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LETTER TO THE EDITOR

Transport in a two-component randomly composite material: scaling theory and computer simulations of termite diffusion near the superconducting limit

Armin Bunde†, Antonio Coniglio, Daniel C Hong and H Eugene Stanley

Center for Polymer Studies‡ and Department of Physics, Boston University, Boston MA 02215, USA

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Abstract. The question of transport in a random two-component mixture is addressed. To this end, two models are precisely formulated that effectively extend to two-component mixtures the de Gennes ant model of one-component systems. We develop and test a scaling theory, and we solve some of the problems associated with the limit where one of the components is superconducting. Our work provides the first practical realisation of the termite model of a random superconducting network, which performs a normal walk in the normal regions of the material but performs a new and unique form of random walk in the superconducting regions. We find that the divergence of the electrical conductivity at the percolation threshold can be described by this random walk, and that the critical exponent s is given by $s = 1.3 \pm 0.1$ in $d = 2$. If we perturb away from the pure superconducting limit, we find that the electrical properties can still be described by the random walk model, with a crossover exponent $\phi \simeq 0.4$ ($d = 2$). Moreover, we find that the diffusion constant in this region is described by a scaling form, so that data can be made to collapse upon a single curve whose form is governed by the exponents s and ϕ.

The problem of diffusion and transport in random materials has been the subject of considerable recent experimental and theoretical interest (de Gennes 1976, Alexander and Orbach 1982, Gefen *et al* 1983, Ben-Avraham and Havlin 1982, Laibowitz and Gefen 1984). This arises in part because of the fundamental scientific questions that arise when seeking to describe how the laws of physics are modified for such complex materials, and in part because of the important realisations in nature of such materials ranging from porous rock to the viscosity of gels (Deutscher *et al* 1983, Jouhier *et al* 1983, Stanley and Coniglio 1984).

One prototype system that has been the object of considerable recent investigation is the *random resistor network* (RRN). In its simplest 'one-component' form, one imagines a lattice each of whose bonds is occupied with probability p by a resistor of resistance R. As p approaches the percolation threshold p_c from above, the conductivity Σ of the RRN approaches zero as $\Sigma \sim \xi^{-\zeta_R/\nu}$ where ξ is the correlation length. Conventionally, one approaches the RRN using techniques based on Kirchoff's laws, which of course apply to the RRN (as well as to the case $p = 1$). A tremendous conceptual advance, which affected our way of thinking about the RRN (and also our way of computing), occurred in 1976 when de Gennes recognised (de Gennes 1976) that one

† Permanent address: Fachbereich Physik, Universität Konstanz, 7750 Konstanz, West Germany.
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could equally think of the RRN as a diffusion problem, since the Einstein relation connecting diffusion to resistivity applies regardless of whether or not the system is random (Scher and Lax 1973). His term 'ant in a labyrinth' to describe the random walker on a random substrate has led to many new results for the RRN (Alexander and Orbach 1982, Gefen *et al* 1983, Ben-Avraham and Havlin 1982, Laibowitz and Gefen 1984, Deutscher *et al* 1983, Jouhier *et al* 1983, Straley 1977, Rammal and Toulouse 1983).

More recently, interest has focussed on an *opposite* extreme of one-component network, the *random superconducting network* (RSN), (de Gennes 1980, Coniglio and Stanley 1984, Herrmann *et al* 1984) in large part due to its applications in materials science and polymer science; e.g., the RSN may describe the shear viscosity of a gel near the gel threshold p_c and also describes the DC dielectric constant of a metal-insulator mixture (Wilkinson *et al* 1983). In contrast with the RRN, the conductivity diverges to infinity as p_c is approached.

'Real' composite materials are often in the intermediate zone between the extremes of the RRN and the RSN. For this reason, one can speak of a *general two-component network* where bonds have conductance σ_A with probability p and conductance σ_B with probability $1-p$ (Efros and Shklovskii 1976, Bergman and Imry 1977, Sen 1981). Clearly the RRN is recovered in the limit $\sigma_B \to 0$, and the RSN in the limit $\sigma_A \to \infty$ (figure 1(*a*)).

Here we propose a novel approach to the two-component network in which the traditional Kirchoff law approach is replaced by a random walker obeying certain rules (figure 1(*b*)). In a sense, we replace the de Gennes ant (de Gennes 1976) and termite (de Gennes 1980, Coniglio and Stanley 1984) by a more general sort of 'hybrid

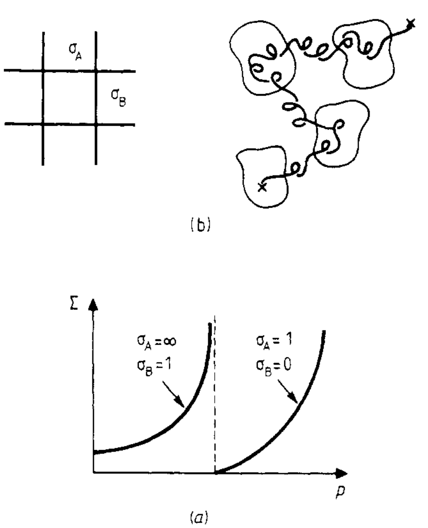

Figure 1. (*a*) The traditional Kirchoff law approach to the random two-component mixture with conductivity σ_A and σ_B is replaced by a random walker which obeys certain rules discussed in the text. (*b*) In the two extreme limits, this model properly describes the de Gennes ant [$\sigma_A = 1$, $\sigma_B = 0$] and the de Gennes termite [$\sigma_A = \infty$, $\sigma_B = 1$].

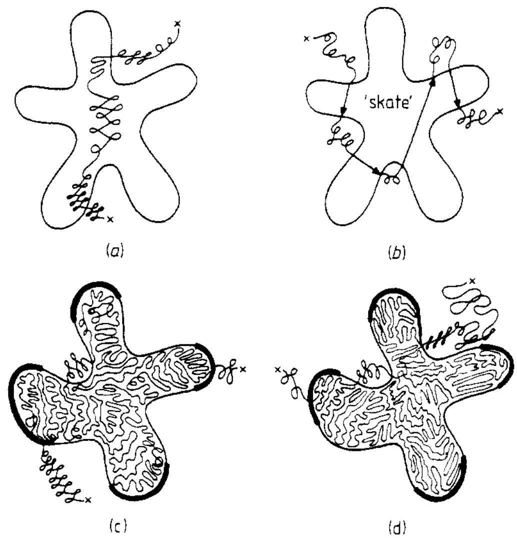

Figure 2. Schematic illustration of the four termite models considered in this paper; for definitions see table 1. (*a*) 'stopwatch' termite model, (*b*) 'skating' termite model, (*c*) 'Boston' termite 1, and (*d*) 'Boston' termite 2 (see also table 1).

animal' whose rules of motion reduce to those of the ant and termite at the two appropriate limits. Accordingly, the goal is to find a set of rules whereby a random walker in the two-component composite reproduces the desired behaviour.

The basic idea of any termite model is different diffusion rules on and off the superconducting cluster (de Gennes 1980). A simple and very tractable model is the so-called 'stopwatch' termite: the clock is stopped whenever the termite walks on a superconducting cluster. Since this is the only effect of the cluster's presence, the trace (or 'trail') of the stopwatch termite is the same as the trace of a simple random walk†. We found, by simulation and by analytic arguments, that $D(p)=1/(1-p)$. Thus a severe drawback is that the stopwatch termite has no singular behaviour at p_c.

A second early model for which we have done calculations is the 'skating' termite (Coniglio and Stanley 1983). Here the termite proceeds with a ballistic trajectory whenever it enters a superconducting cluster (it 'skates'). We found that the skating termite, like the stopwatch termite, has no singular behaviour at p_c except in $d=1$. Table 1 and figure 2 are designed to clarify the relations between the various termite models we have studied. In what follows, we formulate two new models. The first is for the general case of a two-component composite material while the second is for the behaviour in the vicinity of the RSN limit. Calculations presented below for both models provide the first numerical results for the superconductivity exponent in terms of the properties of a random walk. Our work has the virtue that only time ensemble averages are considered.

Table 1. The four termite models for which we have carried out simulations.

Model	Definition	Critical at p_c?
Stopwatch termite	Clock stops when on superconducting cluster; *trail is identical to trail of random walk.*	No
Skating termite	Termite has ballistic trajectory when on cluster.	No
Boston termite 1	Similar to stopwatch termite, but trail is *not* a random walk since next step is weighted in favour of superconducting site.	Yes
Boston termite 2	Similar to 1, except clock is turned off when termite is on a cluster.	Yes

Boston termite 1‡. Physically speaking, we expect that a region of low resistance should correspond to a region where the walker ('termite') moves faster. For example, in the de Gennes ant problem (the RRN limit of our general model), the walker does not move off the cluster since $R=\infty$ there. Guided by these physical considerations, we first set up a time scale precisely ('step 1'). From the Einstein relation, we have $\sigma_A \sim D_A \sim \ell^2/\tau_A$, where D_A is the diffusion constant in the region A, ℓ the mean free path, and τ_A the characteristic time to travel a distance ℓ. The same reasoning applies to species B, so $\sigma_B \sim D_B \sim \ell^2/\tau_B$ and hence

$$\tau_A/\tau_B = \sigma_B/\sigma_A. \tag{1a}$$

The next and final step in formulating our general model is to identify the physically

† We shall see below that the stopwatch termite is identical to a special case of our 'Boston termite 1'.
‡ This model was introduced in footnote 6 of Coniglio and Stanley (1984).

appropriate transition rate ('step 2')†. To accomplish this, we make the *ansatz*‡ that $\Pi_i = k\tau_i^{-1}$ ($i = 1, 2, \ldots, z$, where z is the coordination number), where Π_i is the probability that the termite takes a step to its ith nearest neighbour, $\tau_i^{-1} = \sigma_A$ or σ_B, depending if site i is species A or species B, and k is a normalisation constant. Since $\Sigma_{i=1}^{z}\Pi_i = 1$, we have

$$\Pi_i = \tau_i^{-1}/\Sigma_i\tau_i^{-1}. \tag{1b}$$

In one unit of time, the walker takes $f_A = \tau_A^{-1}$ steps if he is on a large cluster of A sites and $f_B = \tau_B^{-1}$ steps if he is on a large cluster of B sites. The total elapsed time, $t = N_A\tau_A + N_B\tau_B$, is related to the mean-square displacement and the diffusion constant by

$$\langle r^2\rangle \sim D(f_A, f_B, p)t, \tag{2a}$$

where N_A and N_B are the total number of steps in A and B sites.

RSN and RRN limits. The limit $f_A \to \infty$ with N_A/f_A non-zero, $f_B = 1$, gives, for t large, the long-time behaviour of a walk that covers uniformly an A cluster before stepping out of it. We propose to use this walk to describe the critical behaviour of the RSN. In the RSN limit we have

$$\lim_{f_A\to\infty} D(f_A, 1, p) \sim |p - p_c|^{-s}, \tag{2b}$$

since $\Sigma \sim D$ by the Einstein relation.

The RRN, on the other hand, is described by the limit $f_B \to 0$ with $f_A = 1$, and

$$\lim_{f_B\to 0} D(1, f_B, p) \sim (p - p_c)^{\mu}, \tag{2c}$$

where μ is the conductivity exponent.

General case. If we choose f_A and f_B both finite and different from zero, then we describe the general situation of a particle diffusing in a random composite medium. The basic object of interest is the conductivity $\Sigma(\sigma_A, \sigma_B, \varepsilon)$, where $\varepsilon = |p - p_c|/p_c$. If we increase both bond conductances by the factor λ, we find

$$\Sigma(\lambda\sigma_A, \lambda\sigma_B, \varepsilon) = \lambda\Sigma(\sigma_A, \sigma_B, \varepsilon). \tag{3a}$$

Choosing $\lambda = 1/\sigma_A$, we find

$$\Sigma(\sigma_A, \sigma_B, \varepsilon) = \sigma_A\Sigma(1, \sigma_B/\sigma_A, \varepsilon). \tag{3b}$$

† A model with step 1 only (no step 2) is called the stopwatch termite (see discussion in text).

‡ A detailed justification of the *ansatz* is given in Hong *et al* (1984). One heuristic argument (F Leyvraz, private communication) is the following. The macroscopic equations for the current and potential distribution in an arbitrary inhomogeneous medium having conductivity $\sigma(x)$ are:

$$0 = \operatorname{div} j = \operatorname{div}[\sigma(x)\nabla\phi] = \sigma(x)\Delta\phi + \nabla\sigma(x)\cdot\nabla\phi(x).$$

The function $\phi(x)$ can therefore be understood as the stationary state of the equation $\partial\phi/\partial t = \sigma(x)\Delta\phi + \nabla\sigma(x)\cdot\nabla\phi(x)$. This equation, however, exactly describes a diffusion with local drift $\nabla\sigma(x)$ and local diffusion constant $\sigma(x)$. The appearance of the drift term is responsible for the relative probabilities going to the high or low conductivity region when starting from an interface site, as introduced in both models 1 and 2 of this paper.

At $\varepsilon=0$, we expect a power law singularity, (Straley 1976)

$$\Sigma(\sigma_A, \sigma_B, 0) \sim \sigma_A(\sigma_B/\sigma_A)^u \qquad (p=p_c), \tag{4a}$$

where u is a critical exponent. For $|\varepsilon| \ll 1$, this must be modified by a scaling function,

$$\Sigma(\sigma_A, \sigma_B, \varepsilon) \sim \sigma_A(\sigma_B/\sigma_A)^u f[\varepsilon(\sigma_A/\sigma_B)^\phi] \qquad (p \neq p_c), \tag{4b}$$

where ϕ is a second exponent. Below we shall express the new exponents ϕ and u in terms of conductivity exponents μ and s.

Termite limit. ($\sigma_B=1$, $\sigma_A \to \infty$). In this limit, we know that $\Sigma \sim \varepsilon^{-s}$ so we assume $f(x) \sim x^{-s}$, and have

$$\Sigma \sim \sigma_A^{1-u}\sigma_B^u[\varepsilon(\sigma_A/\sigma_B)^\phi]^{-s}. \tag{4c}$$

In order that there should be no dependence on σ_A, we must have $(1-u)/s=\phi$.

Ant limit. ($\sigma_A=1$, $\sigma_B \to 0$). Since $\Sigma \sim \varepsilon^\mu$, we assume $f(x) \sim x^\mu$. In order that the σ_B dependence should vanish, we must have $\phi = u/\mu$. We have derived two equations for the two unknowns u and ϕ, in terms of μ and s, from which we obtain $u=\mu/(\mu+s)$ and $\phi=1/(\mu+s)$.

Since $\Sigma \sim D$, it follows from (4b) that D will be described by a scaling equation of the form

$$D \sim f_A^{1-u} f_B^u H_\pm(\varepsilon(f_A/f_B)^\phi). \tag{5a}$$

Termite limit. ($f_A \to \infty$, $f_B=1$). For fixed p below p_c, D will converge to the constant D_∞ for $f_A \to \infty$. Hence $H_-(x) \sim x^{-s}$ $(x \gg 1)$. For fixed p above p_c, Σ is governed by the infinite network. Thus we expect $D \sim f_A$ so that $H_+(x) \sim x^\mu$ $(x \gg 1)$. In $d=2$, duality argument (Straley 1977) yields $\mu=s$. Thus we can show that for all x (Hong *et al* 1984),

$$h_+(x) = 1/h_-(x). \tag{5b}$$

where $h_\pm(x) = H_\pm(x)/H_\pm(0)$.

Ant limit. ($f_A=1, f_B \to 0$). In this limit, we might allow for a different functional form for D,

$$D = f_A^{1-u} f_B^u A_\pm(\varepsilon(f_A/f_B)^\phi). \tag{5c}$$

However, the same scaling argument used above for the termite limit leads to the same asymptotic functional behaviour for $A_\pm(x)$, $A_+(x) \sim x^\mu$ and $A_-(x) \sim x^{-s}$. Thus we expect the same reciprocal relation (5b) for ant limit $a_+(x) = 1/a_-(x)$, with $a_\pm(x) = A_\pm(x)/A_\pm(0)$. The intriguing result that $a_\pm(x) = h_\pm(x)$ is discussed in Hong *et al* (1984).

Boston termite 2. Model 2 is motivated in part by our intuitive understanding of a superconducting cluster, namely that all the superconducting cluster sites are short circuited. Thus the walker will be with the same probability on each perimeter site of the cluster, and will perform a simple random walk on the normal sites. More precisely, when the walker is on a normal cluster, it chooses at random any direction and proceeds to this neighbour regardless of whether it is a normal site or a superconducting site, the corresponding step frequency $f_N=1$. When the walker is on a superconducting site, it chooses at random in which direction its next attempt to move to a nearest-neighbour site will be. (a) If the attempted site belongs to a superconducting cluster, the walker steps. (b) If the attempted site belongs to a normal cluster, then the walker can either step or wait, with probabilities Π_{SN} and $1-\Pi_{SN}$ respectively. The time is not counted when the walker is on a superconducting cluster. The limit $\Pi_{SN}\to 1$ describes the motion of the termite when the superconducting sites have all been short circuited†. The number of steps spent on a superconducting cluster in unit time is roughly given by $N_S \sim (1-\Pi_{SN})^{-1}$, identical to f_S. For this model, the scaling relation (3) also holds near the superconducting limit $N_S^{-1} \sim f_S^{-1} \to 0$, $f_N^{-1} = 1$. Clearly f_S/f_N corresponds to f in model 1 and we will use the same notation f in the following to simplify the discussion.

Direct simulation. We have succeeded in direct computer simulations of both model 1 and model 2. The simulation was carried out on square lattice of size 800×800 (model 1) and of size 1000×1000 (model 2). The random AB lattice was generated by choosing an A site with probability p, and a B site with probability $1-p$. The starting points for the walker were chosen randomly. Then using the Monte Carlo method walks were simulated according to the rules discussed above. For each walk we calculated the square of the Pythagorean distance, r^2, as a function of time t. To obtain the mean square distance $\langle r^2\rangle$, we averaged over typically 1000 cluster configurations (sometimes we made more than one walk on each configuration).

The asymptotic regime of the walk (where $\langle r^2(t)\rangle = Dt$) was reached after about 400 time steps in model 1 and 200 time steps in model 2. The corresponding number of actual moves of the walker was typically $1/f$ times larger. We have calculated $\langle r^2(t)\rangle$ for t up to 2000 in model 1 and 1000 in model 2 and varied f from 10 up to 20 000 (for p close to p_c). To put the scaling assumption (3) to a first test, we have calculated D at $p=p_c=0.592\,77$ (Gebele 1984) as a function of f. From duality arguments, valid for $d=2$ (Straley 1977), it follows that $\mu = s$ and therefore $u=0.5$. Our results, $u=0.5\pm 0.02$ (see figure 3), confirm this value. By this, we also confirm indirectly the duality argument.

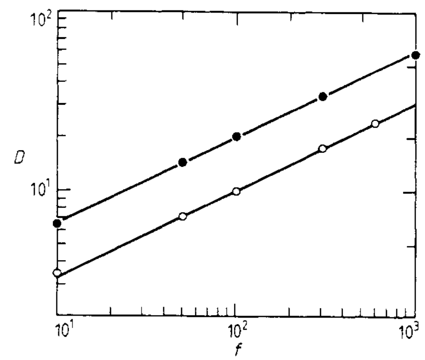

Figure 3. Dependence on $f=f_A/f_B$ of the diffusion constant $D(p,f)$ at the percolation threshold for model 1 and model 2. The slope of the curve, $u=0.5$, is expected from (3) by a duality argument.

† This case was discussed at the end of footnote 6 in Coniglio and Stanley (1984).

From (4) we expect data collapsing, when $D/(H_{\pm}(0)f^{1/2})$ is plotted against $|p-p_c|f^{\phi}$ (figure 4), with $\phi=(\mu+s)^{-1}=(2s)^{-1}$. We have checked this prediction as well as the reciprocal relation (5*b*) by varying ϕ and found complete data collapsing for $\phi=0.40\pm0.03$ which then gives for the superconductivity exponent $s=1.3\pm0.1$. This value is in agreement with the widely accepted value for s (Zabolitsky 1984, Herrmann *et al* 1984, Hong *et al* 1984, Lobb and Frank 1984). The scaling functions behave identically in both models, which shows clearly that *both models belong to the same universality class*†.

In order to determine the diffusion constant in the superconductivity limit at constant $p-p_c$ we have studied $D(1,f,p)$ for f up to 20 000 and performed the final extrapolation to $D(1,\infty,p)$ using the scaling function of figure 2. Our findings for $D(1,\infty,p)$ for both models are shown in figure 5. The slope again is close to the accepted value $s\simeq1.3$.

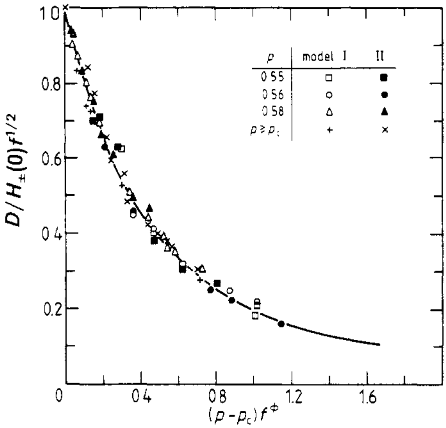

Figure 4. Dependence of the *scaled* variables $D/H_{\pm}(0)f^{1/2}$ upon εf^{ϕ}. The fact that the data for several values of f 'collapse' on the same curve supports the scaling relation (3). The best data collapsing is found for the choice $s=1.3$. Scaling functions above and below p_c are related by reciprocal relation (see (5)).

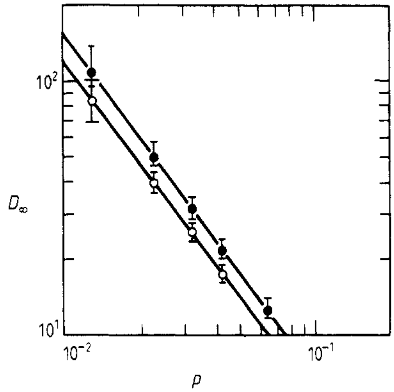

Figure 5. Diffusion constant $D(1,f,p)$ of the termite limit ($f\to\infty$) is plotted against ε below the percolation threshold. Since $D(1,\infty,p)$ is proportional to the bulk conductivity Σ, the slope gives s (we find $s\simeq1.3$).

In summary, we have addressed the question of transport in a random two-component mixture. We have found that a simple random walk, with suitably chosen rules, is sufficient to describe the rich physics of this problem. We have made extensive simulations of two different specific models, and obtained results in agreement with those obtained from conventional methods. After this work was completed, we learned of an approach (Adler *et al* 1985) for the RSN limit, which is quite similar to our 'Boston termite 2' model in the limit $f\to\infty$; model 2 is of course more general in that it describes the *crossover* from the pure RNS limit to the general case of mixed conductors.

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† The reason behind this is that $N_A\tau_A/N_B\tau_B$ in model 1 is finite. Empirically we found that this value is close to $p/(1-p)$.

References

Adler J, Aharony A and Stauffer D 1985 *J. Phys. A: Math. Gen.* **18** L000
Alexander S and Orbach R 1982 *J. Physique Lett.* **43** L625
Ben-Avraham D and Havlin S 1982 *J. Phys. A: Math. Gen.* **15** L691
Bergman D J and Imry Y 1977 *Phys. Rev. Lett.* **39** 1222
Coniglio A and Stanley H E 1983 unpublished report
—— 1984 *Phys. Rev. Lett.* **52** 1068
de Gennes P G 1976 *Recherche* **7** 919
—— 1980 *J. Physique Colloq.* **41** C3-17
Deutscher G, Kapitulnik A and Rappaport M 1983 *Ann. Israel Phys. Soc.* **5** 207
Efros A L and Shklovskii B I 1976 *Phys. Status Solidi* **76** 475
Gebele T 1984 *J. Phys. A: Math. Gen.* **17** L51
Gefen Y, Aharony A and Alexander S 1983 *Phys. Rev. Lett.* **50** 77
Herrmann H J, Derrida D and Vannimenus J 1984 *Phys. Rev.* B **30** 4080
Hong D C, Coniglio A, Bunde A and Stanley H E 1984 *Preprint*
Hong D C, Havlin S, Herrmann H J and Stanley H E 1984 *Phys. Rev.* B **30** 4083
Jouhier B, Allain C, Gauthier-Manuel B and Guyon E 1983 *Ann. Israel Phys. Soc.* **5** 167
Laibowitz R B and Gefen Y 1984 *Phys. Rev. Lett.* **53** 380
Lobb C J and Frank D J 1984 *Phys. Rev.* B **30** 4090
Rammal R and Toulouse G 1983 *J. Physique Lett.* **44** L13
Scher H and Lax M 1973 *Phys. Rev.* B **10** 4491
Sen P N 1981 *Appl. Phys. Lett.* **39** 667
Stanley H E and Coniglio A 1984 *Phys. Rev.* B **29** 522
Straley J 1976 *J. Phys C: Solid State Phys.* **9** 783
—— 1977 *Phys. Rev.* B **15** 5733
Wilkinson D, Langer J S and Sen P N 1983 *Phys. Rev.* B **28** 1081
Zabolitsky J G 1984 *Phys. Rev.* B **30** 4077