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Conductivity of a mixture of conducting and insulating grains: Dimensionality effects

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The percolation behavior of films of thickness d composed of a compact mixture of conducting (concentration p) and insulating (concentration $1-p$) beads is studied by measuring their conductivity $\sigma(d,p)$. A theoretical model based on a renormalization operation to the thickness of the film leads to predictions on the threshold $p_c(d)$, the crossover values between two- and three-dimensional behavior $p_{\pm}(d)$, and the amplitude of the conductivity above threshold. The experiments are analyzed in terms of the model and lead to the determination of several critical exponents.

I. INTRODUCTION

A mixture composed of conducting (with a concentration p) and insulating but otherwise identical grains (concentration $1-p$) undergoes a percolation[1] transition around a threshold p_c. The system is an insulator for $p < p_c$. Conductivity sets in at p_c and its variation above p_c is characterized by the expression, valid close enough to p_c,

$$\sigma \propto (p-p_c)^t \; . \qquad (1)$$

The exponent t has been obtained for various two- and three-dimensional (D) systems[2]

$$t_2 = 1.14 \pm 0.05, \quad t_3 = 1.73 \pm 0.10 \; . \qquad (2)$$

Our results on macroscopic three-dimensional mixtures of packed coated spheres or smaller powders[3] are consistent with the latter value. Thresholds are not expected to display such a universal (lattice-independent) behavior. However experiments on various packed powders lead to a threshold value

$$p_c = 0.27 \pm 0.05 \qquad (3)$$

fairly independent of the nature of the convex objects. An interpretation of this result was given in Ref. 3 using the Scher and Zallen[4] invariant for bond-percolation problems $zp_c = 1.5$; the number of "electrically good" contacts between one object and its neighbors, the coordination number, should be of the order of 6. The value can be shown geometrically[3] to be a good estimate for random loose packing.[5]

An experimental problem connected with the above simulations relates to the finite dimension of the system. We consider here a film of thickness d, made from a compact mixture of grains of diameter a. The film can be considered as infinite (with respect to the size of the individual elements) in the two other directions. The effect of finite thickness is assumed to be equivalent to the introduction of two parallel limiting planes in a material having the structure of the bulk assembly. In particular we will not consider the modifications of the structure which are caused by the plane boundary limits, which may become important in the case of the thinnest films, and those related to the possible anisotropy introduced in the packing.

The finite dimensions of the sample result in a two-dimensional behavior near the threshold and a thickness-dependent shift in the critical density analogous to that in 2D thermodynamic examples.[6,7] We discuss the crossover points, shift of threshold, and variation of conductivity $\sigma(p)$ in Sec. II. Section III presents the experimental techniques. In Sec. IV we present the experimental results and compare them to predictions from other sources.

II. THEORY

Because of the finite thickness of our samples, one expects two-dimensional behavior near the percolation threshold and three-dimensional behavior for sufficiently high (+) and low (−) concentrations. The crossover should occur when the correlation length (ξ) is comparable to the layer thickness. Moreover, the correlation lengths of the two- and three-dimensional regions have to coincide at the crossover points. Except for numerical constants, this is sufficient to predict the behavior of the percolation problem.

One has for the 3D regime:

$$\begin{aligned} \xi_-/a_- &= A_{3-}(p_{c3}-p)^{-\nu_3}, \quad 0 < p < p_{c3} \; , \\ \xi_+/a_+ &= A_{3+}(p-p_{c3})^{-\nu_3}, \quad p_{c3} < p < 1 \; , \end{aligned} \qquad (4)$$

where ν_3 is the critical index for the three-dimensional correlation length on both sides of p_{c3}.

The $a_\pm$ are constants comparable to the particle dimensions. The ratio of the constants (A_{3-}/A_{3+}) is expected to be universal (as is ν_3) and can be used to define a critical density p_{c3}^*. We choose the a so that

$$A_{3-}=p_{c3}^{*\nu_3},\quad A_{3+}=(1-p_{c3}^*)^{\nu_3} \tag{5}$$

[one can check that p_{c3}^* is obtained from p_{c3} from the renormalization operation Eq. (10) defined below].

Crossover between 2D and 3D behavior occurs at two densities p_- and p_+ such that

$$\xi_-(p_-)=\beta_- d,\quad \xi_+(p_+)=\beta_+ d \ , \tag{6}$$

where $\beta_\pm$ are constants (of order unity), reflecting the fact that the crossover points are only defined by extrapolation. In the following we assume, for simplicity, that

$$\beta_-=\beta_+=1 \ . \tag{7}$$

Expressing the conditions (6) in Eq. (4) leads to values for the crossover probabilities

$$\begin{aligned} p_-(d)&=p_{c3}-(a/d)^{1/\nu_3}p_{c3}^* \ , \\ p_+(d)&=p_{c3}+(a/d)^{1/\nu_3}(1-p_{c3}^*) \ . \end{aligned} \tag{8}$$

This assumes [besides Eq. (7)] that d is large enough so that the renormalized expressions (4) are valid.

To describe the crossover, it is convenient to change to a new scale d and to choose a renormalized density p^*:

$$p^*(p)=\frac{p-p_-(d)}{p_+(d)-p_-(d)} \ , \tag{9}$$

such that

$$p_-^*(p_-(d))=0,\quad p_+^*(p_+(d))=1 \ . \tag{10}$$

In the range

$$0<p_d^*<1 \ , \tag{11}$$

the samples behave as a two-dimensional system with a 2D correlation length which takes the values

$$\xi_2(p_\pm)=d \tag{12}$$

at the crossover concentrations. In particular, percolation occurs at a universal density $p^*=p_{c2}^*$ defined analogously to p_{c3}^*. From the definition of p^*, this leads to a threshold $p_c(d)$ shifted from the bulk value p_{c3} by

$$p_c(d)-p_{c3}=(p_{c2}^*-p_{c3}^*)(a/d)^{1/\nu_3} \ . \tag{13}$$

We can now predict the behavior of the conductivity. In the three-dimensional regime $[p>p_+(d)]$ the (3D) conductivity is

$$\sigma_3=\sigma_0(p-p_{c3})^{t_3} \ , \tag{14}$$

and does not depend on d.

In the expression (14) the conductivity σ_0 is a constant obtained from the conductivity of the individual element. Similarly for the 2D regime one can write

$$\sigma_2=\bar{\sigma}_0[p-p_c(d)]^{t_2} \ , \tag{15}$$

where, for convenience, σ_2 is an equivalent three-dimensional conductivity which would result in the relevant 2D conductivity for a layer of thickness d. The constant $\bar{\sigma}_0$ is determined by the requirement that

$$\sigma_2(p_+)=\sigma_3(p_+) \ . \tag{16}$$

This leads to

$$\bar{\sigma}_0=\sigma_0(a/d)^{(t_3-t_2)/\nu_3}(1-p_{c3}^*)^{t_3}/(1-p_{c2}^*)^{t_2} \ . \tag{17}$$

The resulting behavior of σ is described in Fig. 1(b).

We note that Eq. (17) involves the additional assumption that the description of the conductivity problem does not require the introduction of a new

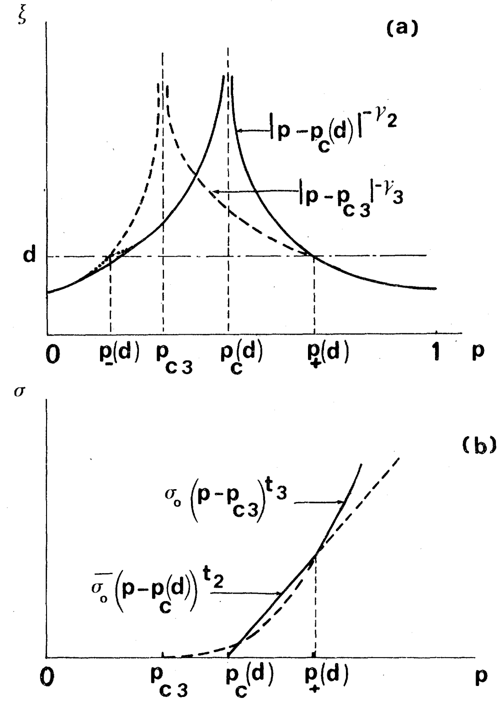

FIG. 1. (a) Schematic description of the behavior of the correlation length for a sample of thickness d. The dashed lines are the extrapolated curves for an infinite sample. Dotted lines indicate the extrapolation implied in the definition of the crossover densities. (b) Schematic description of the conductivity assuming the same crossover point as in (a).

length different from ξ. This is generally believed to hold.[8,9] If an additional length ($\xi' > \xi$) dominates the conducting skeleton, the crossover for σ will occur at a higher density and $\bar{\sigma}_0$ would not be given by Eq. (17).

III. EXPERIMENTAL TECHNIQUES

We have used a mixture of conducting and insulating spheres (diameter 20 μm, dispersion ~30%). The insulating objects are glass beads. The beads have been silver coated to obtain the conducting phase. The Ag thickness is small enough to introduce no appreciable density difference. The statistical homogeneity of the mixture was checked with a stereomicroscope. In order to favor the homogeneity and the compactness of the mixture, the particles were initially put in suspension in alcohol. The suspension was then mixed thoroughly with a magnetic agitator. This method of preparation avoids the formation of clusters which can appear due to electrostatic forces as well as to the presence of interstitial water between the pores.

The suspension is then spread onto a glass plate using a Desaga apparatus[10] which is used to produce thin chromatographic plates. The operation of the "spreader" is described in Fig. 2. The film is produced by moving the container backwards. The adjustable thickness d is defined by the distance between the glass substrate and an adjustable blade parallel to the glass plate moving with the container. (The same concentration of the suspension has been used in all experiments in order to ensure reproducible thickness and compactness results.) The layer is then baked in an oven around 100 °C. Once the film has been formed, its edges are trimmed to a well-defined 20×6 cm^2 rectangular geometry. The thickness value and its homogeneity have been controlled using a dial comparator with an accuracy of ± 10 μm.

The conductivity measurement is done using four parallel conducting indium probes, which had been deposited on the glass surface prior to the splaying. Constant current measurements ($I = 10^{-1} \pm 10^{-5}$ A) are used. The resistance varies typically from 10^9 Ω for an insulating system to 10^{-2} Ω for a conducting one. The doping in conducting spheres was varied from 1 to 0.28, by jumps of 0.05 far from the threshold and 0.025 near the threshold. The values plotted for the conductivity for each p and each d are obtained as an average of five independent experiments with a dispersion of about 10%.

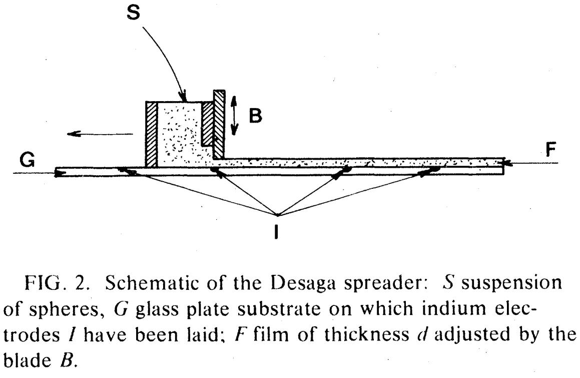

FIG. 2. Schematic of the Desaga spreader: S suspension of spheres, G glass plate substrate on which indium electrodes I have been laid; F film of thickness d adjusted by the blade B.

IV. EXPERIMENTAL RESULTS

We present two types of results: (A) those related to the variation of the percolation threshold $p_c(d)$ with thickness which lead to a determination of ν_3; (B) those obtained from the conductivity above $p_c(d)$.

A. Threshold

The threshold p_c is the value of dopage p from which the conductivity σ becomes different from zero. The variation of $p_c(d)$ as a function of the inverse thickness d^{-1} is given in Fig. 3. Error bars are indicated for several data points. The value $p_c(\infty) = 0.287 \pm 0.05$ has been obtained by an extrapolation described below of the results for thick

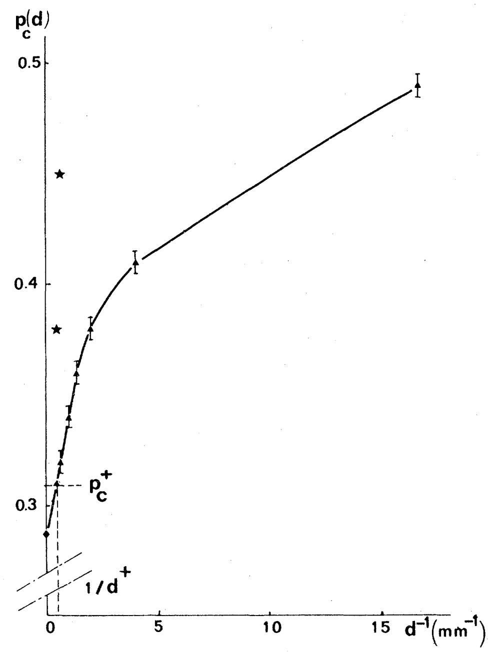

FIG. 3. Percolation threshold $p_c(d)$. The limit p^+, below which the film can never be conducting, is associated with the finite spacing of electrodes; the 3D value p_{c3} is given by a fit described in the text. The two stars represent crossover-doping calculated values.

films. In fact it is found that the film is insulating below a value p_c^+ corresponding to a thickness d^+; the actual experimental curve does not extend continuously to $1/d = 0$. The limit is connected with the finite spacing ($\simeq 6$ cm) of the electrodes in the plane of the layer. Even for an infinitely thick film the current lines only span a finite thickness (measured by d^+) proportional to the spacing between electrodes. The threshold $p_c(\infty)$ is slightly larger than the value obtained for 3D pressed powders. This may be an indication of the more compact structure in the latter case.

In the opposite limit of thin films we expect $p_c(d)$ to saturate to a two-dimensional threshold. Unfortunately we have not been able, in independent attempts, to obtain good percolation experiments with two-dimensional assemblies of spheres comparable to our 3D work of Ref. 3 because it is difficult to apply the pressure needed to establish the electrical contacts in such a plane geometry. Moreover it might well be that for the thinnest films (the value $1/d = 16$ mm^{-1} in Fig. 3, would correspond to three times the diameter of a sphere) the packing of spheres is different from the bulk case due to the strong aligning influence of the glass plate.[11] However a value of p_{c2} of the order of 0.5 to 0.6 is reasonable for two-dimensional lattices with a coordination number around 3 to 4 (Ref. 4).

The value of $p_c(\infty)$ and the best choice of the exponent ν_3 associated with the variation of form (3) are obtained by a classical procedure: We plot $p_c(d)$ as a function of $(d)^{-1/\nu_3}$ for different values of the exponent and we look for the best linear variation. The set of values $p_c(\infty) = 0.287$ and $\nu = 0.85 \pm 0.1$ are obtained in Fig. 4 if the first four data points are used. The value of ν_3 is consistent with published results in three dimensions.[2] In Table I, we compare our results with those given by Straley.[2]

TABLE I. Comparison of critical exponents t (conductivity) and ν (correlation length) in 2D and 3D, as obtained in our measurements with those given by Straley (Ref. 2).

	Straley	Our work
t_2	1.1 ± 0.05	1.25 ± 0.10
t_3	1.725 ± 0.01	1.85 ± 0.10
ν_3	$0.82;0.9 \pm 0.05$	0.85 ± 0.1
ν_2	$1.34;1.33 \pm 0.04$	

B. Conductivity

Figures 5 and 6 give the variation of conductivity for a thin ($d = 0.06$ mm) and a thick ($d = 2$ mm) film above their respective thresholds $p_c(d)$. In the former case, we find a linear variation over two decades of conductivity from which we obtain a critical exponent $t = 1.25 \pm 0.10$. The value is consistent with the two-dimensional exponent t_2 determined from numerical and simulation experiments. On the other hand, in the case of the thicker films, the variation indicates a marked cusp. The linear variation near $p_c(d)$ can again be fitted with a linear variation leading to an exponent $t = 1.28 \pm 0.12$ consistent with the two-dimensional exponent t_2. However, the variation becomes faster for a larger distance from threshold as might be anticipated from the crossover to a three-dimensional problem with an exponent $t_3 = 1.73$ (larger than t_2).

It seems reasonable (although not completely obvi-

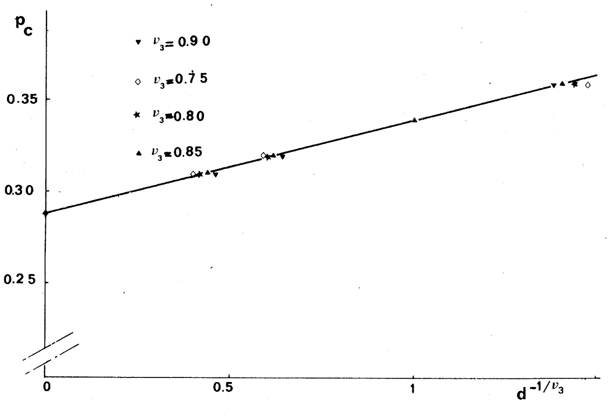

FIG. 4. Corresponds to the data points near $1/d = 0$ on Fig. 3, in units d^{-1/ν_3} vs p for different values of ν_3. The best linear variation is used to get ν_3 as well as the extrapolated value $p_c(\infty)$ [see form (3)].

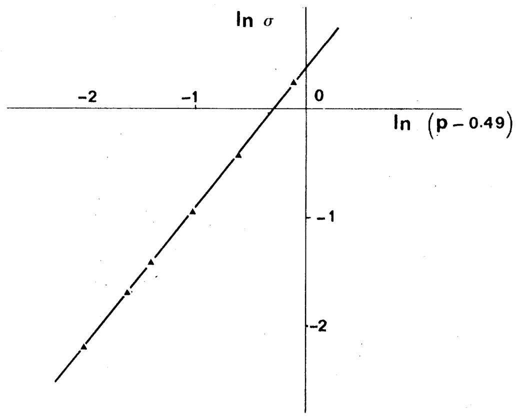

FIG. 5. Log-log plot of the conductivity vs $p - p_c(d)$ for a thin film, $d = 0.06$ mm, showing the slope $t = 1.25 \pm 0.10$ characteristic of the thin-film behavior.

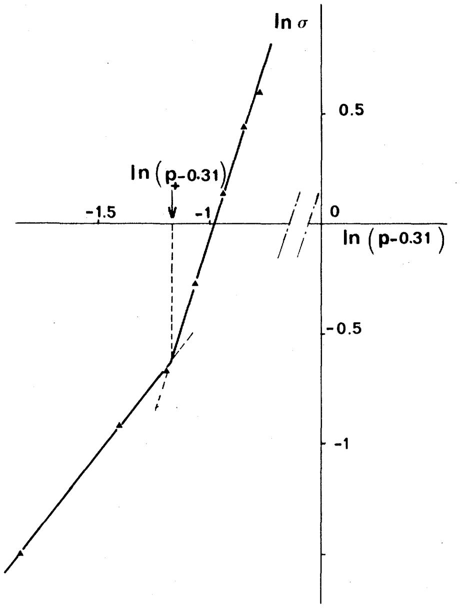

FIG. 6. Log-log plot of σ vs $p - p_c(d)$ for $d = 2$ mm showing a slope $t = 1.28 \pm 0.1$ similar to Fig. 5 and close enough to $p_c(d)$. The intercept is associated with the crossover value $p_+ = 0.38$. A similar sharp break with practically the same value p_+ was obtained by using the value p_{c3} instead of $p_c(d)$ on the abscissa.

ous) to characterize the behavior far from p_c by expressing the critical behavior in terms of the distance to the three-dimensional threshold $p_c(\infty)$. By doing so, we get a value of the exponent $t = 1.5 \pm 0.10$ which agrees reasonably well with the value of t_3.

The variation of the conductivity $\sigma(p)$ for thick films also leads to a determination of p_+. The crossover value, obtained from the intercept of the two linear variations on Fig. 6, appears to be sharply defined, but this might be exaggerated by the construction. We have indicated in Fig. 3 values of p_+ determined for two different film thicknesses. The variation reproduces roughly that of the threshold $p_c(d)$ as expected from the discussion of Sec. II. In order to establish a closer contact with the analysis of the conductivity in Sec. II we normalize the value of σ obtained for different film thicknesses d_2 to that of a reference film (of thickness $d_1 = 1$ mm), with choices of p such that

$$[p_1 - p_c(d_1)] = [p_2 - p_c(d_2)] = 0.1 \ .$$

We suppose that on this interval the power law Eq. (1) is valid near the threshold.

From Eq. (16), we expect

$$\sigma_1/\sigma_2 = (d_2/d_1)^{(t_3-t_2)/\nu_3} \ . \tag{18}$$

From a log-log plot of the two ratios given in Fig. 7 we get a value 0.70 for the slope to be compared with $(t_2 - t_3)/\nu_3$. This determination is compatible with the values for the three exponents given in the Table I.

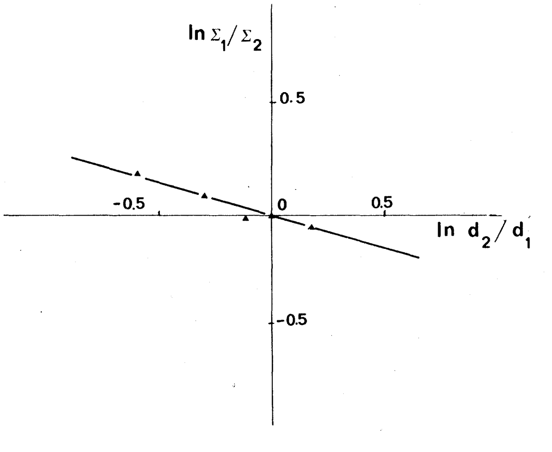

FIG. 7. Determination of the ratio $(t_3 - t_2)/\nu_3$ defined in the model of Sec. II was made by comparing the conductances Σ_2 of films of various thicknesses d_2 to a reference film d_1 of conductance Σ_1.

In a recent letter, Deutscher and Rappaport[12] have shown that thin Pb-Ge composite films with a thickness equal to four times the average grain size showed a threshold and a conductivity exponent approaching two-dimensional results. Unpublished[13] results on the variation of threshold with thickness by the same authors indicate a behavior qualitatively similar to our result of Fig. 3. An interesting feature of the work of Ref. 12, which uses the joint measurement of the superconducting critical current, is that it makes a prediction for the critical exponent μ giving the divergence of the path length $L = (p - p_c)^{-\mu}$, between two nodes of a superlattice of average mesh size ξ.[14] The independent analyses of Skal and Shklovskii[8] and of de Gennes[9] based on this superlattice hypothesis lead to a scaling relation for the conductivity exponent

$$t_D = (D-2)\nu_D + \mu \ , \tag{19}$$

where D is the dimensionality of space. By comparing data on 3D Al-Ge films and the 2D Pb-Ge films. Deutscher and Rappaport show that μ should be of the order of ν_3 in 3D, which is a reasonable (although not justified) result but that it should be smaller than ν_2 in 2D, which is impossible. This means that Eq. (19) is no longer valid.

Our analysis of form (8) leads to a value of 0.70 for the exponent $(t_2 - t_3)/\nu_3$ which can be written, using Eq. (19), as

$$1 - (t_2 - t_3)/\nu_3 = (\mu_2 - \mu_3)/\nu_3 \ ,$$

leading to a value of $\mu_2 - \mu_3 = 0.26$.

V. CONCLUSIONS

The experiments above are a first attempt to simulate the dimensionality crossover in a percolation problem. Such a discussion can have important practical applications as many random experimental systems to which percolation models are applied are done with a finite geometry. Let us quote for example the discussion of Kirkpatrick and Mayadas[15] dealing with the role of limited geometry in the problem of electrical conductivity of narrow heterogeneous strips and some problems of limited penetration of fluids into porous channels of narrow width, discussed in de Gennes and Guyon.[16]

Finally we would like to point out some analogies between the dimensional crossover discussed here due to finite thickness in the limit $1/d \rightarrow 0$ and effects related to crossover met in thermodynamic systems. Size effects in films have been studied in many experimental systems. With a proper consideration of boundary effects, the shift of critical threshold can be estimated by comparing the value of the correlation length at threshold with d as is done in the present study.[6,7]

The existence of anisotropy in a bulk system also leads to a dimensionality crossover but with quite different characteristics: Harbus and Stanley[17] have considered an anisotropic magnetic Ising problem with a small value of the ratio R between the exchange energies for bonds perpendicular and parallel to a reference plane, $J_{\parallel}/J_{\perp}=R$. In this problem the crossover is from 3D to 2D (the classical Ising problem) when $R \rightarrow 0$ instead of 2D to 3D when $1/d \rightarrow 0$ as in the present case. Their analysis (for which they coin the expression "double-power-law behavior") leads to an expression for the susceptibility [from Eq. (2a) of Ref. 17] which displays analogies with the conductivity result (from Ref. 15). In both cases a prediction is made for the amplitude as well as for the critical exponent. This has been made possible because two asymptotic limits are considered in the evaluation of the critical variable. An extension of the anisotropy problem to anisotropic percolation (with $p_{\parallel}/p_{\perp}=R$) has been considered recently by Redner and Stanley[18] but appears to be more complex than the present size-effect problem where a renormalization adjustment has been used. Anisotropy effects can possibly play a role in the present experiments. In order to analyze directly this effect we are developing simulations on anisotropic bulk systems.

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