Family of Exponents for Laplace's Equation near a Polymer

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We study the depletion of a diffusing substance (i.e., of a scalar Laplacian field) near an absorbing fractal, consisting of a random or a self-avoiding walk. We establish a mapping between the moments $\langle u(r)^n \rangle$ of the field $u(r)$ at a distance r from a point on the absorber and the partition functions of certain star polymers. The scaling with r of each moment is governed by an independent exponent $\lambda(n)$, which we calculate to order ϵ^2 ($\epsilon = 4-d$). Nonperturbative results for the limit of high n are also given. We relate the $\lambda(n)$ to the exponents $D(n)$ of a fractal measure.

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Much recent work has been directed towards understanding the physical properties of fractals—structures which are statistically invariant under changes in spatial length scales.[1-4] In this Letter we consider the way in which a fractal interacts with a scalar Laplacian field $u(r)$ obeying

$$\nabla^2 u(r) = 0 \tag{1}$$

with boundary conditions $u=0$ on the fractal, and $u=u_\infty$, a constant, at infinity. This problem is of interest for several reasons. For example, fractal aggregates (such as fumed silica) are used as supports in heterogeneous catalysis.[5] Under many conditions, the rate of reaction is influenced by the steady-state diffusion of one or more chemical species into an aggregate. The density $u(r)$ of reactants in the neighborhood of the substrate then obeys Eq. (1); the rate of reaction at a point x on the aggregate depends on $\phi(x)$, the incident flux of the field u at that point. A closely related problem arises in random kinetic growth processes, such as diffusion-limited aggregation (DLA).[6] In these processes, a field u obeying Eq. (1) describes the probability density for incoming particles. (These particles execute random walks from infinity and are adsorbed upon first contact with the growing cluster.) The behavior of u close to the aggregate determines the distribution of probabilities $\phi(x)$ for the addition of a particle at different points x upon its perimeter. A systematic knowledge of the way an absorbing fractal modifies the surrounding field is thus important if we are to understand the nature of fractal growth in DLA and related systems.

A third reason for studying the depletion of a scalar Laplacian field near an absorbing fractal is because of a close analogy[7] with a more difficult problem—that of calculating the hydrodynamic flow around a (rigid) fractal immersed in a fluid. We expect that valuable insight into the nature of such a flow (and hence into the rheological, transport, and separation properties of fractals such as colloidal aggregates) can be gained by studying the simpler case of a scalar field.

The behavior of the field u far from an absorbing fractal of linear size R is known to be the same as that far from a solid sphere of radius comparable to R, with an absorbing boundary condition at the surface.[2,7] But this "hard sphere" picture tells us little about the behavior of the field in and immediately around the fractal itself. The present work is concerned with studying the field in this inner region. We present below new analytic results for the scaling behavior of $u(r)$ at a distance r from a randomly chosen point on an absorbing fractal, for the case when that fractal is a Gaussian random walk. We have also studied the case of a self-avoiding walk (SAW); the corresponding results will be summarized at the end. Full details of both calculations will be presented elsewhere.[8]

Our results confirm explicitly, for the first time, earlier theoretical arguments[9,10] that the incident flux $\phi(x)$ of the field u onto points on a random fractal absorber has the rich scaling structure of a "fractal measure,[11]" characterized by an infinite family of independent scaling exponents.[12] Similar behavior has been encountered in the current distribution in random resistor networks,[13] and in strange attractors.[9] For incident flux distributions, however, previous quantitative evidence for fractal measure behavior has been limited to numerical studies on some two-dimensional examples.[10,14]

In studying the field $u(r)$, we restrict our attention to the case when r is much less than R, the radius of the fractal absorber. This R obeys $R \sim M^{1/D}$, where M is the absorber's mass and D its fractal dimension; for a Gaussian random walk, $D=2$.[2] Our results are obtained through a mapping between the nth moment of the distribution of u values and the partition function of an $(n+2)$-arm star polymer, with certain (selective) excluded-volume interactions between the arms.

By this trick, we obtain a problem in polymer statistics which can be treated by well-established direct renormalization methods[15,16] for spatial dimensions d near 4. We find, by expanding to second order in $\epsilon = 4-d$, that the positive moments of $u(r)$ scale according to a new family of universal exponents $\lambda(n)$:

$$\langle u(r)^n \rangle \sim u_\infty^n (r/R)^{\lambda(n)}; \tag{2}$$

$$\lambda(n) = n[\epsilon - \epsilon^2(n-1)/4] + O(\epsilon^3). \tag{3}$$

(Here angular brackets denote ensemble average quantities.) These results are applicable for $n \lesssim \epsilon^{-1}$. For the complementary limit of $n >> \epsilon^{-1}$, we have calculated the behavior of $\lambda(n)$ nonperturbatively in dimensions $d \geqslant 3$, using general scaling results for star polymers with many arms.[8,17,18] We find

$$\lambda(n) \sim n^{1/(d-2)} \quad (3 < d < 4), \tag{4a}$$

$$\lambda(n) \sim n/\log(n) \quad (d=3). \tag{4b}$$

From the first of these forms, it is clear that the limits $\epsilon \to 0$ and $n \to \infty$ do not commute.

The results (3) and (4) are notable in that the $\lambda(n)$ for different n bear no simple relationship to one another, but remain essentially independent. In particular, they cannot be collapsed onto a "scaling law" of the form $\lambda(n) = n\lambda(1)$. Hence the probability distribution $P(u(r))$ of the field near a randomly chosen point on the absorbing fractal is very broad. In fact, to order ϵ^2, we can use (3) to reconstruct $P(u(r))$, which is a log-normal distribution.[8] At higher order, one epects $P(u(r))$ to be a more complicated scaling function of $\log(u(r))$; this view is consistent with Eqs. (4).

We have also studied the moments of the distribution of the incident flux ϕ of the field u onto the absorbing fractal. Since ϕ at a point on the absorber is proportional to u at some small distance a from the surface, $\langle\phi^n\rangle \sim \langle u(a)^n\rangle$; hence

$$\langle\phi^n\rangle/\langle\phi\rangle^n \sim (R/a)^{n\lambda(1)-\lambda(n)} \sim R^{(1-n)[D(n)-D(0)]}, \tag{5}$$

where $D(0) = D = 2$ (the fractal dimension), and

$$D(n) = D - n\epsilon^2/4 + O(\epsilon^3). \tag{6}$$

In Eq. (5), the exponents $D(n)$ are defined so as to coincide with those used in Refs. 9–11 to characterize an arbitrary fractal measure.[19]

While Eq. (6) is derived from the strict ϵ expansion (3) of the $\lambda(n)$, we also obtain using Eq. (4) the following limiting forms for $D(n)$ when n is large ($n >> \epsilon^{-1}$):

$$D(n) \to D_\infty + \text{const}\, n^{(3-d)/(d-2)} \quad (3 < d < 4), \tag{7a}$$

$$D(n) \to D_\infty + \text{const}[\log(n)]^{-1} \quad (d=3), \tag{7b}$$

where[20] for $d \geqslant 3$, $D_\infty = D - \lambda(1)$. A further nonperturbative constraint on the λ exponents can be obtained by observing[21] that for $D > d-2$, the total flux $M\langle\phi\rangle$ onto the absorbing fractal scales as R^{d-2}. Comparing with Eq. (2), we find

$$\lambda(1) = D + 2 - d. \tag{8}$$

[Note that this checks with the result obtained by setting $n=1$ in Eq. (2), to the order calculated there.] Thus for an absorbing Gaussian chain in space dimension $d \geqslant 3$, $D_\infty = d-2$. Physically, this means that it is possible to find points on such a chain which are virtually unscreened, insofar as the flux $\phi_{\max}$ onto such "maximally exposed" points (which obeys[8] $\phi_{\max} \sim R^{D-\lambda(1)-D_\infty}$) is independent of the size R of the absorber.

The above results for the $D(n)$ are shown schematically in Fig. 1. In three dimensions, we predict rather large departures from simple scaling behavior [e.g. $\langle\phi^2\rangle/\langle\phi\rangle^2 \sim M^y$ with $y = \epsilon^2 + O(\epsilon^3) \cong 1$]. Hence the present system would be a good candidate for seeing fractal-measure behavior in three-dimensional computer simulations. In any case, our analytic results confirm directly the hypothesis[9,10] that an infinite family of independent exponents is required to describe the incident flux distribution onto a random absorbing fractal.

Such confirmation is important, because this new kind of behavior should have many significant physical consequences. To give one example, Meakin[22] has shown that under certain idealized conditions the rate $Q(n)$ of the diffusion-limited reaction $nA \to B$ in the presence of a fractal catalytic substrate of size R (as discussed earlier) obeys $Q(n) \sim R^{D-\lambda(n)}$. Thus while in the unimolecular case ($n=1$) the conservation law Eq. (8) implies that the reaction near a fractal aggregate is no faster than near a sphere of comparable size, for all higher n the reaction rate for the fractal substrate is enhanced by a positive power of R. More generally, for any process which has a nonlinear

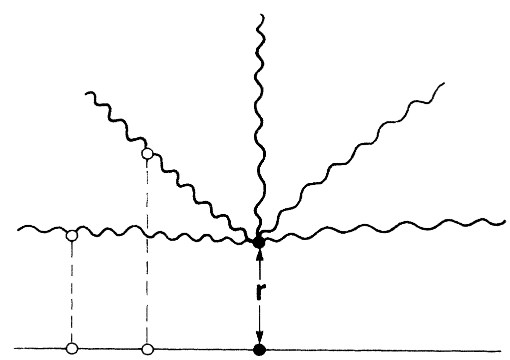

FIG. 1. A set of $n=5$ random walks from infinity to a point close to an absorbing Gaussian polymer, represented as an interaction between two polymers. The n-armed star (wavy lines), and the linear chain (straight line) have no excluded-volume interaction with themselves, but must nonetheless avoid one another. The dashed lines represent excluded volume interactions, for a typical second-order graph in the expansion of $Z_5(R,R,r)$. Because of correlations along the linear chain, the graph is not factorable, even though the interaction lines terminate on different arms of the star. Such nonfactorable contributions are responsible for the term quadratic in n which appears in Eq. (2) at order ϵ^2.

dependence on ϕ (or on u, if that process occurs predominantly in the near-field region) there will be a departure in scaling behavior from the hard-sphere picture mentioned above.[23]

In the remainder of this Letter, we outline the conceptual basis of our calculation and present some further results and comments. The first and main step is to observe that the field $u(\rho)$ at an arbitrary spatial position ρ near an absorbing object X is proportional to the number $N_X(\rho)$ of distinct very long random walks which arrive at ρ without having intersected any point on the absorber X.[24] Moreover, $u(\rho)^n$ is proportional to the nth power of $N_X(\rho)$. This quantity, $[N_X(\rho)]^n$, is itself the number of configurations of a set of n random walks, all of which arrive at ρ without touching X, but which otherwise have no interaction with one another. Next we constrain the point ρ to be a distance r from some monomer (x, say) on our absorbing Gaussian polymer, and, subject to this constraint, perform an ensemble average over the configurations of the absorber. To compute this average, we must sum over all joint configurations of the absorbing polymer and the n random walks. Specifically, we find

$$\langle u(r)^n\rangle / u_\infty^n = \lim_{R'\to\infty} Z_n(R,R',r), \tag{9}$$

where $Z_n(R,R',r)$ is the partition function of a system in which a linear polymer of radius R (representing the absorber) and an n-armed star polymer of radius R' (representing the n incoming walks), neither of which has to avoid itself, are constrained so that the relative separation between the junction of the star and the mononer x is r, and moreover so that the linear chain and the star polymer avoid one another (see Fig. 2). (For $n=1$ or 2 the "junction" of the n-arm star is defined as the end point or midpoint, respectively, of a linear chain.) The normalization of the partition function in Eq. (9) is chosen so that $\lim_{r\to\infty} Z_n(R, R',r)=1$. This ensures that $\langle u(r)^n\rangle = u_\infty^n$ for $r >> R$.

To proceed further, we note that general scaling considerations for linear and star polymers (supported by various field-theory results in limiting cases[15,16,18,25]) indicate the following behavior for $Z_n(R,R',r)$ in Eq. (9):

$$\lim_{R'\to\infty} Z_n(R,R',r) \sim Z_n(R,R,r) \sim (r/R)^{\lambda(n)}. \tag{10}$$

Here $\lambda(n)$ is a one-parameter family of universal exponents which depend only on the dimension of space. The identification of the $\lambda(n)$ with those defined in Eq. (2) follows directly from Eq. (9). In the calculation of $\lambda(n)$ it is convenient to set $r=a$ and thus to consider the partition function $Z_n(R,R,a)$ of a single star polymer having $n+2$ limbs which interact selectively according to the rules given under Eq. (9) above.

By this sequence of simplifications, we have reduced the problem of calculating $\lambda(n)$ to the point where a direct renormalization expansion can feasibly be performed, following the procedure introduced by des Cloizeaux,[15] and modified by Joanny, Leibler, and Ball[16] to account for selective excluded-volume interactions. Using these methods, we have computed $\lambda(n)$ to order ϵ^2; the result is given in Eq. (3) above.

In the complementary limit of large n, one can study the form of the relevant partition function $Z_n(R,R,a)$ using geometrical scaling ideas, based on those used to describe star polymers with excluded volume.[17,18] Such an analysis[8] suggests that the partition function is dominated by configurations in which the two arms of the star representing the absorber are confined to a narrow (hyper)cone of angle a, while the remaining arms (representing the incoming random walks) are excluded from this cone. The partition function of such a system may easily be found.[8] Treating a as a variational parameter and minimizing the resulting free energy yields $a \sim n^{1/(2-d)}$ for $3<d<4$ and $a \sim n^{-1}/(\log a)^2$ in $d=3$. This leads to Eqs. (4), and the asymptotic large-n behavior Eq. (7) for the exponents $D(n)$.

As mentioned previously, we have by similar methods calculated the exponents $\lambda(n)$ defined by Eq. (2) for the case when the absorbing cluster is not a simple random walk, but a self-avoiding walk. The results are most easily expressed in terms of the $D(n)$ of Eq. (6), which become $D(n)=D-9n\epsilon^2/64 + O(\epsilon^3)$, with $D=D(0)=1/\nu$.[2,15] Moreover, the limiting behavior at high n for space dimensions $d \geqslant 3$ is exactly as described under Eqs. (7) and (8) for the Gaussian case.

In summary, by analyzing specific examples, the present work shows concretely how a fractal immersed in an external field exhibits absorbing and/or screening behavior which is richer and more complex than that for simple objects, and which can be associated with the scaling properties of a fractal measure.[9-11] As

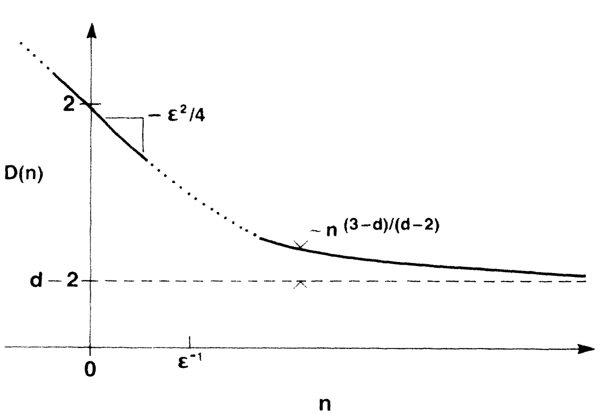

FIG. 2. Schematic plot of $D(n)$ defined by Eq. (5), near four dimensions.

illustrated above by an example from catalysis, this new behavior may prove useful when controllable nonlinear response to an external field is required. We expect several analogous properties to emerge in the electrostatic and hydrodynamic properties of colloidal aggregates and polymers.

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[20]The result $D_\infty = D - \lambda(1)$ will hold for any fractal absorber for which the ratio $\lambda(n)/n$ vanishes as $n \to \infty$. While this occurs also for the SAW in $d \geqslant 3$, it does not hold (for the Gaussian chain or SAW) in $d < 3$; here $\lambda(n)/n \to$ const as n becomes large (see Ref. 8).

[21]The total flux onto any absorber is equal to that across an enclosing surface so large as to be everywhere in the far-field region. So long as $D > d-2$, this is the same as onto an absorbing sphere of radius $\sim R$. Hence $M\langle\phi\rangle \sim R^{d-2}$. See, e.g., R. M. Brady and R. C. Ball, Nature (London) **309**, 225 (1984).

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