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Monte Carlo solution for a lattice of coupled superconducting grains

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We have numerically simulated a Ginzburg-Landau model for a lattice of coupled superconducting grains in a nonsuperconducting matrix. The results unambiguously show the onset of a double superconducting transition when the intergrain normal-state resistance increases above $\sim\hbar/e^2 \sim 4000\ \Omega$: the specific heat changes from Bardeen-Cooper-Schrieffer-like to broadened, and the temperature T_c at which the resistivity vanishes becomes well separated from the single-grain transition temperature T_{c0}.

Composite materials such as granular Al or $(Nb_3Sn)_xCu_{1-x}$, made up of a superconducting (S) constituent and a nonsuperconductor (N), behave radically differently from ordinary bulk superconductors.[1] For example, the specific heat C_V is usually more rounded than the BCS behavior,[2,3] and the resistivity transition is also broadened over a substantial temperature width. This behavior is now widely believed to result, at least in some samples, from a *double* superconducting transition.[4-8] The first, at a temperature T_{c0}, results from the superconducting transition in individual S grains, and the second (the only true phase transition), at $T_c < T_{c0}$, corresponds to the onset of long-range phase coherence and zero resistivity in the composite. Not all superconducting composites are consistent with this picture: There is sometimes evidence[4] of percolation effects,[9] resulting from the formation of infinite connected clusters of S grains extending throughout the composite, and, in very thin films, a vortex-antivortex unbinding transition[10] may play a role.

This paper presents a Monte Carlo solution of a widely discussed thermodynamic model[6] for inhomogeneous superconductors. The model describes small S grains coupled together by Josephson tunneling or the proximity effect and embedded in an N host. For sufficiently weak coupling, the calculation confirms the picture of a double transition, with T_c and T_{c0} well separated with long-range phase order setting in only at the lower temperature. Each transition has its own specific-heat signature, but that at T_c is usually very faint in comparison with the single-grain transition. The lower transition closely resembles the phase transition in a ferromagnetic three-dimensional (3D) XY model. For stronger coupling, the two transitions merge, the C_V anomaly sharpens, phase and amplitude degrees of freedom in the superconducting order parameter become correlated, and the XY model becomes inappropriate. The transition from weak to strong coupling occurs when the intergrain normal-state resistance is of order $\hbar/e^2 \sim 4000\ \Omega$.

According to the model, the Helmholtz free energy F of a granular superconducting composite of N_G grains (in units such that $k_B = 1$) is

$$F = -T\ln\int\left(\prod_{i=1}^{N_G} d^2\psi_i\right)\exp\left(\frac{-\mathfrak{F}}{T}\right) ,$$
$$\frac{\mathfrak{F}}{T_{c0}} = \sum_{i=1}^{N_G}\left(\frac{1}{\delta}(t-1)|\psi_i|^2 + \frac{0.106}{2\delta}|\psi_i|^4\right) + \sum_{i>j}\frac{\pi}{16}\left(\frac{R_0}{R_{ij}}\right)|\psi_i - \psi_j|^2 . \tag{1}$$

Here $\psi_i = |\psi_i|\exp(i\phi_i)$ is the complex gap for the ith S grain; $R_0 = \hbar/e^2$; R_{ij} is the normal-state tunneling resistance between grains i and j; $t = T/T_{c0}$, where T is the absolute temperature; δ is a dimensionless size parameter defined by $\delta = [N(0)vT_{c0}]^{-1}$, where $N(0)$ is the electronic density of states per unit volume at the Fermi energy and v is the volume of the ith grain (all grains are assumed to have the same volume in our calculations); and T_{c0} is the single-grain transition temperature. The integrals run over all possible values of the variables ψ_i. Equation (1) applies to an array (not necessarily ordered) of S grains in an N host, with coefficients numerically appropriate to describe Josephson tunneling between grains in an insulating host.[11]

The physics underlying (1) is quite simple. The single-grain part of (1) causes the mean value of the *amplitude* $|\psi_i|$ to become nonzero below T_{c0} (with rounding due to single-particle fluctuations). The last term causes the *phases* ϕ_i to couple "ferromagnetically" with a consequent phase transition and onset of long-range phase order at a lower temperature T_c. The model implicitly assumes grains small enough to have a spatially uniform order parameter, yet large enough to be treated by a Ginzburg-Landau free-energy functional. Although (1) is applicable in principle only sufficiently near T_{c0}, it can be extended to lower temperatures by quantitatively modifying the functional to include higher powers of ψ_i. Since this is not expected to change the results qualitatively, we have studied the Ginzburg-Landau form for the sake of simplicity.

We have simulated the thermodynamics of (1) by standard Monte Carlo techniques,[12] treating $\mathfrak{F}$ as an effective temperature-dependent classical Hamiltonian for the system. Thus, equilibrium thermodynamic averages (denoted $\langle\theta\rangle$) are equivalent to

$$\langle\theta\rangle = Z^{-1}\int\prod_i (d^2\psi_i)\theta(\{\psi_i\})\exp\left(\frac{-\mathfrak{F}}{T}\right) ,$$

where Z is the argument of the logarithm in (1). $C_V \equiv -T(\partial^2 F/\partial T^2)_V$ can then be found by numerically differentiating the energy, $C_V = (\partial E/\partial T)_V$, where

$$E = F - T\left(\frac{\partial F}{\partial T}\right)_V = \langle \mathfrak{F}_0\rangle ,$$
$$\frac{\mathfrak{F}_0}{T_{c0}} = \sum_{i=1}^{N_G}\frac{-|\psi_i|^2+0.053|\psi_i|^4}{\delta} + \sum_{i>j}\frac{\pi}{16}\left(\frac{R_0}{R_{ij}}\right)|\psi_i-\psi_j|^2 . \tag{2}$$

Alternatively, C_V can be calculated from $C_V = +T^{-2}(\langle\mathfrak{F}_0^2\rangle - \langle\mathfrak{F}_0\rangle^2)$, 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. Calculations were carried out for $5\times5\times5$ and $10\times10\times10$ simple cubic arrays of grains with nearest-neighbor coupling only, assuming periodic boundary conditions, and with 4000 to 10000 Monte Carlo passes through the entire lattice. The results thus are specified by two parameters: δ, and the nearest-neighbor resistance which we denote R.

Figures 1(a) and 1(b) show C_V for $\delta=0.01$ and

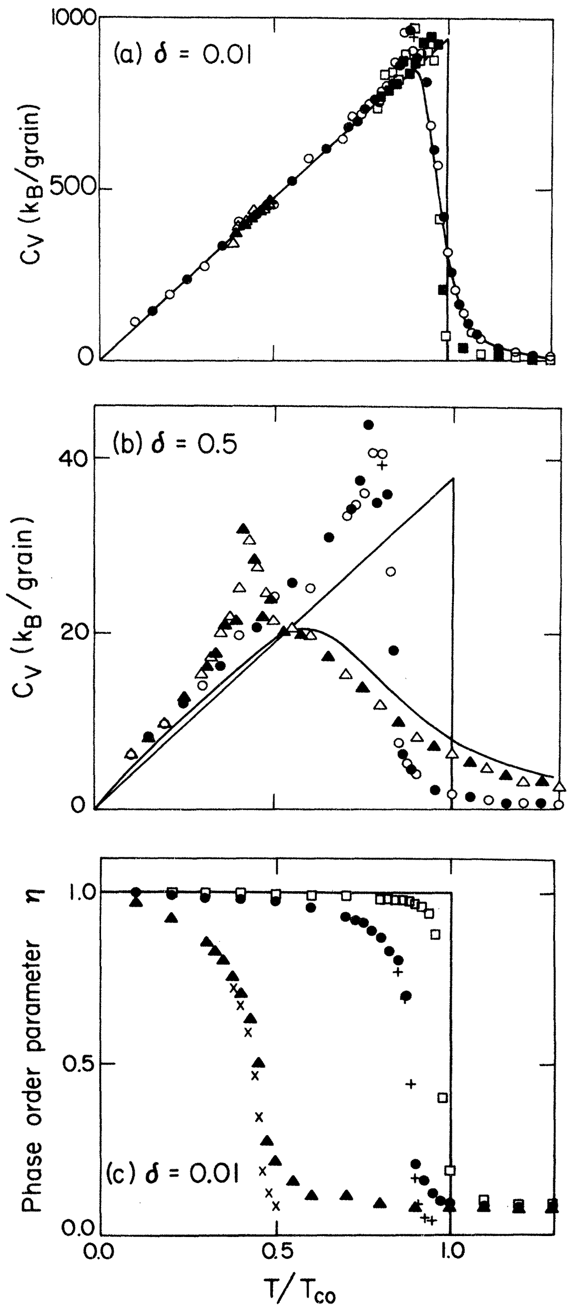

FIG. 1. (a), (b) Specific heat C_V (in units of k_B/grain) for $\delta=0.01$ and 0.5, and $R/R_0=10$ (Δ and ▲), 1 (○ and ●), and 0.1 (□ and ■). Open symbols are from energy fluctuations and closed symbols, from energy differences. All calculations are for a $5\times5\times5$ lattice except at $R/R_0=10$, in (a), which are for a $10\times10\times10$. Symbol + refers to $R/R_0=0.1$, energy difference, and $10\times10\times10$ lattice. Triangular curves in (a) and (b) are the bulk limit ($R\to0$); the other solid curves are the single-particle limit ($R\to\infty$). (c) Phase order parameter η for $\delta=0.01$, and $R/R_0=0.1$ (□), 1 (● and +), and 10 (▲ and ×). All symbols refer to $5\times5\times5$ samples except + and ×, which are for a $10\times10\times10$. The step function is the bulk limit ($R\to0$).

0.5. Also plotted are the infinite coupling (bulk) and zero-coupling (isolated-grain) limits. The former rises linearly with T and is discontinuous at T_{c0}, differing from BCS because of the Ginzburg-Landau assumption. The latter is the limit first treated by Mühlschlegel *et al.*[13] In the case $\delta = 0.01$, the curves for the various R/R_0 differ little from one another, except for a slight reduction in C_V above T_{c0} with increasing R/R_0, due to decreased amplitude fluctuations in that regime. For the weak-coupling case $R/R_0 = 10$, in particular, there is *no* detectable anomaly at the phase-ordering temperature T_c. By contrast, in the plots for $\delta = 0.5$, corresponding to very small particles (e.g., 50 Å in Al), C_V depends strongly on R/R_0. It becomes bulklike for $R/R_0 < 1$; C_V for $R/R_0 = 0.1$ (not shown) is even more similar to the bulk limit. For $R/R_0 = 10$, C_V resolves itself into a single-grain part plus an anomaly near T_c associated with the onset of phase ordering. The phase-ordering peak might thus be seen experimentally in *ordered* arrays of *very small* particles. $\delta = 0.5$ is, however, near the limit at which a continuum model is likely to be reliable.

Figure 1(c) shows the phase order parameter

$$\eta = N_G^{-1} \left\langle \left| \sum_{i=1}^{N_G} e^{i\phi_i} \right| \right\rangle$$

for $\delta = 0.01$ and several values of R/R_0 (results for other δ's are similar). In the limit $R \to 0$ (bulk limit), η becomes a step function as shown, but for finite coupling it becomes rounded, like the magnetization in a ferromagnet, to which it is analogous. The arrows denote the numerically determined values of T_c, at which $\eta \to 0$. (There is some remnant tail in η above T_c, because of finite-size effects in the simulations, which decrease with larger Monte Carlo sample size.) As expected, T_c is much smaller than T_{c0} for $R \gtrsim R_0$, and merges with T_{c0} in the opposite limit. The ratio T_c/T_{c0} roughly satisfies $T_c/T_{c0} = 1/[1 + R/(zR_0)]$, where $z = 6$ is the number of nearest neighbors, as predicted by the molecular-field approximation for T_c suggested by several workers.[4,14]

We have obtained curves corresponding to Fig. 1 for site-diluted lattices of S grains in an N host. The results for C_V are quite similar to the ordered case, except that the phase-ordering peaks are somewhat reduced in height. The effects of this type of disorder are thus probably such as to make the unambiguous detection of a phase-ordering peak in C_V even less likely than in the ordered case.

We turn next to a qualitative comparison of these results with experiment. Our central result is that there is a qualitative change in the behavior of granular superconductors when the intergrain normal-state resistance increases above $\sim 4000\ \Omega$: The sharp transition with a BCS-like specific heat changes to a much broadened one with a specific heat similar to that observed for isolated grains, and with phase ordering occurring at a temperature well below the single-grain transition temperature. A transition from BCS-like specific heat to broadened behavior has been observed by Worthington *et al.* in granular Al,[2] at a resistivity of order $4 \times 10^{-3}\ \Omega$ cm. For an intergrain separation $d = 100$ Å, our theory gives a change in behavior at $\rho = \hbar d/e^2 \sim 4 \times 10^{-3}\ \Omega$ cm, similar to experiment. Since the experiment is for a highly disordered system, it cannot be directly compared with theory; nonetheless, the qualitative correlation is suggestive. The ratio T_c/T_{c0} is observed to decrease considerably from unity in several composites[1] when the intergrain resistance is of order $\hbar/e^2$, and to decrease with increasing ρ, in agreement with our results. Once again, a detailed comparison between theory and experiment is not feasible, because of the disorder in the experimental samples. Nonetheless, our calculations demonstrate unambiguously the onset of a double transition in an idealized model, in which the fiction of no disorder can be maintained.

To summarize, we have presented a numerically exact solution of a model describing a superconducting phase transition in a composite material. Many of the predictions, in particular the single-grain to bulk transition in the specific heat, and the emergence of a double transition with increasing intergrain normal-state resistance, have experimental counterparts. Furthermore, our results establish a clear basis for systematically considering terms neglected by our model, most importantly the effects of disorder, but also the influence of charging energies,[15] on the onset of superconductivity in granular materials. They also suggest potential applications to other materials, such as granular ferromagnets,[16] which may be described by similar Ginzburg-Landau models.

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