^2})}. \tag{3.13}$$

After solving the coupled set of equations (3.7), (3.10), and (3.12) simultaneously for Δ', μ, and λ for each value of $\mathcal{G}$, we can calculate the thermodynamic potential $\Omega(\mathcal{G}) = F - \mu\mathcal{N}$ and hence the partition function using Eq. (3.2)

IV. APPLICATION TO POLYCRYSTALLINE HIGH-T_c MATERIALS

Since the individual grains of sintered polycrystalline high-T_c materials are only very weakly linked (the critical current in these materials is about two orders of magnitude lower than in large single crystals[2]) we treat, as a first approximation, the individual crystallites as isolated from each other.[6] No attempt is made to model the tunneling current between the grains. Furthermore, the supercurrent in these materials seems to be confined (except for tunneling) to the Cu-O planes.[3] In our simple model we consider a small superconducting system with two dimensions determined by the average grain size and the third dimension by the approximate height of the Cu-O planes.

We consequently introduce the following finite-size effects. First, in finite systems at finite temperature, states other than the most probable state (i.e., the state that minimizes the free energy) become accessible to the system, resulting in thermal fluctuations. Thermal fluctuations are especially important for granular high-T_c materials, not only because bulk materials are usually granular, but also since their critical temperature is much higher and their carrier density much lower than in conventional superconducting materials. Secondly, in small systems the mean-field wave functions are no longer exact. This introduces what are commonly called quantum fluctuations. Including quantum fluctuations as a first order perturbation around $Z_{\rm HS}^{\rm SPA}$ we find that their contribution is negligible for the superconducting grains. Thirdly, when evaluating the partition function for small systems one should in principle replace the integral over the density of states by a sum over the single-particle states. However, for particles of the size of the superconducting grains the number of states is still very large and performing the sum is computationally expensive. Instead we use a geometric correction to the density of states.[25,5] Since the current between the grains is only a small tunneling current, we feel that Dirichlet boundary conditions yield a good approximation to the true boundary conditions. The resulting expression for the density of states is

$$g(k) = \left[1 - \frac{\pi A}{4kV} + \frac{\pi L}{4k^2V}\right] g_{\rm TL}(k), \qquad (4.1)$$

where $g_{\rm TL}(k)$ is the density of states in the thermodynamic limit and V, A, and L are the volume, surface, and length parameters for the small superconducting grain. Using geometry fixes the number of particles.

The remaining question is the choice of the Hamiltonian. It seems doubtful that a standard BCS model will be applicable to high-T_c materials since the phonon barrier seems to limit the critical temperature to below 40 K. However, various authors[26,27,18–20] have shown that a BCS-like model, where the pairing need not necessarily be mediated by phonons, might still be valid for the high-T_c materials. This led us to perform the calculations using two BCS-like models. First we used a constant pairing potential of unknown origin and, in order to see whether the momentum dependence of the pairing potential would make any difference in the finite-size effects, we performed the calculations using the model of hole superconductivity.[18–20] We found, however, that the results are qualitatively identical. The figures below show the results obtained with a constant pairing potential.

In Fig. 1 we compare the BCS specific heat curve with the curves obtained using $Z_{\rm HS}^{\rm SPA}$, $Z_{\rm OP}(\Delta)$, and $Z_{\rm OP}(\mathcal{G})$ for the geometries 3 Å×(2000 Å)^2 and 3 Å×(500 Å)^2. The effect of quantum fluctuations was found to be in both cases less than 0.5% and is thus not shown. Note that $Z_{\rm OP}(\mathcal{G})$ approximates $Z_{\rm HS}^{\rm SPA}$ very well indeed while the behavior of $Z_{\rm OP}(\Delta)$ is qualitatively and quantitatively different. For $Z_{\rm OP}(\Delta)$ we observe close to the transition temperature a rise above the BCS peak. This behavior is

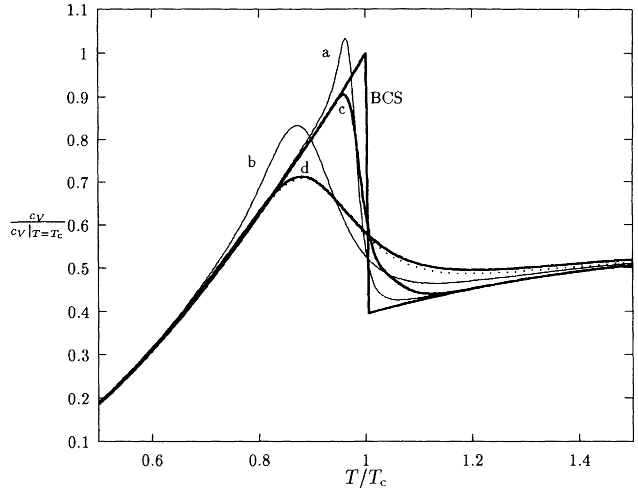

FIG. 1. The specific heat as a function of temperature. The thick solid line labeled BCS is the mean-field BCS result, the two thin solid lines labeled a and b give the result obtained when one uses Δ for the order parameter, a for a particle of size 3 Å× (2000 Å)^2 and b for 3 Å× (500 Å)^2. The two thick solid lines labeled c and d give the result obtained when one uses $\mathcal{G}$ for the order parameter, c for a particle of size 3 Å× (2000 Å)^2 and d for 3 Å× (500 Å)^2. The dotted line gives the SPA result for a particle of size 3 Å× (500 Å)^2. Quantum fluctuations make no visible contribution for both sizes and the SPA result coincides with the result obtained using $Z_{\rm OP}(\mathcal{G})$ for particles of size 3 Å× (2000 Å)^2.

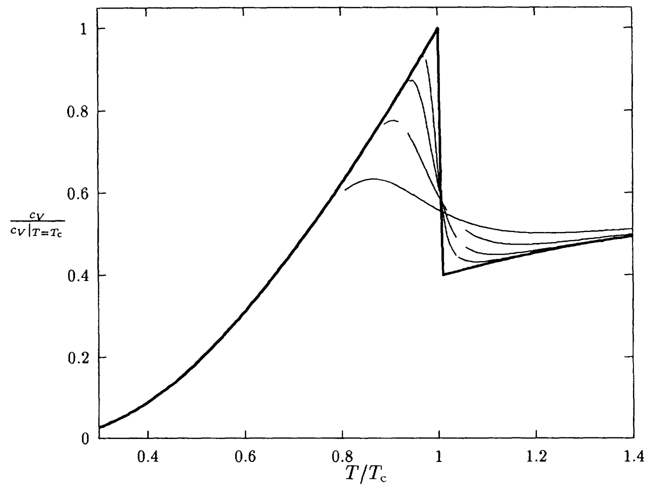

FIG. 2. The specific heat as a function of temperature calculated using $\mathcal{G}$ for the order parameter. The thick solid line gives the result for the thermodynamic limit which coincides with the mean-field BCS result. The thin solid lines are for the geometries 6 Å× (2000 Å)^2, 6 Å× (1000 Å)^2, 6 Å× (500 Å)^2, and 6 Å× (250 Å)^2, respectively. The peak in the specific heat flattens with decreasing crystal size. Note that, contrary to calculations done using Δ for the order parameter, the specific heat curve for $T < T_c$ remains below the BCS curve for all sizes.

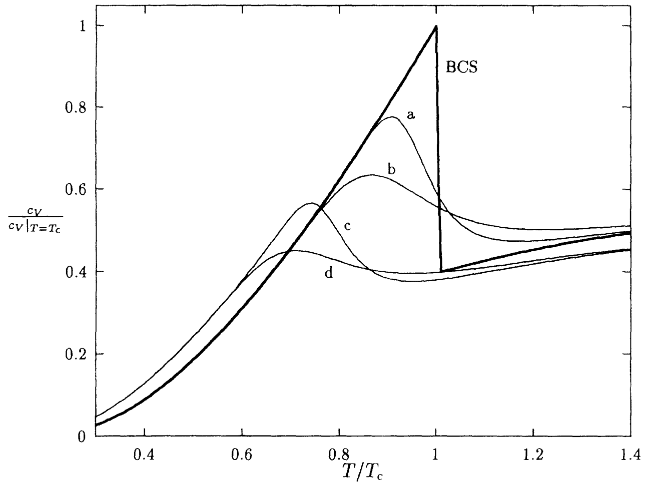

FIG. 3. The specific heat as a function of temperature calculated using $\mathcal{G}$ for the order parameter and including finite-size corrections to the density of states. The thick solid line is the mean-field BCS result, the curves labeled a and b are calculated without finite-size corrections to the density of states, while the curves labeled c and d are calculated by taking into account finite-size corrections to the density of states. Curves a and c are for the geometry 6 Å× (500 Å)^2 while curves b and d are for 6 Å× (250 Å)^2.

indeed observed in polycrystalline high-T_c materials.[10,11] However, we feel that this result is a coincidence arising from the inconsistent choice of the order parameter. One should either use the expectation value of the pairing potential $\mathcal{G}$ for the order parameter or alternatively use the Hubbard-Stratonovich representation of the partition function where the concept of an order parameter is not required.

Figure 2 shows the specific heat as a function of temperature for various grain sizes. The calculations were done using the order parameter representation of the partition function with $\mathcal{G}$ for the order parameter. Note that the specific heat curves remain below the BCS curve for all sizes and for all temperatures $T < T_c$.

In Fig. 3 we see that the effect of the finite-size corrections to the density of states is to lower both the critical temperature and the peak in the specific heat. Note that for the planes to which the supercurrent is confined we have

$$\frac{A}{V} = \frac{2[a^2 + 2ah]}{a^2 h} \simeq \frac{2}{h} \quad \text{for} \quad h \ll a. \tag{4.2}$$

Here h is the height of the plane determined by the Cu-O planes while a is the average side length of the crystallites. In other words the leading term of the finite-size corrections to the density of states is virtually independent of the crystal size.

V. CONCLUSIONS

Comparing the analytical expression for the partition function in the static path approximation of the Hubbard-Stratonovich representation $Z_{\rm HS}^{\rm SPA}$ with that of the order parameter representation $Z_{\rm OP}$ we infer that the expectation value of the pairing potential $\mathcal{G}$ and not the BCS energy gap Δ should be used for the order parameter of a superconducting system described by a BCS-like Hamiltonian. Numerically we have found that the specific heat curves obtained using $Z_{\rm OP}(\mathcal{G})$ are indeed a very good approximation to $Z_{\rm HS}^{\rm SPA}$, while the specific heat curves obtained using $Z_{\rm OP}(\Delta)$ differ significantly.

First order quantum fluctuations were found to be negligible for the superconducting grains and we believe that $Z_{\rm OP}(\mathcal{G})$ gives a good approximation to the exact result. One can thus use either $Z_{\rm HS}$ or $Z_{\rm OP}(\mathcal{G})$ and the choice depends on the particular application since both representations have advantages and disadvantages. The advantages of $Z_{\rm HS}$ can be summarized as follows.

(1) It is an exact representation of the partition function which can be calculated in various well defined approximation schemes (SPA, RPA-SPA, etc.).

(2) For a constant pairing potential it is computationally less demanding than $Z_{\rm OP}$.

(3) Quantum fluctuations can be included.

$Z_{\rm OP}$ has the following advantages.

(1) It is not restricted to pairing potentials which are positive definite.

(2) It can be used for general momentum-dependent pairing potentials.

(3) It introduces the concept of a macroscopic order parameter.

Applying the formalism to polycrystalline high-T_c materials, we found that the specific heat curves obtained using $Z_{\rm OP}(\Delta)$ have a similar structure to those observed experimentally in polycrystalline high-T_c materials in that they have an anomaly rising above the BCS peak. This behavior is not observed when one uses either $Z_{\rm HS}$ or $Z_{\rm OP}(\mathcal{G})$. We feel, however, that this is a coincidence arising from the use of an inconsistent order parameter. In small conventional superconductors, to which the theory should apply, this behavior is not seen; the structure of the specific heat curves in conventional superconducting grains closely resembles that obtained using either $Z_{\rm HS}$ or $Z_{\rm OP}(\mathcal{G})$.

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