Screening of Deeply Invaginated Clusters and the Critical Behavior of the Random Superconducting Network

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Starting with an expression for the fractal dimension d_u of the unscreened perimeter of an arbitrary fractal of dimension d_f, there are derived for the random superconducting network the results $\tilde{s}=(2-d)+d_u$, from which follow $\tilde{\varphi}_s=d_u$ and $d_w=d-d_u$. Here $\tilde{s}$ is the conductivity exponent, $\tilde{\varphi}_s$ the conductance exponent, and d_w the fractal dimension of a random walk on the network. For $d=2$, these results differ from the Alexander-Orbach conjecture by 0.3%.

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How does one define the "surface" of an irregular ramified object, like a biological macromolecule or crosslinked gel? This question is of great current interest as one designs triggering systems that operate by diffusing to specific "target sites" buried at some point on the surface of a large invaginated molecular structure.[1] At first sight, it might seem that this is a trivial question that can be answered geometrically. Indeed, for percolation clusters ("gel macromolecules") it is rigorously known that the number of surface sites is proportional to the number of volume sites. However, of practical importance is not the total number of surface sites but rather the number of surface sites that can be "reached" by a given penetrating object (e.g., the diffusion of an ion into the macromolecule). We shall refer to this as the number of "unscreened" surface sites, M_u. We shall see that M_u is vastly smaller than the total number of surface sites, since the majority of sites are sufficiently "buried" in the macromolecule that they are unreachable for all practical purposes.

We shall first obtain a quantitative prediction for the exponent d_u characterizing the fashion in which M_u increases with the molecular diameter ξ, $M_u \sim \xi^{d_u}$. For an ordinary Euclidean object (e.g., a hypersphere), $d_u=d-1$ of course. To calculate d_u for a general fractal of dimension d_f, we consider the mean penetration depth λ (Fig. 1). Then

$$M_u \sim \xi^{d_f-1}. \tag{1}$$

To see how ξ depends on λ, we consider[2] the average number of steps $N_w^* \sim \lambda^{d_p}$ that a projectile of fractal dimension d_p takes before being absorbed in the shell of width λ. We expect $N_w^* \sim 1/\rho$, where $\rho = M_{\rm tot}/\xi^d \sim \xi^{d_f-d}$ is the number density. Hence $\lambda \sim \xi^{(d-d_f)/d_p}$. Substituting in (1), we have[3]

$$d_u=(d_f-1)+(d-d_f)/d_p. \tag{2}$$

Note that (i) if $d_p=d-d_f$ (the "codimension" of the fractal), then the projectile can penetrate the entire surface: we have $\lambda \sim \xi$ and $d_u=d_f$; (ii) if $d_p \rightarrow \infty$, then $\lambda \sim \xi^0$ and $d_u=d_f-1$.

The above considerations of an "unscreened perimeter" apply also when a particle attempts to *leave* a macromolecule as well as to *penetrate* it (Fig. 1). For example, we can show that (2) can be used to obtain the region of a percolation cluster from which a random walk can "escape" and hence a quantitative expression for the exponent $\tilde{s}$ describing the divergence of the electrical conductivity σ of a random superconducting network. In this system, a fraction p of the bonds of a lattice carry zero resistance and the rest carry unit resistance. This model is also relevant to the divergence of the shear viscosity of a polymer gel.[4] To describe the essential physics of this problem, deGennes suggested that we consider a novel form of random walker, which he called a "termite," which performs a normal random walk ($d_p=2$) when *off* the cluster (the "normal" bonds) but which moves ex-

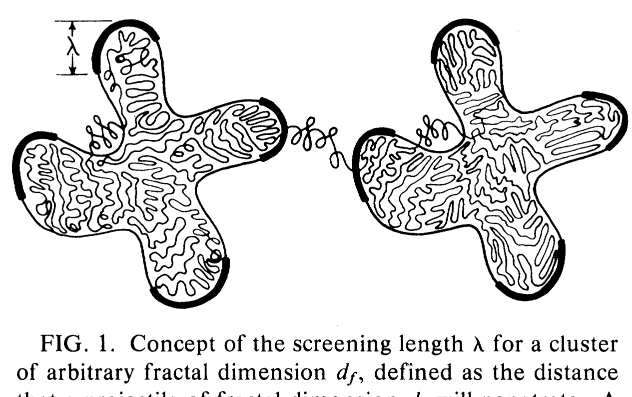

FIG. 1. Concept of the screening length λ for a cluster of arbitrary fractal dimension d_f, defined as the distance that a projectile of fractal dimension d_p will penetrate. A particle *leaving* the unscreened perimeter, indicated by a heavy line, escapes and may be captured by the unscreened perimeter of another cluster.

tremely rapidly when *on* the clusters (the "superconducting" bonds).[4] From the Einstein relation, he concluded

$$\sigma \sim D \sim R^2/\tau, \tag{3}$$

where $R^2 \sim \xi^{2-(d-d_f)}$ is the mean square diameter of a cluster[5] and τ^{-1} is the characteristic frequency for the termite to jump from one cluster to another (Fig. 1).[6] Thus the termite is the complement of the "ant" which models the conductivity of the random-resistor network above the percolation threshold by being required to execute a normal random walk but only on the percolation cluster.[7–9] By definition, if the termite leaves the cluster at a screened perimeter site, it reenters the cluster. Since the termite spends the same amount of time everywhere in the cluster[4,6] and can jump into another cluster only from an unscreened site, we expect that τ^{-1} scales as

$$\tau^{-1} \sim M_u/M_{\text{tot}} \sim \xi^{d_u - d_f}. \tag{4}$$

To evaluate d_u, we need to choose d_p in (2). For $d_f > 2$, a random walk will penetrate the invaginated cluster more than another cluster so we set $d_p = 2$. For $d_f < 2$, the reverse is true and we choose $d_p = d_f$. Thus

$$d_u = \begin{cases} (d+d_f)/2 - 1 \quad (d_f \geqslant 2), & \text{(5a)} \\ d/d_f + d_f - 2 \quad (d_f \leqslant 2). & \text{(5b)} \end{cases}$$

Combining (3)–(5), we find $\sigma \sim \xi^{\tilde{s}}$ with

$$\tilde{s} = 2 - d + d_u = \begin{cases} 1-(d-d_f)/2 \quad (d_f \geqslant 2), & \text{(6a)} \\ d/d_f + d_f - d \quad (d_f \leqslant 2). & \text{(6b)} \end{cases}$$

Relation (6a) was recently conjectured to hold *for all d* by Kertész,[10] but no argument supporting the conjecture was given; (6) agrees with exact results[11] for $d = 1, 6$ and is in accord with calculations of $\tilde{s}$ and d_f for $d = 2$–4. For $d = 2$, $d_f = \frac{91}{48} < 2$, and (6b) reduces to

$$\tilde{s} = 2/d_f + d_f - 2 = 0.9508. \tag{7}$$

Since $\tilde{s} = \tilde{t}$ for $d = 2$, where $\tilde{t}$ is the exponent for the random-resistor network, this result is about 0.3% larger than the Alexander-Orback[7] conjecture $\tilde{t} = \frac{1}{2} d_f = 0.9479$. Had we neglected the intercluster penetration and used $d_p = 2$ for all d, then (6a) would reduce to $\tilde{t} = \tilde{s} = d_f/2$.[10]

We can interpret our result (6) in very physical terms by noting that the superconducting clusters just below p_c play the role of the "nodes" in the "links-nodes-blobs" model of the random-resistor or gelation network just above p_c (Fig. 2). For the random-resistor network, the *conductance* between two nodes separated by a distance of the order of ξ approaches zero with an exponent $\tilde{\varphi} = \tilde{t} - (d-2)$. Similarly, for the superconducting network just below p_c, the conductance between two nodes *diverges* with an exponent $\tilde{\varphi}_s = \tilde{s} + (d-2)$. Using (6), we find that

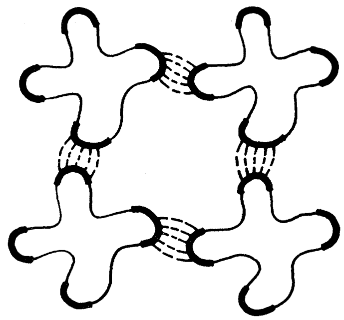

FIG. 2. Large superconducting clusters just below p_c separated by a distance of the order of ξ are connected in parallel by ξ^{d_u} resistors of order of unity joining the unscreened perimeter sites. A complementary model of the "links-nodes-blobs" model of the random-resistor network just above p_c.

$$\tilde{\varphi}_s = d_u. \tag{8}$$

This result can be interpreted as follows: ξ^{d_u} resistors (of order unity) join in parallel the unscreened perimeters of two neighboring clusters (Fig. 2).

We conclude with two remarks: (i) Note that (6) permits us to obtain an expression for the fractal dimension of the random walk performed by the termite. We can write

$$D = d\langle r^2 \rangle/dt \sim \xi^{2-d_w}, \tag{9}$$

since $t \sim \xi^{d_w}$ is the time required for an rms displacement of the order of ξ. Combining (9) and (3), we find $\tilde{s} = 2 - d_w$, with

$$d_w = d - d_u. \tag{10}$$

In "normal" diffusion, $d_w = 2(\langle r^2 \rangle \sim t)$. In the ant problem, $d_w = 2$ for $d = 1$ but $2 < d_w < 6$ for $2 < d < 6$. In the termite problem, we have a different sort of anomalous diffusion: $d_w < 2$, with $d_w = 1$ for a linear chain and $1 < d_w < 2$ for $1 < d < 6$ (Fig. 3). Moreover, (10) allows us to understand why σ does not diverge for $d = 6$: $d_f = 4$ and $d_w = 2$, and so the termite simply cannot find the incipient infinite cluster.

(ii) We can modify the original termite model to describe two domains of interest, (a) $\langle r^2 \rangle << \xi^2$ and (b) $p > p_c$. The original termite model assumes that the motion within a cluster is instantaneous. The predictions for the long-time regime,

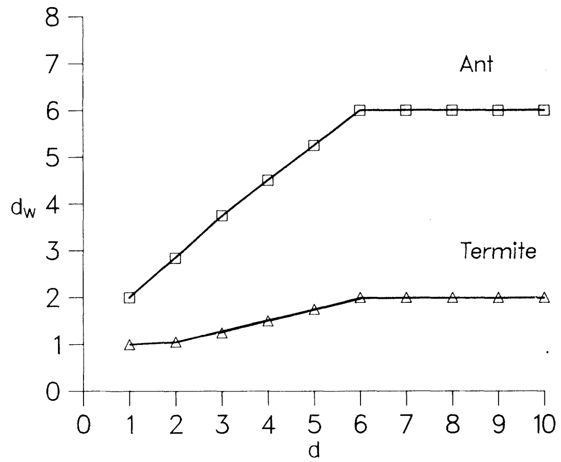

FIG. 3. Dependence on d of the fractal dimension of a random walk d_w ($t \sim \xi^{d_w}$) for anomalous diffusion modeled by the ant (squares) and by the termite (triangles). The value $d_w = 2$ corresponds to normal diffusion, while $d_w > 2$ is anomalously *slow* ("Ant") and $d_w < 2$ is anomalously *fast* ("Termite").

$r^2 >> \xi^2$, are unaffected by this assumption but for short times the termite model predicts instantaneous motion while in reality the termite must take some time to travel within a cluster. To find the motion within the cluster, we note that for $d = 1$ the problem can be solved exactly. One finds from the Langevin equation[12] that $\langle r^2 \rangle \sim t^{2/d_w}$ for $\langle r^2 \rangle << \xi^2$ with $d_w = 1$. If this behavior for short times holds for all d [with $d_w = d_w(d)$ of (10)], then we can describe both short-time and long-time behavior by the scaling form

$$\langle r^2 \rangle \sim t^{2/d_w} f_-(t/\tau^*) \quad (p < p_c), \tag{11a}$$

where $\tau^* \sim \xi^{d_w}$ is an effective collision time[13] and $f_-(x) \to 1$ for $x << 1$ and $f_-(x) \sim x^{-2/d_w+1}$ for $x >> 1$. For $p > p_c$ we expect the same long-time behavior as for $p = 1$ since for large r the motion is dominated by the infinite superconducting network with fractal dimensionality equal to d. For $p = 1$ (all bonds superconductors), it follows from the Langevin equation[12] that $\langle r^2 \rangle \sim t^2$. Scaling therefore predicts for $p > p_c$

$$\langle r^2 \rangle \sim t^{2/d_w} f_+(t/\tau^*) \quad (p > p_c), \tag{11b}$$

where $f_+(x) \to 1$ for $x << 1$ and $f_+(x) \sim x^{-2/d_w+2}$ for $x >> 1$.

In summary, we have seen that the concept of unscreened perimeter (not yet used in percolation) is relevant to the random superconducting network, and have obtained $\tilde{s} = 2 - d + d_u$, $\tilde{\varphi}_s = d_u$, and $d_w = d - d_u$, where d_u is given by (5). We conclude by noting that all the results of this paper can also be obtained if we collapse to a single point all the sites that are joined by superconducting links. The set of clusters then becomes a set of points with many normal bonds emanating from each. Since all the bonds are *normal* conductors, we can apply the random-walk concepts to these bonds. This approach appears to be more useful for the purpose of Monte Carlo simulations and will be reported on elsewhere.

Note added.—Our finding that the Alexander-Orbach conjecture should fail for $d = 2$ has not yet been unambiguously confirmed, despite very recent numerical calculations of high accuracy.[14-18] However, our result that $d_f = 2$ is the critical dimension for our problem *is* consistent with recent arguments[19] for $d_f = 2$ being a critical dimension for the breakdown of statistical independence of fluctuations of growth sites.[20]

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[6]More precisely, we can associate two jump frequencies, $\tau_n^{-1} = 1$ for the normal material and $\tau_s^{-1} >> \tau_n^{-1}$ for the superconducting material. When the termite is at given site, it can choose any one of z bonds for its next step (z is the lattice coordination number). The probability of the termite to choose bond i is given by $\tau_i^{-1}/(\sum_i \tau_i^{-1})$, where $\tau_i = \tau_s$ if the bond is superconducting and $\tau_i = \tau_n$ if the bond is normal. The limit $\tau_s^{-1} \to \infty$ describes the superconducting problem. Note that in one unit of time the termite jumps one step if in the normal region and by τ_s^{-1} steps if on a superconducting cluster. Therefore the total elapsed time is given by $t = N_n \tau_n + N_s \tau_s$, where N_n and N_s are the numbers of steps in the normal and superconducting regions, respectively. The limit $\tau_s \to 0$ with $N_s \tau_s$ finite and t large gives

the long-time behavior of the walk of the termite. Note that in this limit $N_s \to \infty$, which means that the termite covers "uniformly" the entire superconducting cluster before jumping out of it (see Fig. 1). We can generalize this model to τ_n and τ_s finite to describe a *general* random-resistor network. An alternative way is to consider all the superconducting links as short circuited. Therefore the termite will be with the same probability on each parameter site of the superconducting cluster. In this way the termite will always perform a random walk on the normal bonds. However, the topology of the lattice is rather complex because of the presence of long-range connected regions. Since the perimeter is proportional to M_{tot}, Eq. (4) still holds.

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