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# Monte Carlo simulation of a model small-particle superconductor: Effects of disorder

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We describe Monte Carlo simulations of a model three-dimensional inhomogeneous superconductor in which small superconducting grains are coupled together by Josephson tunneling. Disorder is included, but Coulomb effects arising from finite grain capacitances are omitted. An ordered simple cubic array of grains is found to exhibit a phase-ordering transition to a state of long-range phase coherence and zero resistivity. The phase-ordering transition becomes conspicuously well separated from the single-grain transition when the intergrain normal-state resistance is about  $\hbar/e^2 \sim 4000 \ \Omega$ . The specific heat also changes from bulklike to single-particlelike behavior at this resistance. The specific-heat anomaly arising from the phase-ordering transition is found to be very weak. Disorder is studied in a model incorporting random intergrain coupling, via site dilution, and a model with random single-grain transition temperatures. The site-diluted model shows few qualitative differences from the ordered lattice, except that longrange phase coherence disappears as expected below the percolation threshold. If the volume fraction of superconducting grains is a function of temperature, then the phase-ordering temperature is found sometimes to occur above the peak in the specific heat, in agreement with experiments on granular A1.

# I. INTRODUCTION

Inhomogeneous superconductors differ strikingly from conventional, bulk superconductors.<sup>1,2</sup> In particular, the resistivity, instead of dropping abruptly, falls gradually to zero over a range of temperatures, and the specific heat is usually rounded, rather than discontinuous, at the transition.<sup>3-5</sup> Various other anomalies show up in the critical currents, magnetic susceptibility, current-voltage characteristics, and ac response. Many kinds of composites behave in this way, including mixtures of superconductor with normal metal, superconductor with semiconductor, and superconductor with insulator.

It is widely believed that many of these properties can be understood in terms of superconducting grains which are coupled together via Josephson or proximity-effect tunneling.<sup>6-8</sup> According to this picture, the composite may sometimes exhibit two transitions.<sup>9,10</sup> The first is the superconducting transition of the individual grains. The second occurs at the temperature  $T_c$  where the coupling causes the phases of the superconducting order parameter on different grains to line up and produce long-range phase coherence. This corresponds to the resistive transition in the inhomogeneous superconductor, i.e., the temperature at which the resistivity vanishes. These two transitions may be widely separated in temperature and quite distinguishable experimentally especially in resistivity measurements.

In the present work, we analyze this double transi-

tion in terms of an often discussed thermodynamic model for inhomogeneous superconductors.<sup>7,8</sup> The model is basically a discrete version of the Ginzburg-Landau free-energy functional which describes bulk superconductors. The main distinction is that the bulk gradient term is replaced by a discrete tunneling term which represents the superconducting weak links. The model is idealized, but it does allow for the inclusion of disorder, which certainly plays a role in many inhomogeneous superconductors. Disorder can be included in the intergrain coupling or in the single-grain transition temperature.

Our main results are the specific heats and resistive transition temperatures. These can be studied as functions of normal-state sample resistivity, grain size, and other relevant quantities. We find that, in general, the specific-heat peak lies at temperatures at or above the resistive transition. This is not an unexpected result: The specific heat should mainly reflect amplitude degrees of freedom of the superconducting order parameter, which turn on at the single-grain transition, while the resistive transition at  $T_c$  reflects the behavior of the phases, which should become coupled at lower temperatures. This particular sequence persists even if disorder is introduced into the intergrain coupling. However, if the individual grains are assumed to go superconducting over a range of temperatures, then the order can be reversed, i.e., most of the specific-heat peak can lie below the resistive transition. This model thus offers a possible explanation of results reported in granular Al.

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Besides the correlation just mentioned, the paper also provides evidence that  $T_c$  falls smoothly with increasing normal-state resistivity. Results of this nature were already presented earlier, in abbreviated form,<sup>11</sup> and are in accord with widely held beliefs about the behavior of the present model, and of inhomogeneous superconductors.

The methodology we use in this paper is Monte Carlo simulation,<sup>12</sup> which permits us to extract the thermodynamic properties of the model essentially exactly, within the limitations of a finite-sized computer sample. The size limitation is probably unimportant except insofar as it prevents the calculation of quantities such as critical indices, and of percolation effects arising from long tenuously connected superconducting clusters whose correlation length exceeds the size of the sample.

The remainder of the paper is organized in the following way. Section II reviews the model, outlines its justification, and points out which experimental features are included and which neglected. Section III gives results for a perfectly ordered threedimensional array of identical, coupled superconducting grains, supplementing an earlier paper in which a few special cases were shown. Sections IV and V illustrate the effects of introducing disorder into the coupling strengths and into the single-grain transition temperatures. A discussion follows in Sec. VI.

#### **II. MODEL**

The basis of our calculations is the following model for the Helmholtz free energy of a granular superconducting composite (in units such that the Boltzmann constant  $k_B = 1$ ) (Refs. 7, 8, and 11):

$$F = -T \ln \int \prod_{i=1}^{N_G} d^2 \psi_i \exp(-\mathfrak{F}/T) ;$$
  
$$\frac{\mathfrak{F}}{T_0} = \sum_{i=1}^{N_G} \left\{ \frac{1}{t_i^2 \delta_i} (t - t_i) |\psi_i|^2 + \frac{1}{2} \frac{0.106}{\delta_i t_i^3} |\psi_i|^4 \right\}$$
  
$$+ \sum_{i>i} \frac{\pi}{16} \frac{R_0}{R_{ii}} |\psi_i - \psi_j|^2 .$$
(1)

Here  $\psi_i \equiv |\psi_i| \exp(i\phi_i)$  is a dimensionless complex energy-gap parameter for the *i*th grain, related to the energy gap  $\Delta_i$  by  $\psi_i = T_0 \Delta_i$ ;  $T_0$  is a normalizing temperature (for example, the bulk transition temperature); *T* is the absolute temperature;  $t = T/T_0$ ;  $T_i$  is the single-grain transition temperature of the *i*th grain;  $t_i = T_i/T_0$ ;  $\delta_i$  is a dimensionless size parameter defined by<sup>13</sup>  $\delta_i = 1/[N_i(0)v_iT_i]$ , where  $N_i(0)$  is the electronic density of states per unit volume at the Fermi energy for the *i*th grain and  $v_i$  is the volume of the *i*th grain;  $R_{ij}$  is the normal-state tunneling resistance between the *i*th and *j*th grains; and  $R_0 = \hbar/e^2 \sim 4000 \ \Omega$  is a characteristic resistance. The integrals in (1) run over all possible complex values of the variables  $\psi_i$ .

The physics underlying (1) is straightforward.  $\mathfrak{F}$  is the Ginzburg-Landau free-energy functional of the system when the gap parameters have the particular values  $(\psi_1, \psi_2, \ldots, \psi_{N_G})$  where  $N_G$  is the number of grains. In effect the internal degrees of freedom of the various particles have been summed out, except for the gap parameters. The phase-space integral in (1) performs an average over the possible values of the  $\psi_i$ 's. Thus  $\mathfrak{F}$  behaves from the point of view of statistical mechanics as an effective, temperaturedependent classical Hamiltonian.

The functional F is made up of two parts, a singlegrain piece and an intergrain coupling term. The single-grain part is the standard Ginzburg-Landau form in the absence of a magnetic field. It presupposes a spatially uniform order parameter within each grain, but allows for the possibility that different grains have different intrinsic transition temperatures  $T_i$  as well as possibly different volumes and densities of states at the Fermi energy. The coupling arises from Josephson tunneling in the case of a superconductor-insulator composite, and from the proximity effect for normal superconducting mixtures. The coefficients given in (1) are appropriate to Josephson tunneling between identical superconducting grains near their common transition temperatures, or between unlike grains provided the gaps in each are small compared to  $k_B T$ .<sup>14</sup> In the absence of a magnetic field, the coupling is always such as to tend to line up the phases  $\phi_i$  on different sites. For grains with different intrinsic transition temperatures, it also tends to force them to go superconducting at the same temperatures.

Omitted from (1) are "charging energies", i.e., the Coulomb energies associated with the finite capacitances of the grains.<sup>15-21</sup> These tend to inhibit phase ordering, but do not seem to have a major *qualitative* effect on the transition itself, as has been discussed by other workers. The Ginzburg-Landau form of (1) limits its validity, in principle, at temperatures close to the various  $T_i$ 's. Farther away, additional terms should be added to both the single-grain and the coupling terms. But the effects of these additional terms should only be quantitative, and the general types of behavior we find should be unaltered by them. Equation (1) does allow for the effects of quenched disorder, which is certainly one of the most important factors to consider in real composites.

#### III. ORDERED LATTICE OF GRAINS

As a first example, we have considered a simple cubic lattice of identical grains with nearest-neighbor coupling only. The model free-energy functional in

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(1) is then replaced by the simpler form

$$\frac{\sigma}{T_0} = \sum_{i=1}^{N_G} \left( \frac{1}{\delta} (t-1) |\psi_i|^2 + \frac{0.106}{2\delta} |\psi_i|^4 \right) + \frac{\pi}{16} \sum_{i>j} \frac{R_0}{R_{ij}} |\psi_i - \psi_j|^2 , \qquad (2)$$

which (except for  $T_0$  which merely scales the temperature) is characterized by two parameters; the nearest-neighbor coupling R and the size parameter  $\delta$ .

We have simulated the thermodynamics of (1) and (2) by standard Monte Carlo techniques, as briefly outlined in our earlier note. An equilibrium average (denoted  $\langle O \rangle$ ) is obtained from

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$$\langle O \rangle = Z^{-1} \int \left( \prod_{i} d^{2} \psi_{i} \right) O\left( \{\psi_{i}\}\right) \exp\left(-\mathfrak{F}/T\right) ,$$
  
$$Z = \int \left( \prod_{i} d^{2} \psi_{i} \right) \exp\left(-\mathfrak{F}/T\right) .$$
(3)

The specific heat  $C_V = -T(\partial^2 F/\partial T^2)_V$  can be found by differentiating the energy numerically,

$$C_V = (\partial E / \partial T)_V$$
 where

$$E = F - T \left[ \frac{\partial F}{\partial T} \right]_{\nu} = \langle \mathfrak{F}_0 \rangle \quad , \tag{4}$$
$$\frac{\mathfrak{F}_0}{T_0} = \sum_{i=1}^{N_G} \left[ -\frac{1}{t_i \delta_i} |\psi_i|^2 + \frac{0.053}{t_i^3 \delta_i} |\psi_i|^4 \right]$$

$$+\sum_{i>j} \frac{\pi}{16} \frac{R_0}{R_{ij}} |\psi_i - \psi_j|^2 \quad . \tag{5}$$

Alternately,  $C_V$  can be obtained from the fluctuation expression  $C_V = T^{-2}(\langle \mathfrak{F}_0^2 \rangle - \langle \mathfrak{F}_0 \rangle^2)$ , which is the analog for a temperature-dependent Hamiltonian of the usual fluctuation expression for the specific heat. We have calculated  $C_V$  both ways and found very little discrepancy between the two. Calculations were mostly carried out for  $5 \times 5 \times 5$  cubic arrays with periodic boundary conditions, except where conspicuous size effects warranted use of a larger (e.g.,  $10 \times 10 \times 10$ ) samples. Typically 4000 to 10000 Monte Carlo passes were made through the entire lattice.

Figures 1 and 2 show the specific-heat, long-range phase-order parameter  $\eta$ , and mean-square gap



FIG. 1. Specific heat  $C_V$ , phase-order parameter  $\eta$ , and mean-square energy-gap parameter  $\langle |\psi|^2 \rangle$  for an ordered simple cubic lattice of coupled superconducting grains. The three vertical panels represent results for the three coupling strengths corresponding to  $R/R_0 = 0.1$ , 1, and 10. All three cases have particles with size parameter  $\delta = 0.1$ . Arrows denote estimated position of phase-ordering transition. The solid curve in the upper right is for isolated particles  $(R = \infty)$ . Note the two different scales for  $C_V$  at left and right of figure; the right-hand scale gives  $C_V$  in  $k_B$  per cm<sup>3</sup> of the superconductor for a metal of the same free-electron density as Al.



FIG. 2. Same as Fig. 1 but for larger particles ( $\delta = 0.01$ ).

parameter

$$\langle |\psi|^2 \rangle = N_G^{-1} \sum_{i=1}^{N_G} \langle |\psi_i|^2 \rangle$$
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as calculated for a range of the parameters  $\delta$  and R, the nearest-neighbor normal-state resistance.  $\eta$  is defined by the equation

$$\eta = N_G^{-1} \left\langle \left| \sum_{i=1}^{N_G} \exp(i\phi_i) \right| \right\rangle, \qquad (6)$$

and is a measure of the long-range phase coherence in the sample, going to zero at the critical temperature  $T_c$  at which the thermodynamic phase transition occurs (in the same universality class as the threedimensional XY model).  $T_c$  is also the resistive transition temperature, at which the resistivity vanishes. The arrows in Figs. 1 and 2 denote an estimate of  $T_c$ deduced from the behavior of  $\eta$ . In our Monte Carlo calculations,  $\eta$  does not actually vanish at this point but remains nonzero to considerably higher temperatures, because of the finite size of the Monte Carlo sample.  $C_V$  is plotted both in  $k_B$  per grain and also in  $k_B$  per cm<sup>3</sup> of the superconductor; the latter is estimated assuming a density of states at the Fermi energy typical of Al. Finally, we have also included two solid lines in the figures for  $C_V$ ; these represent the single-particle specific heats corresponding to  $R = \infty$ , and may be calculated exactly by numerical evaluation of a Gaussian integral as described by Mühlschlegel et al. 13

The transition temperature  $T_c$  in Figs. 1 and 2 is monotonically decreasing with increasing R, as was already noted in Ref. 11,  $T_c$  reasonably well obeys the mean-field equation<sup>22</sup>  $T_c/T_0 = R_0/(R_0 + zR)$ where z = 6 is the number of nearest neighbors of a given grain. Thus  $T_c$  first begins to separate substantially from  $T_0$  when  $R \sim R_0 \sim 4000 \ \Omega$ . This corresponds to a resistivity  $\rho = R_0 a$ , where a is the intergrain separation, assuming that the normal-state resistivity is dominated by the intergrain tunneling resistance and not by the internal resistivity of the grains themselves. Taking  $a = 100 \ \text{Å}$ , we get  $\rho \sim 4000 \ \mu \Omega \ \text{cm}$ , which is typical of the resistivities for which broad superconducting transitions are observed.

Even for very small particles ( $\delta = 0.1$ ), there is no contribution to the specific heat clearly attributable to the phase-ordering degrees of freedom—these are very few in number (of the order 1 per grain) compared to the number of *amplitude* degrees of freedom, which is of the order of the number of Cooper pairs per grain. In the curves for  $\delta = 0.1$ , there is some indication of a  $\lambda$ -like specific-heat anomaly at  $R/R_0=1$ , but when  $R/R_0$  is as large as 10, this anomaly seems to have shrunk down to just a slight excess over the single-grain specific heat near  $T_c$ . A clear observation of this anomaly is therefore likely to be very difficult (except conceivably by observing changes of the peak in an applied magnetic field).

In the curves for smaller particles ( $\delta = 0.1$ ),  $C_V$  becomes sharper and more bulklike as  $R/R_0$  decreases. This occurs because the phase degrees of freedom are so strongly coupled that the system is tending to behave as one large particle, as was already pointed out in Ref. 11. The crossover from single-particle to bulklike behavior occurs near  $R = R_0$ .

The behavior of the specific heat is largely mirrored in the mean-square gap. Generally,  $\langle |\psi|^2 \rangle$ behaves in a more bulklike manner (varying linearly with temperature) for the samples with smaller  $\delta$  and smaller R. In the other limit, we see (largely singlegrain) zero-dimensional fluctuations producing a tail in the gap above  $T_0$ , the nominal single-grain transition temperature. Since the gap measures the amplitude degrees of freedom, it is little affected by the phase-ordering transition. Only in the curve with  $\delta = 0.1$  and  $R/R_0 = 1$  is there a slight excess value of the gap near  $T_c$ . This anomaly is probably outside the error bars of the simulation, but it is not very large and would be hard to see experimentally.

An issue of experimental interest is the relative positions of  $T_c$  and the temperature at which the peak specific-heat anomaly occurs, which we call  $T_{cv}$ . In Figs. 1 and 2 (and for other parameters we have studied in an ordered lattice)  $T_c$  always lies at or below  $T_{cv}$ . This is easily understood, for the effective coupling between grains is proportional to the product of the order parameters on the different grains. The coupling is therefore nearly absent until the individual grains become superconducting and the specificheat peak forms.

# IV. EFFECT OF RANDOMNESS IN COUPLING STRENGTHS: SITE-DILUTED LATTICE OF GRAINS

We next examine how the results of Sec. III change when the coupling between S grains is made random in some fashion, as would be expected in real materials. The randomness is introduced by means of site dilution. We consider a simple cubic lattice of grains, with nearest-neighbor coupling, the sites being occupied or empty with probabilities p and 1-p, and with no correlation between the occupation probabilities of any two sites. While this model is clearly artificial, it is probably adequate to give a rough idea of real composites with disorder in the coupling strengths. We have, in fact, tested this conjecture by simulating various other ways of including random intergrain coupling, including so-called bond disorder (where the strengths of different bonds are random and uncorrelated), and found results which do not much differ from the ones described below.

We have considered three different site occupancies: p = 0.5, 0.35, and 0.25. The first is well above the percolation threshold  $p_c$  at which there forms an infinite cluster of grains connected by nonzero coupling. The second and third are respectively just above and just below  $p_c$ , which is  $0.312 \pm 0.01$  for a very large site-diluted lattice.<sup>23</sup> In the particular  $10 \times 10 \times 10$  lattices we studied (with periodic boundary conditions) p = 0.25 was, indeed, below percolation, and the other two were above. For the two larger volume fractions a phase-ordering transition should occur, while for the lowest there should be a good amount of short-range phase coherence but no long-range order.

Figure 3 shows the specific-heat, long-range order parameter, and mean-square energy gap as calculated for all three site occupancies, for particles with  $\delta = 0.01$  and  $R/R_0 = 1$  (results for other parameters are similar). Also shown is the short-range phase order parameter S, defined by

$$S = \frac{1}{N_p} \sum_{\langle ij \rangle} \left\langle \cos(\phi_i - \phi_j) \right\rangle \quad , \tag{7}$$

the sum running over all pairs of nearest neighbors connected by bonds ( $N_p$  is the number of such pairs).

The curves for  $C_{\nu}$  and  $\langle |\psi_i|^2 \rangle$  show no substantial dependence on the volume fraction *p* at all: They are insensitive to the occurrence or nonoccurrence of a phase-ordering transition. The reason for this is, as in the ordered case, that these quantities primarily reflect amplitude degrees of freedom. They are largely decoupled from the phase degrees which bring about the resistive transition.

The curves for  $\eta$  show that a resistive transition does occur, as expected, for p = 0.35 and p = 0.5, but not for p = 0.25. For p = 0.35 and 0.5,  $\eta$  approaches a nonzero value at T = 0. This value is different from unity, because some of the occupied sites are attached to finite clusters which are not linked and hence not phase locked to the rest of the sample, even at T = 0. At p = 0.25, the order parameter is zero at T = 0 to within a small value which arises from finite-sample-size fluctuations. This merely reflects the lack of long-range phase coherence below the percolation threshold.

The short-range order parameter S always behaves smoothly, for all three site-diluted samples, and approaches unity at T = 0. Thus, there is essentially perfect *local* phase coherence at T = 0 and the lack of perfect long-range phase coherence is due to the presence of disconnected clusters. The persistence of S above  $T_c$  almost certainly implies a substantial fluctuation paraconductivity in this temperature range. However, the present, *static* theory unfortunately cannot provide an estimate of this paraconductivity.

A feature which seems to distinguish the disordered samples quantitatively from the ordered ones is the shape of the curve for  $\eta(T)$ . In site-diluted samples,  $\eta(T)$  falls off more or less linearly with increasing T, while in the ordered ones (Figs. 1 and 2) the decline is more abrupt, and  $\eta$  approaches zero at  $T_c$ with an exponent less than unity. Since  $\eta$  is the analog of the superfluid density for a granular system, any quantity, such as critical current, which depends

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FIG. 3. Same as Fig. 1 but for site-diluted samples. All three cases are for  $\delta = 0.01$  and  $R/R_0 = 1$ . In center panel, dots represent  $\eta$ ; squares, the short-range order parameter S. The three vertical panels represent concentrations of 25%, 35%, and 50% site occupancy and are carried out for  $12 \times 12 \times 12$ ,  $11 \times 11 \times 11$ , and  $9 \times 9 \times 9$  lattices with periodic boundary conditions.

on this density should show similar effects of disorder. A similar quasilinear falloff with increasing T has been reported for the order parameter of amorphous ferromagnets.<sup>24</sup> In both cases, the gradual onset of long-range order is probably related to local fluctuations in the coupling strengths.

Figure 3 also shows the variation of mean-squared energy gap with temperature for the three cases described above. As expected, the energy gap is unaffected by phase ordering, at least for the moderate coupling strengths shown—that is, the gap is controlled by single-grain properties.

To summarize, the site-diluted lattices (and other models we have examined with randomness in the coupling strengths) show no qualitative differences from the corresponding ordered-lattice results, except for the obvious effects of a lack of infinite cluster below  $p_c$ . This does not rule out unusual effects from large clusters that might form on a statistical basis in a real composite. But since we are really studying a quasiperiodic system in this work (because of the periodic boundary conditions), our samples are too small to see such behavior in our calculations.

## V. EFFECT OF RANDOMNESS IN SINGLE-GRAIN TRANSITION TEMPERATURES

Besides random intergrain coupling, a real composite might have random single-grain properties. For example, the grain size or the single-grain transition temperature might vary from grain to grain. The first is not likely, by itself, to cause any striking change in the thermodynamics of the composite. But a randomly varying transition temperature can lead to unusual effects, as we show in this section. A variable single-grain transition temperature might occur, for example, in granular Al. This metal often has a higher  $T_c$  as a composite or a thin film than as in conventional bulk form.<sup>25, 26</sup> The reason for this effect is not known, but perhaps the large surface area, and soft surface phonons, enhance the electron-phonon coupling and raise  $T_c$ . Since the effect seems to require small particle dimensions, we consider a model in which the single-grain transition temperature is correlated with particle size; smaller grains having higher transition temperatures (up to a certain lower limit of size).

Figure 4 shows the specific-heat, long-range order parameter, and mean-square energy gap for a model of this kind. The free-energy functional is Eq. (1). The single-grain temperature  $T_i$  is assumed to be a random variable, with  $T_i$  uniformly distributed between 1 and 3.  $\delta_i$  is taken to be related to  $t_i$  by the equation

$$\delta_i = 0.01 t_i^2 \quad , \tag{8}$$

so that small grains correlate with high  $t_i$ 's within this range of sizes. These choices are arbitrary, but are intended to simulate what might be occurring in



FIG. 4. Same as Fig. 1 but for model of Sec. V, with random single-grain transition temperatures and nonrandom couplings as indicated. Solid line represents  $R = \infty$ .

granular Al. However, our results do not depend strongly on how the  $t_i$ 's are distributed, or how they are correlated with  $\delta_i$ . In order to focus specifically on random single-grain properties, we also assume that the intergrain coupling is nonrandom. Figure 4 shows results for three coupling strengths as indicated.

The three vertical panels of Fig. 4 show very different behavior which correlates with the coupling strength. For weakest coupling,  $T_c$  is relatively low; it occurs in the middle of the specific-heat peak. The specific heat and mean-square gap are typical of a collection of isolated particles of a range of sizes and transition temperatures. To make this connection more apparent, the specific-heat curve for  $R = \infty$  is superimposed as a solid line on the upper right of Fig. 4. On the other hand, for the strongest coupling  $(R/R_0=0.1)$ , the proximity effect forces the entire system to act somewhat like one large particle, all of which goes superconducting at the same temperature. Thus, the specific heat sharpens towards a bulklike shape, and the mean-square energy gap does the same.

The most novel behavior is at  $R/R_0 = 1$ . Here, we have sufficiently strong coupling that, as soon as enough grains have gone superconducting to form an infinite cluster, the entire sample acquires long-range phase coherence. On the other hand, the coupling is not so strong to force the entire sample to behave as a single grain. The result is that  $T_c$  lies above the temperature  $T_{cv}$  of the specific-heat peak. The latter occurs where the bulk of the amplitude degrees of freedom turn on, whereas the phase ordering occurs when only about 30% of the grains (and the smaller ones, with fewer amplitude degrees of freedom) have gone superconducting.

Figure 4 also shows that  $T_c$  does not increase monotonically with increasing coupling. For the strongest coupling, the grains with the highest transition temperature have their superconducting temperature depressed by the proximity effect from neighboring normal grains (in the model), and so  $T_c$ decreases slightly. This effect has not been observed experimentally, although there is no objection in principle to its occurrence.

#### **VI. DISCUSSION**

The most surprising result of this paper is that, for an appropriate model, the resistive transition temperature  $T_c$  may lie *above* the peak  $T_c$  in the specific heat. Since this behavior has occasionally been observed in real superconducting composites, it is worthwhile to examine this result in more detail. It is obtained only in the model of Sec. V, which invokes a temperature-dependent volume fraction of the superconductor arising from a variable singlegrain transition temperature  $T_i$ . Aside from this feature, the details of the model are not very important, as we have found by doing similar calculations with different distributions of  $T_i$  and particle size. Random coupling models generally give  $T_{cv} > T_c$ . Thus we find that the experimentally observed results in Al need a model in which the superconducting volume fraction is temperature dependent.

It is not clear if the model of Sec. V applies specifically to granular Al. The assumption of the model is that each grain is essentially a different material, with a different transition temperature. Since the resistive transition temperature of Al definitely rises above the bulk  $T_c$  for samples made of very small particles, one might speculate, as have others,<sup>2</sup> that the phonon structure or electron-phonon coupling is stronger in small particles than in bulk. This suggests that the coupling, and hence  $T_i$ , will also vary from particle to particle, even possibly if they are nearly the same size. However, the effect seems greatest for very small ( $\sim 100$ -Å radius) particles, and those are near the limit for the use of a Ginzburg-Landau theory. Thus a complete explanation of experiment may require a more microscopic theory than is presented here.

Deutscher *et al.*<sup>27</sup> have presented a somewhat different percolation model to explain resistivity and specific-heat data in granular Al. They consider a random variation of coupling strengths, and assume that each grain becomes part of an infinite superconducting cluster as the transition temperature for the

- <sup>1</sup>For recent reviews and a series of experimental and theoretical studies on this subject, see the articles in *Inhomogeneous Superconductors*-1979, edited by T. L. Francavilla, D. V. Gubser, J. R. Leibowitz, and S. A. Wolf, AIP Conf. Proc. No. 58 (AIP, New York, 1980).
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bond is passed. Our results suggest that the same kind of effect can be obtained by having random grain transition temperatures. Possibly the two models could be reconciled by imagining that our "grains" are actually clusters of more or less strongly coupled *clusters* of grains, although verification of this point of view would require a study beyond the scope of our numerical simulation.<sup>28</sup>

To summarize, we have presented in this paper a numerical study of a model of granular superconducting composites, including the effects of disorder. For ordered samples, we confirm the behavior found previously, that the superconducting transition becomes substantially broadened when the intergrain resistance approaches  $\hbar/e^2$ . For disordered samples, we find no very surprising effects arising from random coupling strengths. The persistence of short-range order in this case (and also in all the others studied) suggests that there is a considerable paraconductivity arising from Josephson fluctuations. A model in which the volume fraction of superconductor depends on temperature can lead to an inversion of the specific heat and resistive transition temperatures, and may help explain some experimental work in which such an inversion is observed.

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represented by a composite with a temperature-dependent volume fraction of superconductor. The transition considered here is basically the d = 3 xy transition, which has a specific-heat exponent of zero to within experimental uncertainty [G. Ahlers, Phys. Rev. A §, 530 (1973)], and thus could be either inhomogeneous or homogeneous. Our work here could be interpreted as showing that an inhomogeneous model leads to agreement with some aspects of experiment.