Divergent Diamagnetism in Superconducting and Normal Metal Composites near the Percolation Threshold

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The bare diamagnetic susceptibility χ of a composite superconductor below the percolation threshold p_c has been numerically calculated. A novel fitting procedure gives $\chi \propto (\Delta p)^{-b}$ near p_c, with $b = 1.29$ in dimension $d = 2$, $b = 0.35$ in $d = 3$, the exponents agreeing between site and bond percolation to within 0.02 in both cases. Similar effects give a far-infrared absorption coefficient α in normal-metal–insulator composites varying as $\alpha \sim \omega^2 (\Delta p)^{-(s+b)/2}$ where s is the dielectric-constant exponent.

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In this Letter, we describe a calculation of the diamagnetic susceptibility in a composite superconductor at very low temperatures and near the percolation threshold p_c. The calculations show, for the first time, that in three-dimensional samples the "bare" susceptibility (i.e., the susceptibility calculated before taking into account local-field corrections due to dipolar interactions between the finite clusters) diverges, although weakly. In two dimensions, we find a much stronger divergence for both site and bond percolation. The two-dimensional bond results differ slightly from the earlier results of Rammal and Angles d'Auriac,[1] obtained on considerably smaller samples. For both $d = 2$ and $d = 3$ the divergence is described by a power law, and the exponent characterizing the divergence is approximately 1.29 in $d = 2$, 0.35 in $d = 3$, the exponents agreeing between site and bond percolation in both dimensionalities within the expected error of the fit. Our calculations apply not only to disordered superconducting networks below the percolation threshold, but also to clusters of normal metal in an insulating host, where they describe the variation in the far-infrared absorption coefficient due to eddy currents circulating in loops of normal metal near the percolation threshold. This connection is described further below.

The divergent diamagnetic susceptibility originates in supercurrents which circulate in loops of superconductor in response to an applied dc magnetic field. As pointed out by de Gennes,[2] this contribution is the only source of diamagnetism in a network of superconducting wires which are thin compared to a penetration depth. It is expected to show critical behavior, possibly diverging, near p_c because the clusters that form at such concentrations may be very large, and may, in consequence, have large loops which can support substantial magnetic moments.

To calculate the susceptibility arising from such loops, we have considered a somewhat stylized superconducting network, namely, an array of superconducting grains, coupled together by Josephson tunneling, and subject to an external applied magnetic field B. The Hamiltonian for such an array is

$$H = \sum_{(ij)} J_{ij} \cos(\varphi_i - \varphi_j - A_{ij}), \tag{1}$$

where J_{ij} is the Josephson coupling energy between the i th and jth grains, φ_i is the phase angle describing the superconducting order parameter on the ith grain, and $A_{ij} = (2\pi/\Phi_0)\int_i^j \vec{A} \cdot d\vec{l}$ is a phase factor arising from the variation of Josephson coupling energy with vector potential A. $\Phi_0 = hc/2e$ is a flux quantum, and the sum runs over all distinct bonds between pairs of grains. We assume a bimodal distribution of couplings, all coupling energies being either J or zero. In site percolation, grains are placed on the sites of a lattice at random with probability p, whereas in bond percolation the bond energies are J or zero with probability p or $1-p$. The zero-field *bare* diamagnetic susceptibility is defined at zero temperatures by the condition

$$-\chi = \frac{1}{V}\left(\frac{\partial^2 E}{\partial B^2}\right)_{B=0}, \tag{2}$$

where E is the energy, V is the volume of the system, and B is the external field. For small values of the field, and finite clusters, the cosine factors in (1) can be expanded in powers of their arguments, and the phase-dependent part of the energy takes the form

$$\frac{E}{J} = \min \sum_{(ij)} (\varphi_i - \varphi_j - A_{ij})^2. \tag{3}$$

For the purpose of calculating the *zero-field* susceptibility *below* the percolation threshold (where there are only finite clusters), the flux through any cluster is much less than a flux quantum and therefore this expansion is exact. The equations

of minimization are

$$\sum_j(\varphi_i-\varphi_j-A_{ij})=0, \quad (4)$$

where the sum runs over all neighbors which are connected to site i by nonvanishing bonds. For a given value of B, this is a system of coupled linear equations of dimensionality equal to the number of grains in the cluster. (One phase in each cluster can, of course, be chosen arbitrarily.) The effective size of the linear system can be reduced by removing all dead ends, and all bonds whose removal would cut a given cluster into two unconnected parts; these bonds do not contribute to the susceptibility. The solution of (4) gives values of the phase angles which are linear in B, and hence an energy which is quadratic in B, from which the relevant susceptibility can be extracted.

For a simple loop of perimeter P and projected area S perpendicular to the field, it is readily shown that (4) gives a moment which is proportional to S^2/P. For several connected loops, Eq. (4) can be converted into an expression equivalent to de Gennes's, involving projected loop areas perpendicular to the field and perimeters as variables. In practice, we find that for large clusters containing N_s sites, the effective value of S^2/P tends to increase faster than N_s, with great statistical fluctuations, giving rise to a divergent susceptibility. The large clusters are usually very "stringy" with not many large loops.

We have calculated χ from Eq. (4), for both site and bond percolation on square and simple cubic lattices. The relevant linear systems of equations were solved with an envelope-reduction algorithm for large, sparse, positive-definite matrices.[3] Sample configurations were obtained by either of two methods: (i) Sites or bonds were put down at random with probability $p<p_c$ on an $N\times N$ or $N\times N\times N$ lattice with periodic boundary conditions; or (ii) individual clusters were grown one at a time from an initial seed of one site by adding sites or bonds to the perimeter with probability p, as described in the literature.[4] The latter method gives a larger proportion of large clusters, and cannot exhibit any finite-size effects, but yields the same values of χ as method (i). In all calculations carried out by method (i), χ was obtained by averaging over twenty runs on a 216^2 or 36^3 lattice, while those based on (ii) involved $(1-2)\times10^6$ sites. Our numerical "samples" are thus comparable in number of superconducting grains to many experimental superconducting arrays,[5] although smaller than the disordered

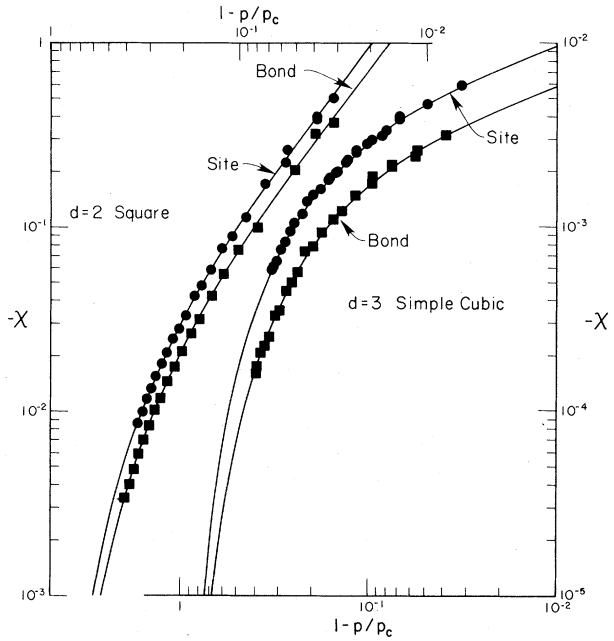

FIG. 1. Calculated susceptibility for square and simple cubic superconducting lattices below the percolation threshold. The circles denote calculated points for site percolation, the squares denote bond percolation, and the solid lines are the analytic fits as described in the text.

superconductors in which magnetic field effects have been studied to date.[6]

Our results are shown in Fig. 1. In both numbers of dimensions, some data points are obtained by method (i) (except near p_c) and some by (ii); we have not distinguished between them because they both lie on the same curve to within statistical fluctuations. Our units are such that an elementary square loop oriented perpendicular to the field contributes 0.25 to the magnetic moment per unit field [this is S^2/P for a square of unit edge]. The results, especially for $d=3$, do not approach an expected asymptotic power-law behavior in p_c-p at least until $1-p/p_c\leq0.1$, presumably because very few loops are formed at all until p is relatively close to p_c.

Because the critical part of the susceptibility is apparently rather small, we have fitted the four curves with an analytic form which interpolates between the calculable power-series form, $-\chi=\sum a_n p^n$, at low p and the expected power law, $-\chi=A[(p_c-p)/p_c]^{-b}$, in the critical region. For all present lattices, $-\chi=a_4p^4+a_6p^6+\ldots$ at small p, with $a_4=\frac{1}{4}$ for all four cases, and $a_6=\frac{1}{3}$ ($d=2$, site), $\frac{4}{3}$ ($d=2$, bond), $\frac{7}{15}$ ($d=3$, site) and $\frac{8}{3}$ ($d=3$, bond). Including both of these coeffi-

TABLE I. Calculated exponent b describing the divergence of $-\chi$ in $d=2$ and 3. The corresponding values of A are 6.41×10^{-3} ($d=2$, site), 5.06×10^{-3} ($d=2$, bond), 1.99×10^{-3} ($d=3$, site) and 1.35×10^{-3} ($d=3$, bond). The bracketed values represent the predictions $b=2\nu-t+\beta$ (Ref. 9) and $b=2\nu-t$ (Ref. 2), respectively [using the values of (Ref. 12) for the exponents].

Lattice	$d=2$, site	$d=2$, bond	$d=3$, site	$d=3$, bond
Exponent	1.30	1.28	0.35	0.33
	[1.54 ± 0.08, 1.40 ± 0.08]		[0.26 ± 0.15, −0.15 ± 0.15]	

cients, we used the analytic form

$$\chi=-a_4p^4\left(\frac{A}{a_4p_c^{\,4}}\right)^{(p/p_c)^3}\exp\left[\frac{a_6}{a_4}\,p^2\left(1-\frac{p}{p_c}\right)\right]\left\{\left(1-\frac{p}{p_c}\right)\exp\left[\frac{p}{p_c}\left(1-\frac{p}{p_c}\right)\left(1+\frac{3}{2}\,\frac{p}{p_c}\right)\right]\right\}^{-b}. \tag{5}$$

While this expression may appear unnecessarily complex, it is the simplest form we could invent which has the proper analytic behavior in both limits and which allows a simple fitting procedure to determine independently the values of A and b in the singularity at p_c. Simplification of Eq. (5) would mean we could not keep a_4 and a_6 matched to their proper values (with $a_0=a_1=a_2=a_3=a_5=0$) or A and b would become functionally related and hence not independent parameters. With use of Eq. (5), A and b are obtained by plotting

$$(p/p_c)^3\ln[\,|\chi|/(a_4p^4)]-(a_6p_c^{\,2}/a_4)(p_c/p-1)$$

against the variable

$$(p_c/p)^3\ln(1-p/p_c)+(p_c/p+\tfrac{3}{2})(p_c/p-1)$$

in which case, $\ln[(A/(a_4p_c^{\,4})]$ and $-b$ are the y intercept and slope of a least-squares fit. The quality of the fits is shown in Fig. 1; the correlation coefficients of the fits are 0.997 ($d=2$, site), 0.996 ($d=2$, bond), 0.995 ($d=3$, site), 0.969 ($d=3$, bond).[7] The resulting exponents are shown in Table I.[8]

It is of interest to compare the present results with scaling predictions and other previous work. Rammal, Toulouse, and Lubensky[9] have postulated a scaling description of superconducting diamagnetism near the percolation threshold, which leads to the prediction $-\chi\propto(\Delta p)^{-(2\nu-t+\beta)}$, where t, ν, and β are standard percolation exponents. A simpler argument by de Gennes[2] leads to $-\chi\propto(\Delta p)^{-(2\nu-t)}$. The numerical values corresponding to these exponents are also listed in Table I. Numerical results from small lattices by Rammal and Angles d'Auriac[3] give $b=1.54$ in $d=2$. All of these values, for $d=2$, differ sharply from the analytic result of Stephen[10] for the self-similar model of a two-dimensional percolation cluster known as a Sierpinski gasket, for which $b=-0.77$ (i.e., no divergence in $-\chi$). Our present results are in very good agreement with the scaling predictions[9] in $d=3$. For $d=2$, they disagree by a small amount that appears to lie outside the possible inaccuracies of our calculation. The prediction $b=2\nu-t$,[2] on the other hand, gives the wrong sign in $d=3$. We tentatively conclude that the scaling theory requires some modification in order to bring it into agreement with numerical experiment. Note also that our work provides support for the hypothesis of universality: Agreement between site and bond percolation is extremely good in both $d=2$ and $d=3$.

Note that for a weakly linked superconductor such as is modeled here, the numbers plotted in Fig. 1 must be multiplied by $4\pi^2Ja/\Phi_0^{\,2}$, where a is the lattice constant of the "grain lattice," J the Josephson coupling energy, and $\Phi_0=hc/2e$ an elementary flux quantum. For a 10-μm grain separation and a 10-K coupling energy, this factor is $\sim4\times10^{-4}$.

Another possible method of observing this divergence would be in a composite of *normal* metal and insulator below the percolation threshold. In such materials, a long-wavelength electromagnetic wave (of frequency ω) will set up oscillating diamagnetic currents in loops of metal grains, and hence an energy absorption varying as ω^2 and with a coefficient that diverges near the percolation threshold. Loops of cross section S, perimeter P, composed of wires of cross-sectional area πr^2 and conductivity σ, and placed perpendicular to magnetic field $Be^{-i\omega t}$, will exhibit an induced moment $\vec{m}=i[\omega\sigma(\pi r^2)/(2c^2)]\vec{B}S^2/P$. The

geometrical factor involved in this response is the same as in the superconducting case. From this we estimate that a diluted square or cubic mesh composed of such wires will have a magnetic *permeability*

$$\mu \sim 1 + 4\pi i[\omega\sigma(\pi r^2)/2c^2]\,\chi_d \equiv \mu_1 + i\mu_2, \qquad (6)$$

where χ_d is the susceptibility shown in Fig. 1.

The propagation constant is given by $k = (\omega/c)(\epsilon\mu)^{1/2}$ where $\epsilon = \epsilon_1 + \epsilon_2$ is the dielectric constant of the medium. Now $\epsilon_1 \sim (p_c - p)^{-s}$ near p_c,[11] where s is another percolation exponent ($s \sim 1.3$ in $d = 2$, 0.7 in $d = 3$).[12] If the effects of divergent dielectric and diamagnetic response can be treated independently by invoking a multiplicative index of refraction $n = (\epsilon\mu)^{1/2}$, then the loops produce an infrared absorption coefficient $\alpha \equiv \mathrm{Im}k \sim \frac{1}{2}(\omega/c)\epsilon_1^{1/2}\mu_2$ or

$$\alpha \sim \left(\frac{\sigma r^2}{c^2}\right)\frac{\omega^2}{c}(p_c - p)^{-(s+b)/2}. \qquad (7)$$

This is to be compared with a magnetic dipole absorption coefficient $\alpha = 2\pi\omega^2\sigma r^2 p/5c^3$ for a small volume fraction p of conducting spheres of radius r. The presence of closed loops thus greatly enhances this magnetic dipole absorption, and may therefore contribute to the anomalously large coefficient of α that has often been reported in far-infrared absorption by small metal particles.[13] It would be of great interest to see this divergence experimentally. Quite apart from the divergence, furthermore, such loops could greatly enhance the far-ir absorption even at low p, if some mechanism (e.g., short-range order) existed which tended to form more large loops than would be expected randomly. Such a mechanism could possibly account for the large discrepancy between far-ir measurements and previous theories.[13]

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