# Superconducting phase transitions in granular systems

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We consider a model for granular superconductors consisting of an array of small superconducting particles interacting by Josephson coupling through insulating barriers. We obtain systematically the various critical regions, critical temperature shifts, and crossover regions between zero- and three-dimensional behavior as functions of measurable sample parameters. The qualitative behavior of the system in the various regimes is analyzed and results for the specific heat and fluctuation conductivity in the Gaussian region above $T_c$ are obtained. The possibility of obtaining large critical regions is emphasized. The conditions for observing the phase-locking transition distinct from quasiordering within the grains are found. Theoretical predictions are compared with existing experimental results.

## I. INTRODUCTION

The physics of small superconducting particles has recently attracted considerable attention. The behavior of isolated, so-called zero-dimensional (0-D), particles is quite well understood theoretically, at least insofar as their size is not in the microscopic limit.[1-3] The predictions[2] for the magnetic behavior have recently received a beautiful experimental confirmation.[4] However, our understanding of systems that are composed of small and weakly coupled particles is of a rather preliminary nature. The reason for the interest in such systems is that by varying both the particle size and the interparticle coupling one may span a very wide range of physically interesting situations. In particular, the crossover between 0-D and 3-D (or 2-D for thin films) critical behaviors may be systematically studied. Recent theories[5,6] have emphasized the dependence of the critical behavior on the dimensionality of the system, and the importance of understanding the crossover between different dimensionalities. Furthermore, there is evidence that the systems under consideration can be realized experimentally with grain sizes and inter-grain couplings kept under control.[7-11] One can therefore hope that theoretical predictions may be directly checked by experiment.

The calculations that we present here are a development of two preliminary notes[12,13] where the basic physical ideas and the relevant model were presented. Here we emphasize the similarity of our model, based on Landau-Ginzburg theory for the grains and Josephson coupling[14] among the grains, to modern general models for critical behavior.[5] In fact, the granular systems appear to be a physical discrete realization of the field-theoretical models used by Wilson[5] and others, with widely varying ranges of the parameters. In this paper we do not emphasize the critical behavior (e.g. the values of critical indices), we focus our attention on questions like what are the magnitudes of the various regions and shifts of the critical temperature due to fluctuations,[15,16] and what determines whether the system is 0-D or 3-D. These questions will be dealt with in Sec. II and III. It will turn out that, from the theoretical point of view, the discussion presents a number of relevant cutoff problems, our answers for which can be checked experimentally. The most relevant result is perhaps that we compute the critical region as a function of measurable quantities and show that one can easily make it large enough to be experimentally accessible for a superconducting system. We also discuss the possibility of two distinct transitions[17] and give well-defined criteria for its occurrence. In Sec. IV we calculate the specific heat and the paraconductivity in the Gaussian regime and discuss the 3-D to 0-D crossover. Section V is devoted to a summary and to some concluding remarks.

## II. THE MODEL, CORRELATION LENGTHS, AND THE VARIOUS TEMPERATURE REGIONS

Our model (see Fig. 1) for the granular system has the following[13] free energy as a function of the order parameters of the grains, $\psi_i$:

$$F=\sum_i V_i\left(a|\psi_i|^2+\tfrac{1}{2}b|\psi_i|^4\right)+\frac{1}{2}\sum_{\langle i,j\rangle}C_{ij}|\psi_i-\psi_j|^2\,, \quad (1)$$

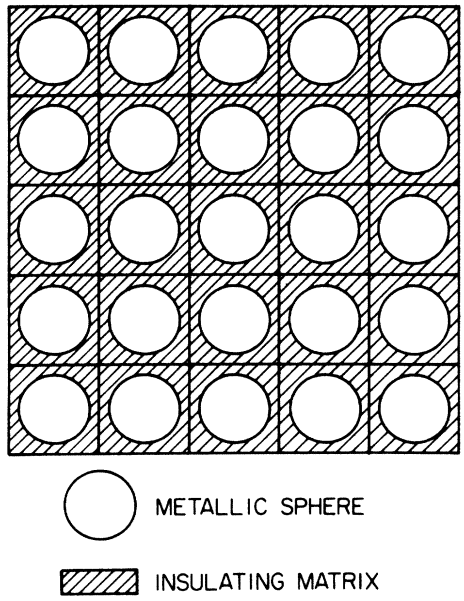


FIG. 1. Model for granular systems: a lattice of metallic spheres embedded in an insulating matrix.

where the last term, operating only between nearest-neighbor grains, is a Josephson-type coupling among the grains,[13] $V_i$ is the volume of the $i$th grain, and $a$ and $b$ are the usual Landau-Ginzburg coefficients characterizing the grain material, including some $T_c$ renormalizations due to surface effects, dielectric barriers, etc. but no fluctuation effects, $a=\bar{a}(T-T_c^0)/T_c^0\equiv\bar{a}t$ with $t$ the usual reduced temperature, $\bar{a}=N(0)$, the electronic density of states at the Fermi level, and $b=0.106N(0)(k_BT_c^0)^{-2}$. For simplicity, we take the grains to be equivalent, and to form a cubic lattice of $N$ lattice points with a lattice constant $d$ so that $V_i=V\sim d^3$ and $C_{ij}=C$. We shall consider the case where the lattice is 3-D; the 2-D case, relevant to thin films of large grains, can be similarly discussed. We notice that the model (1) looks like a discrete version of, e.g., Wilson's field-theoretic $x$-$y$ (or $n=2$) like model,

$$F_W=\int d\vec{x}\left[a|\psi(x)|^2+\tfrac{1}{2}b|\psi(x)|^4+c|\nabla\psi|^2\right], \qquad (2)$$

with $c\sim C/d$.

As long as the Gaussian approximation holds, one can calculate easily the order-parameter correlation function (using a normal-mode transformation for the "harmonic" model[13]). This yields the familiar $(k^2+\xi^{-2})^{-1}$ form for the Fourier transform of the correlation function, which is thus of the Ornstein-Zernicke type and is characterized by a correlation length $\xi(T)$, where

$$\xi(T)^2=\begin{cases} C/da & \text{for } T>T_c^0, \\ -C/2da & \text{for } T<T_c^0. \end{cases} \qquad (3)$$

Note that although this correlation length has the same temperature dependence as the superconducting Ginzburg-Landau (GL) correlation length $\xi_{GL}(T)=\xi_{GL}(0)t^{-1/2}$, its magnitude is very different, and it is typically much smaller than $\xi_{GL}(T)$. $\xi_{GL}(0)$ is on the order of the coherence length $\xi_0$ for clean materials, and $(\xi_0 l)^{1/2}$ for dirty ($l\ll\xi_0$ where $l$ is the electronic mean free path) materials. Here $l$ refers to the mean-free-path characteristic of the material of a single grain. We shall assume throughout this article that $\xi_{GL}(T)\gg d$. This is the condition for a separate grain to be zero-dimensional (0-D), so that the order parameter is approximately uniform within each grain, as is assumed in Eq. (1). The correlation length, Eq. (3), can be shown to be of the same order of magnitude as that found in Refs. 7, 10, and 14 from entirely different considerations (which led, for $\tau\ll1$, to $\xi(0)^2\sim\xi_0 l_{eff}$, with $l_{eff}=d\tau$, $\tau$ is the transmission coefficient of the barrier, $C\propto\tau$).

Let us now characterize the strength of the coupling $C$ in terms of the ratio between $\xi(T=0)$ and $d$ by introducing the following terminology. We shall refer to our system as being "strongly coupled" or "weakly coupled" according to whether $\xi(0)\gg d$ or $\xi(0)\ll d$ which is equivalent to whether

$$C\gg|\bar{a}|V \text{ or } C\ll|\bar{a}|V, \qquad (4)$$

respectively. Furthermore, as long as $\xi(T)\gg d$, the sample will be referred to as 3-D, while if $\xi(T)\ll d$, the grains are decoupled, and the system will be referred to as 0-D. Clearly, a strongly coupled system will be 3-D for any $T<T_c$ and for a large temperature region above $T_c$. A weakly coupled system will become 3-D, in the Gaussian approximation above $T_c$ [wherein $|\psi|^4$ in (1) is neglected], close enough to $T_c$, once $|t|\ll t_t$ where

$$t_t=C/\bar{a}V. \qquad (5)$$

The estimate (5) will be valid, however, only if $t_t\gg t_g$ where $t_g$ is the critical region[15,16] inside which the Gaussian approximation breaks down.

The size of the critical region, $t_g$, depends strongly on the physical range of the parameters of the system. For the 0-D case[1-3] the Gaussian approximation for a single grain breaks down inside the critical region $t_{g0}$, where[1-3]

$$t_{g0}=\left(\frac{1}{N(0)kT_c^0d^3}\right)^{1/2}=\left(\frac{d_0}{d}\right)^{3/2}. \qquad (6)$$

This defines a characteristic length $d_0=(1/N(0)kT_c^0)^{1/3}$ where large grains ($d\gg d_0$) will have $t_{g0}\ll1$ and in small grains ($d\lesssim d_0$, $t_{g0}\gtrsim1$) size effects are so important as to completely smear out the superconducting transition for a single grain. $d_0$ is of the order of magnitude of 30 Å for typical metals ($k_F\sim2$ Å$^{-1}$, $T_c^0\sim1$ °K). For the 3-D case,

the situation is more complicated. As long as $\xi(0) \gg d$ (strong coupling), we are allowed[15,16] to use the Ginzburg criterion, which yields, in 3-D:

$$t_{g3} = \left(\frac{kT_c b}{\bar{a}^2 \xi(0)^3}\right)^2 = \frac{(kT_c b)^2 V}{\bar{a} C^3} \quad . \tag{7}$$

For the weak-coupling case we are on much shakier theoretical grounds. The Ginzburg criterion employs a $1/\xi(T)$ cutoff on $k$-space summations. This cutoff was justified[16] only for $\xi(0) \gg d$. For weak coupling $[\xi(0) \ll d]$, a necessary condition for the relevance of the $1/\xi(T)$ cutoff is that $\xi(T) \gg d$ at $t_g$. Making the physically plausible assumption that this is the relevant condition[16] for the validity of (7), it is equivalent to the condition that at $t_{g3}$ the system is 3-D, or that

$$t_t \gg t_{g3} \text{ or } C^2 \gg kT_c bV \, . \tag{8}$$

Note that (8) is also the condition for the validity of the estimate (5) for $t_t$. From (5), (7), and (8) we find that the weak coupling range, where (8) is valid is

$$(\bar{a} V)^2 \gg C^2 \gg kT_c bV \, . \tag{9}$$

By (6), a range like this will exist only for large grains ($t_{g0} \ll 1$). For small grains, $kT_c bV \gg (\bar{a} V)^2$. If they are strongly coupled, we can use the Ginzburg criterion (7) anyway, as discussed below. If the small grains are weakly coupled, then the inequality $t_t \gg t_g$, as well as our estimates (5) and (7), do not hold. We shall return to this case after the discussion of $T_c$ shifts.

It should be kept in mind that the above estimates for the critical region $t_g$ are valid[15,16] with $t$ being defined with respect to the true transition temperature $T_c < T_c^0$ (renormalized by fluctuation effects). We shall now estimate this $T_c$ shift, $t_s \equiv (T_c^0 - T_c)/T_c^0$. According to Hohenberg[15(b)] it appears that this may be estimated for $\xi(0) \gg d$, by calculating the fluctuation $\langle |\psi|^2 \rangle$ in the Gaussian approximation and equating it to $|a|/b$, where a cutoff $1/\xi(0)$ is employed for $\sum_k \langle |\psi_k|^2 \rangle$. This yields

$$t_s \cong \frac{kT_c b}{\bar{a}^2 \xi(0)^3} = \frac{kT_c b d^{3/2}}{\bar{a}^{1/2} C^{3/2}} = t_{g3}^{1/2} \quad . \tag{10}$$

This calculation does not apply in the weak-coupling case. Since there $1/d \ll 1/\xi(0)$, a reasonable assumption is to repeat the above calculation using $1/d$ as a cutoff. This yields

$$t_s \sim \frac{kT_c b}{\bar{a}^2 \xi(0)^2 d} = \frac{k_B T_c b}{C\bar{a}} \sim \frac{1}{C k_B T_c} \quad . \tag{11}$$

For $t_{g0} \ll t_s \ll 1$, one can also arrive at the same order of magnitude as the result (11) from a molecular field or from a Bethe[17] type approximation on (1), noticing that the single grain terms constrain $\psi$ to be a temperature-dependent "spin" with a coupling $C$. The inaccuracy of the molecular field $T_c$ can only multiply (11) by an $O(1)$ factor. Thus, at least for $t_{g0} \ll t_s \ll 1$ the result (11) is valid. In the case $1 > t_s \gg t_{g0}$ the situation is of a great interest since the system would appear to show two transitions[17]: a strict phase transition at $T_c$, and a smeared quasitransition around $T_c^0$, whose width, however, is much less than $T_c^0 - T_c$. Thus the two transitions are quite distinct. The condition $t_s \gg t_{g0}$ is

$$C^2 \ll kT_c bV \, , \tag{12}$$

which we recognize as the opposite inequality to the one in (8). One important consequence of the above results is that for weakly coupled small grains $C^2 \ll kT_c bV$ and therefore $t_s \gg t_{g0}$. Now, the small grains have $t_{g0} \gtrsim 1$. This implies that $t_s \gg 1$. It should be kept in mind however that all the critical regions and shifts we are considering are meaningful only insofar as they are smaller than unity. Thus it would follow that in this case the system would either not order at all, or order at a temperature much lower than $T_c$.

## III. ENUMERATION OF THE VARIOUS REGIMES FOR A GRANULAR SYSTEM

We would like now to obtain systematically the various ratios among the parameters $t_{g0}$, $t_t$, $t_s$, and $t_{g3}$ in the weak-coupling case. In the strong-coupling case the situation is simpler, and we shall return to it later. Assuming Eq. (9) to be valid, which justifies our estimates (5) and (7) for the weak-coupling case and denoting

$$t_t / t_{g0} = \alpha = (C^2 / 2bVkT_c)^{1/2} \, , \tag{13a}$$

we find

$$\frac{t_t}{t_{g3}} = \alpha^4 \, , \quad \frac{t_s}{t_{g0}} = \alpha^{-1} \, , \quad \text{and} \quad \frac{t_{g3}}{t_{g0}} = \alpha^{-3} \, . \tag{13b}$$

If Eq. (9) holds, it follows from it that $t_t / t_{g3} \gg 1$ and $\alpha \gg 1$, which implies $t_t \gg t_{g0} \gg t_s \gg t_{g3}$. This means that the 0-D Gaussian system will become 3-D Gaussian at $t_t$, then it will become 3-D critical at $t_{g3}$. It will never become 0-D critical.

In the case $\alpha \ll 1$ our expressions (5) for $t_t$ and (7) for $t_{g3}$ do not hold. Then, for the interesting case of large grains we expect the system to complete its 0-D quasitransition before it makes the 3-D transition. For this to be valid we would also like $t_t \ll t_s$ so that the system will stay 0-D throughout the 0-D critical region. We note that the only relevant cutoff in $k$ space is $1/d$ in this case, which means $t_s \cong t_{g3}$; and since $t_t \ll t_{g3}$, we shall also have $t_t \ll t_s$. Also, in this case it will turn out for the large-grain situation that the magnitude of $t_t$ will be of interest. This can be estimated as follows. At $T_c^0$, which is just around the edge of the

critical region, the correlation length is given both by $\xi(0)/t_s^{1/2}$ using the Gaussian expression, and by $\xi_0^*/t_s^{\nu}$ using the "critical" expression,[6] where $\nu$ is the critical index for the correlation length and $\xi_0^*$ a constant with the dimension of length. This determines that $\xi_0^* \sim \xi(0) t_s^{\nu-1/2}$. Now at $t_t$, $\xi(T) \sim d$, which implies

$$t_t \sim \left(\frac{\xi_0^*}{d}\right)^{1/\nu} \sim \left(\frac{\xi(0)}{d}\right)^{1/\nu} \left(\frac{k T_c b}{C\bar{a}}\right)^{(2\nu-1)/2\nu} , \quad (14)$$

where we used the strong-coupling expression (11) for $t_s$. Note that in this case $t_t \propto C^{1/\nu-1}$. We emphasize that to get (13) we used the Gaussian approximation around $T_c$, the justification for which is less clear here than in the case $\alpha > 1$.

We shall now express our theoretical parameters in terms of measurable quantities and give some illustrative orders of magnitude. $C$ is given in terms of the junction normal resistance $R_n$ by[18] ($R_n^{-1}$ is also proportional to the transmission coefficient of the barrier, $\tau$):

$$C = \frac{\pi\hbar}{16 e^2 R_n k_B T_c} \cong \frac{10^3}{R_n[\Omega] k_B T_c} , \quad (15)$$

where $R_n[\Omega]$ means $R_n$ measured in ohms. There are two relevant orders of magnitude for $R_n$. The first, which we call $R_1$, separates the weak- from the strong-coupling regime and is given by $C(R_1) = \bar{a}V$, thus

$$R_1[\Omega] \cong \frac{1.5\times 10^3}{k_B T_c N(0) V} \cong \frac{3\times 10^4 E_F/k_B T_c^0}{V k_F^3} \sim \frac{10^9}{V k_F^3} , \quad (16)$$

where we used $\bar{a} = N(0)$ for the first equality and a free-electron picture for the second one. $R_1$ ranges from $\sim 10^4$–$10^5\ \Omega$ for $d \sim 30$ Å to $\sim 0.1$–$1\ \Omega$ for $d \sim 1000$ Å. The corresponding resistivity is $\rho_1 \sim R_1 d$, or $\rho_1[\Omega\,\mathrm{cm}] \sim B/d^2$ with $B \sim 1$–$10$, where $d$ is measured in Å. The second resistance value, $R_2$, is the one for which $t_t \sim t_{g3}$ or $\alpha \sim 1$; i.e., for $R_n < R_2$ the system becomes 3-D outside of the 3-D critical region. $R_2$ is given by $C^2(R_2) = k T_c b V$; using (15) we find

$$\rho_2 \cong \rho_1 [3 k_B T_c N(0) V]^{1/2} \sim \rho_1 (d/d_0)^{3/2} \sim \rho_1 / t_{g0} , \quad (17)$$

where $d_0$ [cf. Eq. (6)] is the order of magnitude of the length distinguishing between large and small grains.

For convenience we express below the various critical regions, etc., in terms of the resistance $R_n$ and the grain size $d$. Equations (5), (7), (10), and (11) are respectively rewritten ignoring $O(1)$ numerical constants as

$$t_t \sim R_1/R_n , \quad (5')$$

$$t_{g3} \sim \left(\frac{R_n}{R_2}\right)^3 \left(\frac{d_0}{d}\right)^{3/2} \sim \left(\frac{R_n}{R_2}\right)^3 t_{g0} \sim \left(\frac{R_n}{R_1}\right)^3 t_{g0}^4 , \quad (7')$$

$$t_s \sim t_{g3}^{1/2} \sim \left(\frac{R_n}{R_1}\right)^{3/2} \left(\frac{d_0}{d}\right)^3 , \quad \text{for } R_n \ll R_1 \quad (10')$$

$$t_s \sim \left(\frac{R_n}{R_2}\right)^2 \frac{R_1}{R_n} = \frac{R_n}{R_2} \left(\frac{d_0}{d}\right)^{3/2} \sim \frac{R_n e^2}{\hbar} \quad \text{for } R_n \gg R_1 . \quad (11')$$

The parameter $\alpha$ [cf. Eq. (13a)] is simply given by

$$\alpha = R_2/R_n . \quad (18)$$

We can now completely characterize the qualitative behavior of the various regimes of the granular systems as follows:

*a. Large grains* ($d \gg d_0 \sim 30$ Å), $\rho_2 \gg \rho_1$. For $\rho_n \gg \rho_2$: Two transitions; the shift given by Eq. (11′). For $\rho_1 \ll \rho_n \ll \rho_2$: A single transition; $t_s$, $t_t$, and $t_g$ are given, respectively, by (11′), (5′), and (7′), with $t_t \gg t_{g0} \gg t_{g3}$. For $\rho_n \ll \rho_1$: Strong coupling, 3-D system, $t_s$ given by (10′), $t_{g3}$ by (7′).

*b. Small grains* ($d \ll d_0 \sim 30$ Å), $\rho_2 \ll \rho_1$. For $\rho_n \gg \rho_1$: Superconductivity either does not exist or it exists only at very low temperatures ($T_c \ll T_c^0$). For $\rho_2 \ll \rho_n \ll \rho_1$: Equations (5′) and (7′) are inapplicable but Eq. (10′) holds for the $T_c$ shift. For $\rho_n \ll \rho_2$: Equations (5′), (7′), and (10′) are applicable, $t_t \gg t_g$.

The case $d \sim d_0 \sim 30$ Å is also of interest. Here $\rho_2 \cong \rho_1$ and the region $\rho_2 \ll \rho_n \ll \rho_1$ does not exist.

To analyze the case of small grains, we note that for $\rho_n \ll \rho_2$ we get for the shift from Eq. (10′) that $t_s$ becomes of $O(1)$ for $\rho_n \sim \rho_1 (d_0/d)^{6/5}$. This is on the order of $10^{-2}$–$10^{-3}\ \Omega$ cm for $d \sim 20$ Å, in qualitative agreement with the results of Ref. 8. In the case where $t_s < 1$, we predict a critical region proportional to $R_n^3$, which is in a fair agreement with the experimental results of Ref. 8. Another result that follows from Eq. (7′) is that for $d \sim 30$ Å, $t_{g3}$ will be of $O(1)$ once $\rho \sim \rho_2$, again in a fair agreement with experiment.[8]

A further important order of magnitude for $R_n$ occurs when it is low enough such that $\xi(T)$ in the 3-D regime is of the same order of magnitude as the coherence length of the clean superconducting material. For this we need

$$C/d \cong N(0)\xi_0^2 \quad (19)$$

which yields, using (15),

$$\rho_n = \frac{\pi\hbar}{8 e^2 k_B T_c N(0) \xi_0^2} \sim \frac{\hbar}{e^2 k_F^2 \xi_0} \sim \frac{10^3}{k_F^2 \xi_0}\ \Omega\,\mathrm{cm} .$$

This is independent of $d$, and on the order of magnitude of $\sim 10^{-7}\ \Omega$ cm, similar to the resistivity

of a simple normal metal with a mean free path equal to $\xi_0$ (which is, roughly, $\sim \hbar/k_F^2 e^2 \xi_0$). In such a way the "3-D" system approaches, when $R_n$ is so low that (19) holds, the clean continuum limit. Replacing $\xi_0^2$ in Eq. 19 by $\xi_0 l$ (where $l$ is the sample mean free path, assuming $l \ll \xi_0$) will similarly yield the dirty continuum limit. A complete discussion of these questions, which depends both on intrinsic properties of the grain material and on the properties of the barrier, is beyond the scope of this paper.

## IV. THE SPECIFIC HEAT AND PARACONDUCTIVITY IN THE GAUSSIAN APPROXIMATION

In this section we evaluate the specific heat and paraconductivity in the Gaussian approximation (or outside of the critical region) above $T_c$. We assume $R \ll R_2$ so that the 0-D to 3-D crossover occurs in the Gaussian regime. Here the quartic terms in (1) can be neglected and what remains is diagonalized[13] by a normal-mode transformation in the same way as for a harmonic lattice. Denoting the normal modes by $q_k$ and the eigenfrequencies by $\omega_k$ (Ref. 13) ($\omega_k^2 \cong aV + s^2 k^2$, $s^2 = 2Cd^2$ for $k \ll \pi/d$), we find for the partition function [with $\beta \equiv (k_B T)^{-1}$]

$$Q = \int \prod_k dq_k e^{-\beta \omega_k^2 |q_k|^2} = \prod_k \frac{1}{(\beta\omega_k^2)^{1/2}} \times \text{const.} \qquad (20)$$

From this, we can evaluate the specific heat per unit volume

$$c(T) = \frac{k_B \partial}{VN\partial T}\left(T^2 \frac{\partial \ln Q}{\partial T}\right) = \frac{k_B}{2NV}\sum_k \left(1 - \frac{2\bar{a}V}{\omega_k^2}\frac{T}{T_c} + \frac{(\bar{a}V)^2 T^2}{\omega_k^4 T_c^2}\right); \qquad (21)$$

one is easily convinced that the important term for the leading singularity in $c(T)$ is the last one. To compute $c(T)$ we replace the sum by an integral and use a Debye-type approximation[13] $\omega_k^2 = aV + s^2 k^2$ with a cutoff, $k_{\max} \sim 1/d$. The result depends on the effective dimensionality of the system, namely on the ratio $\xi(T)/d$.

(a) In the 3-D case, $\xi(T) \gg d$ and we can to a good approximation replace the upper limit of the integral by infinity:

$$c(T) \cong \frac{(\bar{a}V)^2 T^2 k_B}{4\pi^2 T_c^2}\int_0^\infty \frac{k^2 dk}{(aV + s^2k^2)^2} \cong \frac{(\bar{a}V)^2}{4\pi^2 s^3 (aV)^{1/2}}\int_0^\infty \frac{u^2 du}{(1+u^2)^2}, \qquad (22)$$

where $u = sk(aV)^{-1/2}$. As might be expected, the Gaussian specific heat behaves like $t^{-1/2}$, as in the continuum case. From (7) one also finds that (22) can be written as

$$c(T) \cong \Delta c (t_{g3}/t)^{1/2}. \qquad (23)$$

where $\Delta c$ is on the order of the mean-field specific-heat jump $\bar{a}/2bT_c$.

(b) In the 0-D case $\xi(T) \ll d$ and $s^2k^2 \ll aV$ over the integration region, which leads to

$$c(T) = \Delta c (t_{g0}/t)^2, \qquad (24)$$

in agreement with the single-grain result.[1-3] The two expressions (23) and (24) merge into each other at $t_t$, where $\xi(T) \cong d$.

Using the time-dependent Ginzburg-Landau (TDGL) picture,[19,20] which in 1-D, 2-D, and 3-D gives similar results to the Aslamazov-Larkin[21] (AL) microscopic calculation, one can obtain the paraconductivity outside the critical region above $T_c$. This is given by[20]

$$\sigma = (2e)^2 \sum_k \langle n_s(k)\rangle \frac{\tau_s(k)}{2m}, \qquad (25)$$

where $\langle n_s(k)\rangle$ is the average fluctuating superfluid (pair) density with a wave vector $\vec{k}$ and $\tau_s(k)$ its relaxation time. $\langle n_s(k)\rangle$ is proportional to $\langle |\psi_k|^2\rangle$ where the normalization of our order parameter is such that it has the dimension of an energy gap while in order that $\langle |\psi_k|^2\rangle$ represent pair superfluid density, the field $\psi$ has to be normalized such that the coefficient of $|\nabla\psi|^2$ is $\hbar^2/4m$. This yields

$$\langle n_s(k)\rangle = \frac{2\bar{a}\xi(0)^2 m}{\hbar^2}\langle |\psi_k|^2\rangle = \frac{2m\xi(0)^2 k_B T}{\hbar^2 NVt}\frac{1}{1+k^2\xi^2} \qquad (26)$$

where $NV$ is the total volume. For $\tau_s(k)$ one gets from the TDGL equation[19,20] (this is independent of the normalization of $\psi$):

$$\tau_s(k) = \frac{\pi\hbar}{16 k_B T(1+k^2\xi^2)t}. \qquad (27)$$

Thus

$$\sigma = \frac{e^2\pi\xi(0)^2}{4NV\hbar t^2}\sum_k \frac{1}{(1+k^2\xi^2)^2} = \frac{e^2\pi\xi(0)^2}{t^2\hbar}\int_0^{1/d}\frac{d^d k}{(2\pi)^d}(1+k^2\xi^2)^{-2}. \qquad (28)$$

Let us first use this formula for the case of a single isolated 0-D metallic grain[22] of a volume $d^3 = V$. The coherence length $\xi$ in (28) must then be replaced by $\xi_{GL}(T)$. When $d \ll \xi_{GL}(T)$ one cannot replace the summation over $k$ by an integration since most of the contribution to (28) comes from the $k = 0$ term; thus

$$\Delta\sigma_{0\text{-}D}(\text{single grain}) = \frac{e^2\pi\xi_{GL}(0)^2}{4V\hbar t^2} \sim \sigma_m\left(\frac{t_{g0}}{t}\right)^2, \qquad (29)$$

where we assumed the grain to be dirty (should be valid for $d < \xi_0$ and realistic grain surface) and used (6). $\sigma_m$ is the normal conductivity of the grain, $\sigma_m \cong ne^2 l/v_F m$.

We now return to the case of a granular array, here the integral in (28) is the same as for the specific heat, and we obtain the following two limiting cases:

(a) 0-D, $\xi(T) \ll d$:

$$\Delta\sigma_{0\text{-}D} \cong \frac{e^2\pi\xi(0)^2}{4t^2V} \sim \sigma_n\left(\frac{t_{g0}}{t}\right)^2 , \tag{30}$$

where we have used (6) and (15). $\sigma_n$ is the sample conductivity $\sigma_n \sim 1/R_n d$. Although (29) and (30) both pertain to 0-D cases, they differ (their ratio is $\sigma_m/\sigma_n \gg 1$) due to the fact that the $\xi^2_{GL}(0)$ appearing in (29) is appropriate to the metal, while $\xi(0)$ is the $\langle\psi_i\,\psi_j\rangle$ correlation length of the granular system. The $\Delta\sigma_0$ (single grain) of Eq. (29) is the fluctuation conductivity just of the metallic grain while $\sigma_{0\text{-}D}$ of Eq. (30) is the fluctuation conductivity of the whole sample. The fact that their ratio is equal to $\sigma_m/\sigma_n$ is also very clear. Since in the granular system the grains are connected by high resistance barriers, a relative increment $\Delta\sigma_m/\sigma_m$ in the grain conductivity will have a much smaller effect on the network conductivity which is dominated by $1/R_n d$, the much smaller barrier conductivity. In fact, the simplest expression for the network conductivity is $(1/\sigma_m + R_n d)^{-1} = \sigma_n$. Since $R_n d \gg \sigma_m^{-1}$, the change $\Delta\sigma_n$ induced in $\sigma_n$ due to a change $\Delta\sigma_m$ in $\sigma_m$ is given by $\Delta\sigma_n/\sigma_n \sim (\Delta\sigma_m/\sigma_m) \times (\sigma_n/\sigma_m)$. The enhancement of $\sigma_n$ due to this effect was recently measured[22] and found to agree with Eq. (30).

(b) 3-D, $\xi(T) \gg d$: Here, similarly to (23) and (29);

$$\Delta\sigma_{3\text{-}D} \sim \sigma_n(t_{g3}/t)^{1/2} . \tag{31}$$

Equations (30) and (31) merge into each other at the 0-D to 3-D crossover at $t_t$.

It is instructive to note that Eqs. (30) and (31), as well as (23) and (29), are related by an interdimensional-scaling[6]-type argument. Imagine the 3-D case as consisting of "supergrains" of size $\xi(T)$, the effective $t_{g0}$ of the supergrains will be given by $[N(0)kT_c\xi(T)^3]^{-1/2} = t_{g0,\,eff}$. Let us use this $t_{g0,\,eff}$ in the 0-D form:

$$\frac{t^2_{g0,\,eff}}{t^2} = \frac{1}{N(0)kT_c\xi(T)^3t^2} = \frac{V}{\xi(0)^3}\,\frac{t^2_{g0}}{t^{1/2}} \sim \left(\frac{t_{g3}}{t}\right)^{1/2} , \tag{32}$$

where we used (3) and (7). In the same way the Gaussian-type singularities can be derived for 1-D and 2-D, e.g., from the 0-D one.

Our results (29) and (30) for the 0-D case need some cautionary comments. Arguments have been put forward in the literature against the $k = 0$ contribution to the superfluid current on the grounds that: (a) The $k = 0$ state carries no current,[23] and (b) the microscopic[21] AL-like theory, and for that matter also the TDGL with the Kubo formula approach,[24] give a different expression for the paraconductivity. In the latter expression, the term $(1 + k^2\xi^2)^{-1}$ in Eq. (28) is replaced by $(4/d)k^2\xi^2(1 + k^2\xi^2(1 + k^2\xi^2)^{-3}$, where $d$ is the space dimensionality. This gives the same result for $\sigma$ as (28) as long as the cutoff $k_c$ over $k$-space summations satisfies $k_c\xi \gg 1$, which is the case in 1-2-3-D systems. However, the microscopic expression weights down strongly the $k \to 0$ contribution, and therefore its results do not agree with those of (28) in 0-D.

As far as (a) is concerned, the $k = 0$ state does indeed carry no current, but the calculation of the conductivity is done for the limit of zero current. For a small but finite current, the $k = 0$ state will be slightly modified such that it will have a small gradient in the order parameter that will correspond to the assumed current. This remark may also be a partial answer to (b), although a complete answer is difficult at the present stage. The difference between (28) and the microscopic result is that between a physically motivated but quite unfounded phenomenological expression and an incomplete microscopic theory. Related to this is also the question of the Maki terms[23(a)] in the microscopic theory. They were evaluated for 0-D by Hurault, Maki, and Beal-Monod,[23(b)] giving a result different from our Eq. (29). However, the Maki term contribution depends strongly on the $T_c$ shifts due to pair-breaking mechanisms.[25] While one contribution to this was taken in Ref. 23(b), others were not. For example, the large shift between $T_c^0$ and $T_c$ due to the fourth-order terms in the GL free energy is an important "pair-breaking" effect which will have to be considered in the future fully renormalized theory of fluctuation conductivity. This shift, neglected in the present stage microscopic theory, is $t_s$ [Eq. (11)] in 3-D and renormalizes $T_c^0$ to $T_c = 0$ in the pure 0-D case. In view of these comments, one has to regard the 0-D results of this paper as well as the microscopic ones both of the AL and of the Maki diagrams as being of a rather tentative nature.

Our formulas (30) and (31) also take into account in the appropriate temperature range the reduction of $R_n$ due to an incipient Josephson effect caused by fluctuations.[24] This physical idea was used in Ref. 17, together with the theory of Ref. 26 to obtain the total fluctation conductivity. On first sight it might seem that our result (31) does not agree with this idea. For example, at $t_t$ the average barrier Josephson coupling energy is of the order of $k_BT$, which should[17,26] result in a relative enhancement of $\sigma_n$ by a finite $O(1)$ factor while our Eqs. (30) and (31) predict an enhancement factor of $1 + (t_g/t)^{1/2}$ whose difference from unity is much smaller than 1. However, it turns out[22,27] that the latter situation, as described by our Eqs. (30) and (31) is valid. For $t \gtrsim t_t$ the fluctuations in

different junctions are to a good approximation decoupled. One can now calculate the enhanced conductivity of the junction[24] by the Kubo formula using the current correlation functions $f(t)$. Now, the time decay of $f(t)$ is due to two reasons: fluctuations of the relative phase across the junction, and fluctuations of the order-parameter amplitudes $\Delta_1$ and $\Delta_2$ in the two sides of the junction. If one of those fluctuations is much faster than the other, then it will dominate the decay in time of $f(t)$. Kulik[27] finds that the characteristic frequency for the phase fluctuations is

$$\gamma = \left(\frac{2e}{\hbar}\right)^2 R_n k_B T = \frac{\pi}{2\hbar C} \tag{33}$$

(which is not be be confused with the $\gamma$ of Refs. 17 and 26). While the characteristic frequency for the amplitude fluctuations is $\Gamma = \tau(k=0)^{-1}$ [see Eq. (27)]. Thus the modified barrier resistance will have two regimes: For $\gamma \gg \Gamma$, phase fluctuations dominate the conductivity; in the calculation of $f(t)$, $\Delta_1 \Delta_2$ can be replaced by the static average $\langle \Delta^2 \rangle$ for a single grain; the theory of Ref. 26 is applicable and yields for the reduced resistance of the junction $R_n^{f1}$ for $t > t_t$,

$$R_n^{f1} = R_n[1 - O((t_t/t)^2)] \ . \tag{34}$$

$R_n$ is the normal quasiparticle junction resistance. On the other hand, for $\gamma \ll \Gamma$, amplitude fluctuations dominate, and a calculation[22,27] similar to that of Ref. 24 yields for $t > t_t$,

$$R_n^{f1} = R_n[1 - (\gamma/\Gamma)\, O((t_t/t)^2)] \ . \tag{35}$$

Equation (34) is valid for $t \ll t_1$ while Eq. (35) is valid for $t \gg t_1$ where $t_1$ is defined by $\gamma = \Gamma$ or

$$t_1 \cong (\pi e^2/2\hbar)\, R_n \sim R_n R_1/R_2^2 \sim t_s \sim 10^{-3} R_n[\Omega] \ . \tag{36}$$

where for $t_s$ we took (11′), the weak-coupling relation. We notice using (5), (15), and (17) that $t_1/t_t \sim (R_n/R_2)^2 \ll 1$ for the case of interest. Thus for $t_2 \gtrsim t_t$ Eq. (35) holds. Around $t_t$, $(\gamma/\Gamma)t_t^2 \sim (t_1/t_t)t_t^2 = (R_1/R_2)^2 = t_{g0}^2$, using (5′), (16), and (17). Thus, around $t_t$ Eq. (35) does agree with Eqs. (30) and (31). On the other hand, for $t \gg t_t$ the intergrain coupling is much less than $k_B T$ and the 0-D conductivity enhancement due to fluctuations inside the grains is much larger than the incipient Josephson effect (35). For $t \ll t_t$ the grains are no longer independent, and therefore different barriers are coupled; thus neither (34) nor (35) hold. For this region the correct conductivity enhancement (as long as $t \gg t_g$) is given by our expression (31). In summary, it is only around $t_t$ where the incipient Josephson effect should be both calculable using independent junctions and important for the fluctuation conductivity of the whole sample. Just around $t_t$, our expressions do match with Eq. (35) obtained from this fluctuation Josephson effect. However, for $t \ll t_t$ one has a multigrain effect while for $t \gg t_t$ intragrain effects become dominant.

## V. CONCLUSIONS AND DISCUSSION

We summarize here the various regimes of behavior of granular films, this was compared qualitatively in Sec. III with existing experimental results. Notice that we have treated the 0-D–3-D case. There are cases where there is, for example, only one grain in the film thickness. These are 0-D–2-D situations. In principle, the treatment there is the same, except that some characteristic powers [cf. Eqs. (7), (9), (10), (11)] may be different. For the 0-D–3-D situations our classification is summarized in Table I.

We would like to make a few remarks about the case of large grains with $\rho_n \gg \rho_2$. Here the 0-D quasitransition is expected to take place fully above $t_t$, and phase locking should occur at lower temperatures. Experimentally, the upper transition can be detected by specific heat, quasiparticle tunneling, or magnetic-susceptibility[4] measurements. During the lower transition the resistance of the sample should go to zero along with some structure (presumably a peak or a weak singularity) in $c(T)$. It should be noted, however, that the total entropy change is on the order of $k_B$ per grain for the phase-locking transition and $k_B(d/d_0)^3$ per grain for the 0-D transition.

Recently, Solinsky and Goldman[11] measured the specific heat and the resistive transition of films with grain sizes of 200–1000 Å. Their results might be interpreted as showing two transitions. However, this interpretation is inconsistent with our estimates since $\rho_n \sim \rho_1$, which means that their anomalous specific heat cannot be a pure locking of almost fluctuation free units.

One of the drastic approximations in our model is the neglect of disorder effects—the distributions in grain sizes and barrier resistances. This feature can vary widely among different experi-

TABLE I. A Summary of the various regimes of behavior for 3-D arrays of superconducting grains.

| Large grains, $d \gg d_0$, $\rho_2 \gg \rho_1$ | Small grains, $d \ll d_0$, $\rho_2 \ll \rho_1$ |
|---|---|
| $\rho_n \gg \rho_2$. Two transitions, $t_s$ given by (11′), $t_s \gg t_{g0}$, very weak coupling. | $\rho_n \gg \rho_1$. Weak coupling. $T_c \ll T_c^0$ (possibly no transition). |
| $\rho_2 \gg \rho_n \gg \rho_1$. A single transition weak coupling. Equations (5′), (7′), (11′) hold. $t_t \gg t_g$, $t_{g0} \ll t_t$. | $\rho_2 \ll \rho_n \ll \rho_1$. Strong coupling. Equations (5′) and (7′) do not hold. $t_s$ given by (10′). |
| $\rho_n \ll \rho_1$. Strong coupling, 3-D system. Equations (7′) and (10′) hold. | $\rho_n \ll \rho_2$. Very strong coupling. Equations (7′) and (10′) hold. |
| $d_0 = [N(0)k_B T_c]^{-1/3}$, $R_1[\Omega] \sim \frac{10^9}{(dk_F)^3}$, | |
| $\rho \cong Rd$ | $R_2 \sim R_1(d/d_0)^{3/2}$ |

mental samples, according to the method of their preparation. We feel, however, that for narrow enough distributions (such as may be the case with some of the samples of Ref. 8) and in cases where the order-parameter correlation length is much larger than the characteristic length for the disorder—the latter should not be qualitatively important. Also, in the 0-D case, the only relevant distribution is that of grain size which can easily be taken into account.[4] However, one may envisage cases where, due to slow spatial variations of the parameters, or to percolation regions, different parts of the sample may order at different temperatures and there may even be no ordering of the whole sample.

Recently,[28] it was suggested that the superconducting transition becomes weakly first order, due to fluctuations in the electromagnetic field. The "size" of this transition is however very small and is proportional, for dirty samples, to the magnitude of the critical region. If this theory is also relevant to inhomogeneous granular systems—the effect may be more easily observable here due to the large critical regions.

It would be of interest to study, both experimentally and theoretically, further properties of the model considered in this article. We hope to discuss in future publications the magnetic properties,[2,4,7] density-of-states effects, NMR relaxation times, and electromagnetic properties.[14,27] We note that recently Saxena, Crow, and Strongin[29] found interesting coherent phenomena and magnetic field dependence in the response of a granular superconducting sample to rf electromagnetic fields, see also Refs. 30 and 31.

Finally, we would like to remark that, although we treated here the specific case of a granular superconductor, similar situations can exist also for other phase transitions. A well-known case is that of an array of superparamagnetic particles. The general problem is that of phase transitions in a system composed of a large number of weakly interacting small particles and the crossover from 0-D to higher-D behavior. A simplifying feature of the superconducting case is the typically large value of $\xi_0$. Nonetheless, much of our considerations can be used in these other cases, too. Also of interest are the related problems of weakly coupled chains or layers with crossover[6] between different dimensionalities.

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