Adsorption in models of ideal polymer chains on fractal spaces

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We study critical adsorption in models of ideal polymer chains situated on fractal spaces in the vicinity of an impenetrable surface. The obtained exact results on fractal lattices, with a coordination number that can vary from site to site of the lattice, reveal a critical behavior that might be quite different from that established for lattices with the same coordination. Specifically, in the cases where localization of the chain takes place, i.e., when the mean end-to-end distance of the chain grows more slowly than any power of its length N, we found that various generating functions of interest usually display multiplicative singular corrections to the leading power law singularities (confluent logarithmic singularities, for example). We have demonstrated with specific examples that the average fraction of steps of the chain on adsorbing surface, at critical adsorption point, vanishes according to the asymptotic law $\sim \ln^{\psi_1} N$ (where $\psi_1 < 0$ is a given constant) or $\sim \exp(-c \ln^{\psi_2} N)$ (where c and ψ_2 are certain positive constants).

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I. INTRODUCTION

Statistical properties of a single polymer chain near an attractive surface have been studied for a long time (see, for example [1]). The general picture that emerges from these studies reveals that a polymer chain can undergo an adsorption-desorption transition. At low temperatures, the chain is basically localized in the vicinity of the adsorption surface, with a finite fraction M/N of its monomers lying on the surface, while at higher temperatures a nonadsorbed behavior prevails. Later, this transition was fruitfully described in the framework of surface critical phenomena [2]. Most of the reported theoretical works are based on the study of suitable models of polymer adsorption on standard homogeneous spaces. Recently, considerable research activity has appeared in the study of the critical adsorption in various models of polymers which reside on fractal spaces [3–8]. In all these models excluded-volume effects have been taken into account, and a simple scaling picture of critical adsorption, of the type found earlier in the case of Euclidean spaces [9], has been established. A similar conclusion was reached in the case of polymer chains represented by simple random walk paths (without constraint of self-avoidance) on fractal lattices with a uniform coordination number [10].

In the more general case of random walks on fractals with coordination numbers that can vary from site to site of the lattice, one can consider several types of statistics [11]. The statistical weight associated with a particular path of such a *kinetic random walk* depends on both the number and type of visited sites [12]. On the other hand, one can associate the same weight K^N with each path having N steps irrespective of the coordination number of visited sites. This model, known also as the *ideal chain* model [13], is closely related to the equilibrium statistical problem of an ideal polymer in solution. Recently obtained results [13,14] show that the ideal chain model and kinetic random walks in an inhomogeneous environment do not belong to the same universality class. It is obvious, on the other hand, that both statistics become equivalent on a Euclidean basis, and on those fractal lattices that have the same coordination number.

In a previous work [10] we studied the problem of critical adsorption of random walks on a class of exact fractals with uniform coordination. Using an appropriate Gaussian model and a renormalization group approach, we have been able to express a set of pertinent critical exponents in terms of spectral and fractal dimensions of the fractal substratum and the adsorbing boundary fractal dimension. In this paper we develop an approach suitable to treat a similar Gaussian model on fractals with nonuniform coordination numbers in the presence of a fractal boundary. The exact results obtained show that critical adsorption of ideal polymer chains in this case can be rather different from that described in Ref. [10]. In particular, there is not the simple connection established in [10] between the crossover exponent ϕ ($M \sim N^{\phi}$) and the surface susceptibility exponents. What is more, in the cases when mean the end-to-end distance of the chain grows more slowly than any power of its length N, various bulk and surface generating functions do not display simple power law singular behavior, which means that standard critical exponents are not defined. As we shall show, in such cases the leading singular behavior of the generating functions of interest can be expressed as a product of several confluent singular terms.

This paper is organized as follows. In Sec. II we present our model and its solution on some simple exam-

ples. In Sec. II A we consider the adsorption problem on a simple treelike lattice—the T fractal. Then in Sec. II B we study the properties of an ideal chain on a modified Koch curve with loops on all scales. There we shall analyze the critical behavior of the chain for two different choices of adsorbing wall. In Sec. III we turn to cases where one may expect localization [13] of an ideal chain: We study adsorption on fractals where the sites of the highest coordination number of the lattice do not form an infinite connected network—two- and three-dimensional modified gaskets with a space scaling factor equal to 3.

II. MODEL AND ITS SOLUTION ON SIMPLE EXAMPLES

It is well known (see, for instance, [15]) that statistics for random walks on lattices can be captured by using a suitable Gaussian model. Indeed, the two-spin correlation function of a Gaussian model represents the generating function of numbers of random walk paths between two given points. In a similar way, the generating function for numbers of all walks on the lattice can be related to the susceptibility, whereas the probability of return to the origin of a walk can be obtained from the free energy of the model [15]. For these reasons, critical adsorption of an ideal polymer chain near an impenetrable wall can be described by using an appropriate Gaussian model.

A. Ideal chain on a T-fractal lattice

Consider first, for simplicity, only the bulk partition function of the usual zero-field Gaussian model on a T-fractal lattice at the rth stage of its iterative construction [see Fig. 1(a)]

$$Z^{(r)}(K)=\int_{-\infty}^{\infty}\cdots\int dS_1\cdots dS_N \exp\left[-\frac{1}{2}\sum_i S_i^2 + K\sum_{\langle ij\rangle} S_iS_j\right], \tag{1}$$

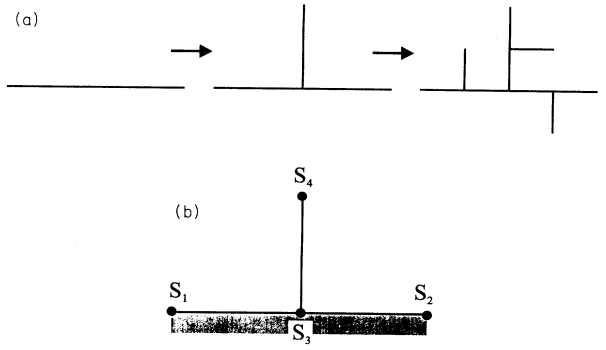

FIG. 1. (a) First two stages in the iterative construction of the T-fractal lattice. The final object has a fractal dimension $D=\ln 3/\ln 2$. (b) Schematic representation of an rth stage T fractal with the adsorbing boundary (shadow region). To obtain the partition function $Z^{(r)}(S_1,S_2)$, one has to perform integration over two internal spins S_3 and S_4 [see relation (6)].

where S_i is the continuous spin variable at site i, K stands for the interaction between each nearest-neighbor pair of spins, and $\langle ij\rangle$ denotes the summation over all such pairs. Let us imagine that we have performed the integration over all internal spins of an rth order lattice. It is clear, from symmetry considerations, that resulting function should take the form

$$Z^{(r)}(S_1,S_2)=D^{(r)}\exp[A^{(r)}(S_1^2+S_2^2)+B^{(r)}S_1S_2], \tag{2}$$

where S_1 and S_2 denote two outer spins from Fig. 1(b) (separated by the distance $R=2^r$), while parameters $A^{(r)}$, $B^{(r)}$, and $D^{(r)}$ depend on the interaction parameter K. It is clear that partition function (1) can be expressed in terms of these parameters,

$$Z^{(r)}=\int\int dS_1dS_2Z^{(r)}(S_1,S_2)\exp[-\tfrac{1}{2}(S_1^2+S_2^2)] = \frac{2\pi D^{(r)}}{\sqrt{1-4A^{(r)}+4A^{(r)2}-B^{(r)2}}}. \tag{3}$$

Thus, knowledge of $A^{(r)}$, $B^{(r)}$, and $D^{(r)}$ enables us to learn all thermodynamic properties of the model. Furthermore, it is a simple matter to see that the correlation function can be expressed in terms of these parameters as well,

$$\langle S_1S_2\rangle\equiv G^{(r)}(K) = \frac{1}{Z^{(r)}}\int\int dS_1dS_2S_1S_2Z^{(r)}(S_1,S_2) \times\exp[-\tfrac{1}{2}(S_1^2+S_2^2)]. \tag{4}$$

After a simple integration, we obtain

$$G^{(r)}=\frac{B^{(r)}}{(1-2A^{(r)})^2-B^{(r)2}}. \tag{5}$$

The parameters $A^{(r)}$ and $B^{(r)}$ entering the above relations can be determined recursively. Indeed, the rth order partition function (2) can be obtained from similar $(r-1)$th order partition functions,

$$Z^{(r)}(S_1,S_2)=\int\int dS_3dS_4Z^{(r-1)}(S_1,S_3) \times Z^{(r-1)}(S_3,S_4)Z^{(r-1)}(S_3,S_2) \times\exp\left[-\frac{(S_3^2+S_4^2)}{2}\right]. \tag{6}$$

Taking (2) into account, it is not difficult to obtain the following recursion relations:

$$A'=\frac{2A-16A^2+24A^3+B^2-4AB^2}{2(1-8A+12A^2-B^2)}, \qquad B'=\frac{(1-2A)B^2}{1-8A+12A^2-B^2}, \tag{7}$$

and

$$D'=\frac{2\pi D^3}{\sqrt{1-8A+12A^2-B^2}}, \tag{8}$$

where, for clarity, we have suppressed the superscript $(r-1)$ on the right-hand sides of the above equations,

and have substituted the superscript (r) with the prime on the left-hand sides. This system of recursion relations has to be supplemented with the initial conditions

$$A^{(0)}=0\ ,\quad B^{(0)}=K\ ,\quad \text{and}\quad D^{(0)}=1\ . \tag{9}$$

It turns out that critical behavior of an ideal polymer chain on a T fractal can be related to a certain peculiar singular behavior of the recursion relations (7), which occurs for large r, when we start with initial conditions (9) and a value of the interaction strength K lying in the vicinity of its critical value K_c. It seems that singular structure of the above recursions has a nature similar to the one found recently in a study of the same problem, but using a somewhat different approach [13]. It is also worth mentioning here that similar singular forms have been noticed earlier, in a study of branched polymers on fractals [16], and more recently [17] in the problem of diffusion on ramified fractal structures in the presence of a biasing field. Looking forward, we may say that critical adsorption of an ideal polymer chain on fractals depends sensitively on the character of the singular behavior of relevant recursion relations. Therefore, it is very useful to examine our approach first on the simple bulk case, which provide a good pedagogical example. We are now going to derive the leading asymptotic behavior of the ideal polymer chain which follows from the above recursion relations.

As mentioned above, the correlation function (5) represents the generating function for the numbers $\mathcal{G}^{(r)}(N)$ of all N-step random-walk paths that join two opposite horizontal vertices of an rth order T fractal,

$$G^{(r)}(K)=\sum_N \mathcal{G}^{(r)}(N)K^N\ , \tag{10}$$

where K should be interpreted as the fugacity per step of the walk. The average number $N^{(r)}$ of steps of all walks between two vertices depends on K, and can be expressed in terms of the first derivative of $G^{(r)}(K)$: $N^{(r)}=K(d\ln G^{(r)})/dK$. For large r ($r\to\infty$), there exists a critical value of the fugacity K_c which corresponds to the limit of very long polymer chains ($N^{(r)}\to\infty$). In this regime one usually tries to express the leading asymptotic behavior of the mean end-to-end distance R of the walks in the form of a simple function of N (as a rule, it is a power law: $R\sim N^{\nu}$, ν being the critical exponent). The asymptotic behavior of $N^{(r)}$ is closely related to the comportment of $A^{(r)}$, and $B^{(r)}$ and their derivatives $\partial A^{(r)}/\partial K$ and $\partial B^{(r)}/\partial K$ in the vicinity of $K=K_c$.

If the value of the fugacity K in (9) is less than $K_c=0.394\,293\ldots$, then, under successive iterations of system (7), $B^{(r)}$ decreases to zero, while $A^{(r)}$ tends to a certain K dependent constant. If K is larger than the threshold value K_c, then both $A^{(r)}$ and $B^{(r)}$ displays some spurious instabilities reflecting the appearance of an unphysical region (Gaussian model is not defined in the low temperature region $K>K_c$, see, e.g., [15]). Finally, precisely at $K=K_c$ all successive iterations of $A^{(r)}$ and $B^{(r)}$ lie on an invariant line starting at the point $A^{(0)}=0$, $B^{(0)}=K_c$ and ending at the point $A=\frac{1}{6}$, $B=0$ (see Fig. 2). It is easy to see that recursion relations (7) become

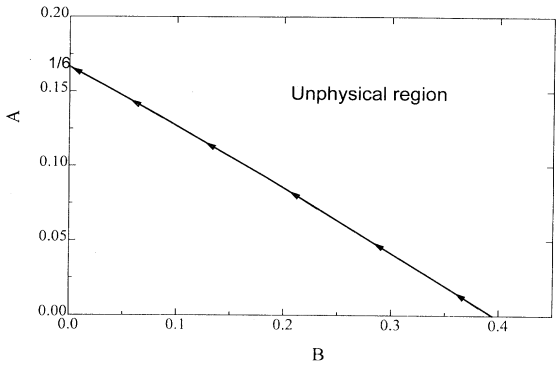

FIG. 2. Phase diagram on the A-B plane for an ideal polymer chain on the T-fractal lattice bulk. Under recursion relations (7), all sets of initial conditions (9) with $K<K_c=0.394\,29$ flow toward the A axis ($A<\frac{1}{6}$), which corresponds to finite polymer chains. This region is limited by an invariant line signifying the appearance of an infinite chain. The invariant line joins the points ($A^{(0)}=0$, $B^{(0)}=K_c$) and ($A^{(\infty)}=\frac{1}{6}$, $B^{(\infty)}=0$).

singular at the latter point. It turns out, however, that just this point controls the critical behavior of the ideal polymer chain. A numerical analysis reveals that this point represents a sink for all points lying on the invariant line. To overcome this difficulty, and to find a proper form of recursion relation in the neighborhood of the sink, it is useful to know at least an asymptotic equation of the invariant line. Fortunately, its asymptotic form is quite simple, and can be obtained analytically, by making a perturbative expansion in powers of B. This leads to the asymptotic equation of the required invariant line

$$A(B)=\frac{1}{6}-\frac{1+\sqrt{13}}{12}B-\frac{29-\sqrt{13}}{184}B^2+O(B^3)\ , \tag{11}$$

which is valid for small values of B. Taking into account (7), we find that along this line the recursion relation for B acquires the simple form

$$B'=\frac{\sqrt{13}-1}{6}B+O(B^2)\ , \tag{12}$$

implying $B^{(r)}\sim[(\sqrt{13}-1)/6]^r$.

Taking partial derivatives of Eqs. (7) with respect to K, we can obtain recursion relations for $\partial A^{(r)}/\partial K$ and $\partial B^{(r)}/\partial K$. These relations can be written in matrix form,

$$\begin{bmatrix}\dfrac{\partial A^{(r)}}{\partial K}\\[2ex]\dfrac{\partial B^{(r)}}{\partial K}\end{bmatrix}=\begin{bmatrix}\dfrac{\partial A^{(r)}}{\partial A^{(r-1)}} & \dfrac{\partial A^{(r)}}{\partial B^{(r-1)}}\\[2ex]\dfrac{\partial B^{(r)}}{\partial A^{(r-1)}} & \dfrac{\partial B^{(r)}}{\partial B^{(r-1)}}\end{bmatrix}\begin{bmatrix}\dfrac{\partial A^{(r-1)}}{\partial K}\\[2ex]\dfrac{\partial B^{(r-1)}}{\partial K}\end{bmatrix}\ . \tag{13}$$

It is clear that the asymptotic behavior of these derivatives substantially depends on the comportment of the matrix appearing in (13). One can show that for $K=K_c$, elements of this matrix do not depend on r (for large r), and that its largest eigenvalue is equal to 2, implying $\partial A^{(r)}/\partial K\sim\partial B^{(r)}/\partial K\sim 2^r$. Using these results, we can extract the leading asymptotic behavior of $N^{(r)}$: $N^{(r)}\sim(1/B^{(r)})\partial B^{(r)}/\partial K\sim\lambda_1^r$, with $\lambda_1=1+\sqrt{13}$. This allows

us to express the average end-to-end distance $R \sim 2^r$ as a function of $N^{(r)}$: $R \sim \exp(r \ln 2) \sim \exp[\ln 2 \ln(N^{(r)})/\ln\lambda_1]$, i.e.,

$$R \sim N^{\nu} \quad \text{with } \nu = \frac{\ln 2}{\ln \lambda_1} = 0.453\,849 , \tag{14}$$

which coincides with the corresponding result of Ref. [13]. Knowledge of the asymptotic properties of $A^{(r)}$, $B^{(r)}$, $\partial A^{(r)}/\partial K$, and $\partial B^{(r)}/\partial K$ along the invariant line suffices to establish the leading singular forms of the free energy density and its first derivative with respect to K. Indeed, by iterating the recursion relation (8) we can express the partition function (3) in terms of A and B. The expression obtained provides a good starting point to deduce the way in which diverges internal energy, i.e., generating function $P(K)$ for the numbers of random-walk paths that return to the starting point of the walk. Thus, for $K \to K_c$ from below, we found the power law

$$P \sim (K_c - K)^{\ln 3/[\ln(1+\sqrt{13})-1]} , \tag{15}$$

which means that for large N the number of all N-step closed paths scales as $K_c^{-N} N^{\alpha-2}$, with the critical exponent $\alpha = 2 - \ln(3)/\ln(1+\sqrt{13}) = 1.280\,67$.

The above described approach can be extended to the case of the presence of a finite magnetic field. The free energy of such a model naturally splits into two terms, one of them being the above mentioned zero-field free energy, while the other one involves the magnetic field. It is convenient, therefore, to express the partition function $Z^{(r)}(S_1, S_2)$ in the form

$$Z^{(r)}(S_1,S_2) = D^{(r)} \exp[A^{(r)}(S_1^2 + S_2^2) + B^{(r)} S_1 S_2 + C^{(r)}(S_1 + S_2) + E^{(r)}] , \tag{16}$$

where parameters $C^{(r)}$ and $E^{(r)}$ spring from the interactions of the Gaussian spins with the (reduced) magnetic field H. If we put this form into (6), and multiply the integrand of such obtained relation by $\exp[H(S_3 + S_4)]$, we can then use it to determine the recursion relations for parameters C and E. In this way, we obtain

$$C' = \frac{C(1 - 8A + 12A^2 + 3B - 6AB) + H(B - 2AB + B^2)}{1 - 8A + 12A^2 - B^2} \tag{17}$$

$$E' = 3E + \frac{C^2(5 - 12A + 3B) + 4CH(1 - 3A + B) + H^2(1 - 4A + B)}{1 - 8A + 12A^2 - B^2} , \tag{18}$$

whereas initial conditions for these variables have the form $C^{(1)} = 0$ and $E^{(1)} = 0$. It is useful to note here that magnetic field H enters recursion relations (17) and (18) in both explicit and implicit ways.

The above relations can be used to determine the field dependent part of the free energy of the model. In particular, the susceptibility of the Gaussian model, i.e., the generating function for the numbers $\Omega(N)$ of all N-step paths per lattice site, can be constructed by using the above recursions. Here we give only a few details concerning the leading singular behavior of the zero-field susceptibility χ. Iterating the recursion relation (18), and retaining only the most divergent term of such obtained expression, we obtain the estimate

$$\mathcal{N}^{(r)} \chi^{(r)} \sim (\partial^2 E^{(r)}/\partial H^2)|_{H=0} \sim (\partial^2 E^{(r)}/\partial C^{(r-1)^2})(\partial C^{(r-1)}/\partial H)^2 \sim (1/B^{(r)})(\partial C^{(r)}/\partial H)^2 ,$$

where $\mathcal{N}^{(r)} \sim 3^r$ denotes the number of sites of an rth stage T fractal. Taking the first derivative of (17) with respect to H, it is easy to construct an exact recursion relation for derivatives $\partial C^{(r)}/\partial H$. Using such a relation we find that $\partial C^{(r)}/\partial H$, at $H = 0$ and $K = K_c$, follows the asymptotic law $\partial C^{(r)}/\partial H \sim [(1+\sqrt{13})/2]^r$. Putting these results together, we have $\chi^{(r)} \sim [(5+2\sqrt{13})/3]^r$, which yields

$$\chi(K) \sim (K_c - K)^{-\gamma}$$

$$\text{with } \gamma = \frac{\ln\left[\dfrac{5+2\sqrt{13}}{3}\right]}{\ln(1+\sqrt{13})} = 0.919\,117 , \tag{19}$$

in agreement with [13].

The extension of the above described approach to the case of the presence of a surface is straightforward. We suppose that the reduced interaction strength takes the value K for all nearest-neighbor pairs of spins, except for pairs lying on the lattice boundary [the shadow region of Fig. 1(b)], for which it is K_s. It is also convenient to introduce a reduced surface magnetic field H_s which couples only to the spins on the boundary, while the usual bulk magnetic field H couples to all other spins.

To proceed, we relate the rth order partition function

$$Z_1^{(r)}(S_1,S_2) = D_1^{(r)} \exp[A_1^{(r)}(S_1^2 + S_2^2) + B_1^{(r)} S_1 S_2 + C_1^{(r)}(S_1 + S_2) + E_1^{(r)}] , \tag{20}$$

to the corresponding $(r-1)$th order partition functions [see Fig. 1(b)],

$$Z_1'(S_1,S_2)=\int\int dS_3 dS_4 Z_1(S_1,S_3)Z(S_3,S_4)Z_1(S_3,S_2)\exp[-\tfrac{1}{2}(S_3^2+S_4^2)+H_s S_3+HS_4]\ ,$$

where the $(r-1)$th order bulk partition function $Z(S_3,S_4)$ has been defined in (16) (to simplify notation we have suppressed the iteration index r). Having determined $Z_1^{(r)}(S_1,S_2)$, all thermodynamic properties of the above mentioned Gaussian model can be derived from the partition function

$$Z_1^{(r)}(K,K_s,H,H_s)=\int\int dS_1 dS_2 Z_1^{(r)}(S_1,S_2)\exp[-\tfrac{1}{2}(S_1^2+S_2^2)+H_s(S_1+S_2)]\ .$$

The first of these two relations enables us to derive relevant recursion relations. We find that parameters A_1 and B_1 must satisfy the recursion relations

$$A_1'=\frac{2A_1(1-4A+4A^2-4A_1+8AA_1-B^2)+B_1^2(1-2A)}{2(1-4A+4A^2-4A_1+8AA_1-B^2)}\ ,$$
$$B_1'=\frac{(1-2A)B_1^2}{1-4A+4A^2-4A_1+8AA_1-B^2}\ , \tag{21}$$

and initial conditions $A^{(1)}=0$ and $B^{(1)}=K_s$. In the context of the adsorption of a polymer chain, it is convenient to express the interaction strength K_s as the product of two weighting factors $K_s=Kw$—the first of them being the usual one-step fugacity, while the second represents an additional weight for each step (monomer) lying on the adsorbing boundary [if, for example, one assigns an energy $\epsilon=-|\epsilon|$ for each step along the attractive surface, w may be interpreted as a suitable Boltzmann factor $w=\exp(-\epsilon/T)>1$, which leads to an increased probability of making a step along this surface]. The correlation function for two spins lying on the boundary takes the following form:

$$G_1^{(r)}=\frac{B_1^{(r)}}{(1-2A_1^{(r)})^2-B_1^{(r)^2}}\ , \tag{22}$$

and it provides the generating function for the numbers $\mathcal{G}^{(r)}(N,M)$ of all N-step walks on an rth order lattice, M of which lie on the surface, provided both ends of the walk are attached to the surface $[G_1^{(r)}(K,w)=\sum_N \mathcal{G}^{(r)}(N,M)K^N w^M]$. This function can be used, therefore, to obtain both the average number of monomers $N^{(r)}=K(d\ \ln G_1^{(r)})/dK)$ and the average number of adsorbed monomers $M^{(r)}=w(d\ \ln G_1^{(r)})/dw$.

Here we focus our attention on the phenomenon of critical adsorption of an ideal polymer chain, which is described by recursion relations (7) and (21) and correlation function (22). Both numerical and analytical analyses of these relations reveal that, for a given value of w, there exists a value of the fugacity $K_c(w)$ corresponding to a certain critical behavior of the chain. Specifically, we find that for all values $w>1$ there exists an invariant surface which controls the adsorbed state of the chain. An asymptotic equation of the invariant surface can be represented by the plane

$$A_1=\tfrac{1}{4}-\tfrac{1}{2}A-\tfrac{1}{2}B_1\ . \tag{23}$$

Along this plane, parameter B_1 follows the simple recursion relation $B_1'=\frac{1}{2}B_1$, while parameter B very rapidly goes to zero under iterations (it renormalizes according to the law $B'\sim B^2$). Using (23) it is easy to derive asymptotic behavior of the derivatives $(\partial A_1^{(r)}/\partial K)\sim(\partial B_1^{(r)}/\partial K)\sim 2^r$, which implies $N^{(r)}\sim(1/B_1^{(r)})(\partial B_1^{(r)}/\partial K)\sim 4^r$. It is obvious, therefore, that the average end-to-end distance of the chain in this regime follows the usual power law $R\sim 2^r\sim N^{1/2}$ with a value of the critical exponent ν, $\nu=\frac{1}{2}$, which reflects its one-dimensional critical behavior [18]. A similar conclusion may be reached by studying the fraction M/N of monomers adsorbed at the boundary. Results of our numerical analysis of the generating function (22) and its corresponding derivatives support the expectations that this quantity should be finite in the region $w>1$.

In contrast to the above case, we find that critical fugacity keeps the same value, $K_c(w)=K_c(1)$, in the region $w<1$, implying a vanishing fraction of random-walk steps in contact with the boundary $(M/N=(w/K_c)[dK_c(w)/dw])$. This corresponds to a desorbed state of the chain [19]. For $w<1$, parameter $B_1^{(r)}$ goes very rapidly to zero under iterations (much faster than $B^{(r)}$), while $A_1^{(r)}$ reaches certain finite value which depends on $w[A_1^{(\infty)}(w)<\frac{1}{6}]$. Precisely at $w=1$ another type of critical behavior sets in, corresponding to the critical point of the adsorption transition of an ideal polymer chain. We have found that bulk and concomitant surface variables at this point follow the same asymptotic law. For example, we have found $B^{(r)}\sim B_1^{(r)}\sim[(\sqrt{13}-1)/6]^r$, while both $A^{(r)}$ and $A_1^{(r)}$ tend to $\frac{1}{6}$ at $K=K_c(1)$. One can show that derivatives of these parameters with respect to K follow the previously established law $\partial A^{(r)}/\partial K\sim\partial A_1^{(r)}/\partial K\sim\partial B^{(r)}/\partial K\sim\partial B_1^{(r)}/\partial K\sim 2^r$, which means that asymptotic behavior of the average number of all monomers remains unchanged and that, therefore, the bulk critical exponent (14) still governs the average end-to-end distance.

It is of interest to study behavior of the fraction of adsorbed monomers at the point of adsorption transition. To deduce the asymptotic law of the average number of adsorbed monomers, $M^{(r)}\sim(1/G_1^{(r)})(\partial B_1^{(r)}/\partial w)$, one can consider recursion relations for derivatives $\partial A_1^{(r)}/\partial w$ and $\partial B_1^{(r)}/\partial w$, which may be written in a matrix

form similar to (13). The largest eigenvalue of pertinent matrix governs the asymptotic behavior of these derivatives, $\partial A_1^{(r)}/\partial w \sim \partial B_1^{(r)}/\partial w \sim [(13+2\sqrt{13}+\sqrt{329-56\sqrt{13}})/18]^r$, which leads to the law $M^{(r)} \sim \lambda_2^r$ with $\lambda_2=(13+5\sqrt{13}+\sqrt{350-14\sqrt{13}})/12$. Taking into account that $N^{(r)} \sim \lambda_1^r$, we conclude that at criticality $K=K_c(1)$ the usual power law $M \sim N^{\phi}$ holds (see, e.g., [9]), where the crossover exponent ϕ is given by

$$\phi=\frac{\ln\lambda_2}{\ln\lambda_1}=0.912\,246\ . \tag{24}$$

Now we turn to a study of asymptotic behavior of zero-field surface susceptibilities $\chi_1=\partial^2 f_s/\partial H \partial H_s$ and $\chi_{11}=\partial^2 f_s/\partial H_s^2$, where $f_s=f_s(K,K_s,H,H_s)$ represents the surface free energy density of the model. The function χ_1 (function χ_{11}) provides the generating function for the numbers $\Omega_1(N)$ [$\Omega_{11}(N)$] of all N-step walks with one (both) end(s) attached to the adsorbing boundary. It is generally believed that these numbers follow the asymptotic laws

$$\begin{aligned}&\Omega_1(N) \sim K_c^{-N} N^{\gamma_1-1}\ ,\\ &\Omega_{11}(N) \sim K_c^{-N} N^{\gamma_{11}-1}\ ,\end{aligned} \tag{25}$$

where $K_c=K_c(w)$ and γ_1 and γ_{11} are the associated critical exponents which can assume distinct values in different adsorption regimes. If (25) holds, then the above surface susceptibilities should display the power law singularities, when $K \to K_c$ from below, $\chi_1 \sim (K_c-K)^{-\gamma_1}$, and $\chi_{11} \sim (K_c-K)^{-\gamma_{11}}$.

To construct the generating functions χ_1 and χ_{11}, it is enough to consider only the field-dependent part of the surface free energy. This part of the free energy is closely related to the comportment of parameters $E_1^{(r)}$ and $E^{(r)}$ under iterations. In particular, one can show that the asymptotic behavior of $E_1^{(r)}$ determines the asymptotic behavior of χ_1 and χ_{11}

$$\begin{aligned}&\mathcal{N}_s^{(r)}\chi_1^{(r)} \sim \left.\frac{\partial^2 E_1^{(r)}}{\partial H \partial H_s}\right|_{\substack{H=0\\H_s=0}}\ ,\\ &\mathcal{N}_s^{(r)}\chi_{11}^{(r)} \sim \left.\frac{\partial^2 E_1^{(r)}}{\partial H_s^2}\right|_{\substack{H=0\\H_s=0}}\ ,\end{aligned} \tag{26}$$

with $\mathcal{N}_s^{(r)}$ being the number of surface sites ($\mathcal{N}_s^{(r)} \sim 2^r$, in this case). We have already studied in some detail recursion relations (17) and (18) for bulk variables C and E. It is not difficult to establish the recursion relations for concomitant surface variables C_1 and E_1,

$$C_1'=\frac{(1-2A)[C_1(1-2A-4A_1+2B_1)+B_1(C+H_s)]+B(B_1C+BC_1+B_1H)}{1-4A+4A^2-4A_1+8AA_1-B^2}\ , \tag{27}$$

$$\begin{aligned}E_1'=&2E_1+E+\frac{2(C+H)(BC+2BC_1+BH_s-2A_1H-2A_1C)}{2(1-4A+4A^2-4A_1+8AA_1-B^2)}\\ &+\frac{(1-2A)[(C+H)^2+(C+2C_1)^2+H_s(2C+4C_1+H_s)]}{2(1-4A+4A^2-4A_1+8AA_1-B^2)}\ .\end{aligned} \tag{28}$$

Then a study of these relations and their derivatives with respect to H and H_s suffices to learn the leading asymptotic behavior of (26).

For low values of the interaction parameter w ($w<1$), we find that the leading singular behavior of $\mathcal{N}_s^{(r)}\chi_1^{(r)}$ can be represented by a term of the type $(\partial^2 E_1^{(r)}/\partial C^{(r-1)}\partial C_1^{(r-1)})(\partial C_1^{(r-1)}/\partial H_s)(\partial C^{(r-1)}/\partial H)$. One can verify that along invariant line (11) the first two factors of this expression approach certain constant values. The asymptotic behavior of $\partial C^{(r)}/\partial H$ has been established earlier [see (19)], so that we can write $\chi_1^{(r)} \sim 2^{-r}[(1+\sqrt{13})/2]^r$, which leads to

$$\chi_1 \sim (K_c-K)^{-\gamma_1}$$

$$\text{with } \gamma_1=\frac{\ln\left[\dfrac{1+\sqrt{13}}{4}\right]}{\ln(1+\sqrt{13})}=0.092\,301\ . \tag{29}$$

In a similar way we find $\gamma_{11}=-1$, which mean that χ_{11} is not diverging for $w<1$. On the other hand, at the point of the adsorption transition [$K=K_c(1)$] we obtain the following estimates: $\partial C_1^{(r)}/\partial H_s \sim [(2+\sqrt{13})/3]^r$, and $\partial^2 E_1^{(r)}/\partial C_1^{(r-1)^2} \sim \partial^2 E_1^{(r)}/\partial C_1^{(r-1)}\partial C^{(r-1)} \sim 1/B^{(r)} \sim [(1+\sqrt{13})/2]^r$. This allows us to derive the asymptotic behavior of the susceptibilities:

$$\begin{aligned}\chi_1 &\sim 2^{-r}(1/B^{(r)})(\partial C^{(r)}/\partial H)(\partial C_1^{(r)}/\partial H_s)\\ &\sim [3(3+\sqrt{13})/4]^r\end{aligned}$$

and $\chi_{11} \sim [(23+7\sqrt{13})/12]^r$, yielding to

$$\begin{aligned}\gamma_1&=\frac{\ln\left[\dfrac{9+3\sqrt{13}}{4}\right]}{\ln(1+\sqrt{13})}=1.0478\ ,\\ \gamma_{11}&=\frac{\ln\left[\dfrac{23+7\sqrt{13}}{12}\right]}{\ln(1+\sqrt{13})}=0.910\,95\ .\end{aligned} \tag{30}$$

Using the above described approach one can also determine the asymptotic behavior of the surface susceptibility $\chi_s=\partial^2 f_s/\partial H^2|_{H=0}$, which provides a generating

function for the numbers $\Omega_s(N)$ of all N-step random walks given that both end points of the random walk path lie in the bulk. We find that this function for $K \to K_c(w)$ from below display the usual power law type of singularity: $\chi_s \sim (K_c - K)^{-\gamma_s}$, where the critical exponent γ_s takes the same value,

$$\gamma_s = \frac{\ln \frac{5+2\sqrt{13}}{2}}{\ln(1+\sqrt{13})} = 1.1846 , \tag{31}$$

in the desorbed phase ($w < 1$) as well as at the point of adsorption transition ($w = 1$). This means that the numbers $\Omega_s(N)$ follow the asymptotic behavior of the type (25), $\Omega_s(N) \sim K_c^{-N} N^{\gamma_s - 1}$. One can also check that the above presented values of the critical exponents satisfy the standard scaling relation of surface phase transitions $\gamma_s = 2\gamma_1 - \gamma_{11}$ (see, for example, [9]), in the whole region $w \leq 1$.

We shall make some further comments below concerning results presented here—after consideration of the critical adsorption of an ideal polymer chain on a branching Koch curve. Before leaving the case of adsorption on the T fractal, let us mention that the parameter D_1 from partition function (20) enters the filed independent part of the free energy density and can be used to deduce critical behavior of corresponding quantities. Such quantities are not, however, of very great interest for polymer physics, and will not be considered here.

B. Ideal chain on branching Koch curves

As a second example, we study the adsorption problem of an ideal polymer chain on the branching Koch curve which contains loops [Fig. 3(a)]. We consider two cases of the adsorbing boundary: In the first case, shown in Fig. 3(b), the adsorbing wall is presented by a one-dimensional line, while the second one represents a fractal boundary—the nonbranching Koch curve with fractal dimension $D_s = \ln 4 / \ln 3$ [see Fig. 3(c)].

To write the appropriate recursion relations, one can follow the lines of Sec. II A. In particular, the general form of partition function $Z_1^{(r)}(S_1, S_2)$ is still described by relation (20), and an integration over three internal spins leads to pertinent recursions. Resulting relations are more cumbersome than in the case of the T fractal, so here we give only the recursion relations for bulk variables A and B,

$$A' = \frac{2A - 32A^2 + 168A^3 - 288A^4 + (1 - 16A + 56A^2)B^2 - 4AB^3 - B^4}{2(1-6A+B)(1-10A+24A^2-B+4AB-2B^2)} ,$$
$$B' = \frac{B^3(1-4A+B)}{(1-6A+B)(1-10A+24A^2-B+4AB-2B^2)} . \tag{32}$$

Let us note here that the correlation function still has the form (5). The critical behavior of the chain sets in near the threshold value $K = K_c = 0.362\,890\ldots$, for which Eqs. (32) become singular under successive iterations ($A \to \frac{1}{6}$, $B \to 0$ at K_c). It turns out that, as in the case of the T fractal, there exists an invariant line which controls the critical behavior of the chain. The structure of that line is rather similar to the one described in Sec. II A (see Fig. 2), and its asymptotic equation can be written in the form

$$A(B) = \frac{1}{6} - \frac{\sqrt{5}}{6} B - \frac{14+6\sqrt{5}}{43} B^2 + O(B^3) . \tag{33}$$

Along this line parameter B renormalizes according to the law $B' = B/4 + O(B^2)$, while derivatives with respect to K follow the asymptotic law $\partial A^{(r)}/\partial K \sim \partial B^{(r)}/\partial K \sim (\frac{11}{4})^r$. This allows us to deduce the exact value of the end-to-end critical exponent ν, $\nu = \ln 3 / \ln 11 = 0.458\,16$, in agreement with the corresponding finding of Ref. [13].

In contrast to the bulk behavior of the chain, its surface critical properties depend on a particular choice of adsorbing boundary. For this reason, one has to consider the two cases separately [see Figs. 3(b) and 3(c)]. As we mentioned above, a complete system of recursion relations is somewhat cumbersome and will be omitted here. Nevertheless, we give the leading asymptotic behaviors of some main parameters affecting the surface critical behavior of the chain. So, at the point of adsorption transition $w = 1$, for case (b) we found $\partial A_1^{(r)}/\partial w \sim \partial B_1^{(r)}/\partial w \sim [(21+\sqrt{249})/16]^r$, whereas in case (c) we have $\partial A_1^{(r)}/\partial w \sim \partial B_1^{(r)}/\partial w \sim [(9+\sqrt{65})/8]^r$. Using these results, and taking into account correlation function (22), it is easy to establish the following asymptotic form for the average number of steps on the surface: $M^{(r)} \sim (\lambda_2^{(b)})^r$ and $M^{(r)} \sim (\lambda_2^{(c)})^r$, with $\lambda_2^{(b)} = (21+\sqrt{249})/4$ and $\lambda_2^{(c)} = (9+\sqrt{65})/2$ for cases (b) and (c), respectively.

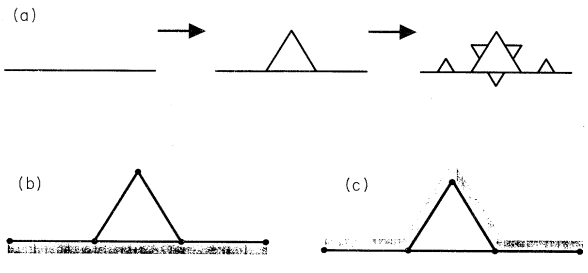

FIG. 3. (a) First two stages in the iterative construction of the branching Koch curve. We consider two cases of adsorbing boundaries—the one-dimensional line (b) and the nonbranching Koch curve (c).

This allows us to obtain the exact values of the crossover exponents presented in Table I. Due to a larger number of available sites on the adsorbing wall in case (c) than in (b), it seems somewhat surprising that the number $M^{(r)}$ diverges more slowly in the former case than in the latter one [$\lambda_2^{(b)} \approx 9.195 > \lambda_2^{(c)} \approx 8.531$, which entails a larger value of the exponent ϕ in case (b) than that in case (c)—see Table I]. This effect is subtle, and we attribute it to a tendency of the ideal chain to visit sites of higher coordination number preferentially [20].

Following the lines of Sec. II A, we have been able to extract the surface susceptibility critical behavior. It is interesting to note here that corresponding derivatives with respect to the fields H and H_s follow the same asymptotic law in both cases (b) and (c). For example, at $w=1$ in both cases we have found $\partial C_1^{(r)}/\partial H_s \sim [(3+\sqrt{5})/2]^r$, and $\partial C_1^{(r)}/\partial H \sim \partial C^{(r)}/\partial H \sim [(7+3\sqrt{5})/4]^r$. This means that the difference appearing between the values of concomitant surface susceptibility critical exponents for cases (b) and (c)—see Table I—has to be attributed only to different number of surface sites in these two cases ($\mathcal{N}_s^{(r)} \sim 3^r$ and $\mathcal{N}_s^{(r)} \sim 4^r$, respectively). This explains why all surface susceptibility generating functions in case (c) display a slightly weaker singular behavior than their counterparts in case (b).

Speaking in more general terms, critical adsorption of an ideal polymer chain appears to be qualitatively rather similar in all three cases presented in Table I. In particular, it seems that the presence of loops in the lattice structure (Koch curves, in contrast to the case of the T fractal) does not affect the critical behavior of the chain very much. One can also verify that the scaling relation $2\gamma_1 - \gamma_{11} = \gamma + \nu(D - D_s)$, which has been established for the adsorption of self-avoiding walks on fractal lattices [4], is satisfied both at the point of adsorption transition and in the regime of desorbed phase. A similar conclusion holds in the case of the scaling relation [9] $\gamma_s = 2\gamma_1 - \gamma_1$ [for the adsorption problem on the branching Koch curve for both cases (b) and (c) we have found $\gamma_s = \ln[(47+21\sqrt{5})/6]/\ln 11 = 1.14729$ in the whole range $w \leq 1$]. On the other hand, it is interesting to note here that there is no simple connection between critical exponent ϕ and susceptibility critical exponents, corroborated in the study of the adsorption of an ideal polymer chain on fractal lattices with the same coordination number [10] (in this case, for example, at the point of the adsorption transition it has been found that $\phi = \gamma_{11}$; the values of ϕ from Table I are, however, slightly larger than the values of γ_{11} at $w=1$).

III. CASES OF LOCALIZATION

Now we turn to the adsorption problem for an ideal polymer chain on fractal lattices where the sites of the highest coordination do not form an infinite network of nearest-neighbor sites. Here we shall consider two such examples, depicted in Figs. 4 and 5. Both fractal lattices presented here have a space scaling factor equal to 3, and they provide a generalization of the well-known two- and three-dimensional Sierpinski gaskets. The main topological difference from standard gaskets is that the local coordination number in this case fluctuates significantly from site to site.

A. Ideal chain on a two-dimensional modified Sierpinski gasket

Now we are going to study critical adsorption of an ideal chain on a two-dimensional modified gasket, in the presence of an impenetrable wall sketched in Fig. 4. This can be done by using an approach quite similar to the one described in Sec. II. In analogy with (20), an appropriate partition function $Z_1^{(r)} = Z_1^{(r)}(S_1, S_2, S_3)$ can be taken in the form

$$Z_1 = D_1 \exp[A_1(S_1^2 + S_2^2) + A_2 S_3^2 + B_1 S_1 S_2 + B_2(S_1 S_3 + S_2 S_3) + C_1(S_1 + S_2) + C_2 S_3 + E_1] ,$$

where S_1 and S_2 denote two corner spins lying on the adsorbing wall, while S_3 represents the third corner spin of an rth order triangle (see Fig. 4). Now we can express the rth stage partition function as an integral which involves six corresponding partition functions of the order $(r-1)$. To write recursion relations for pertinent parameters, one has to perform an integration over seven internal spin variables—a simple task, in principle, but rather cumbersome in practice. The complete system of recursive relations take up too much space to be given here, and we present only the recursions for bulk variables A and B:

$$A' = \frac{\Gamma}{\Delta} \quad \text{and} \quad B' = \frac{\Lambda}{\Delta} , \tag{34}$$

where

TABLE I. Critical exponents for the adsorption problem of an ideal polymer chain on T-fractal and branching Koch curves with the adsorbing boundaries depicted in Figs. 3(b) and 3(c).

Lattice	$w \leq 1$		$w < 1$		$w = 1$		
D, D_s	ν	γ	γ_1	γ_{11}	γ_1	γ_{11}	ϕ
1.585, 1[a]	0.4538	0.9191	0.09230	−1	1.048	0.9110	0.9122
1.465, 1[b]	0.4582	0.9343	0.05550	−1.036	1.035	0.9227	0.9253
1.465, 1.262[c]	0.4582	0.9343	−0.06447	−1.156	0.9150	0.8027	0.8940

[a]Figure 1(b).
[b]Figure 3(b).
[c]Figure 3(c).

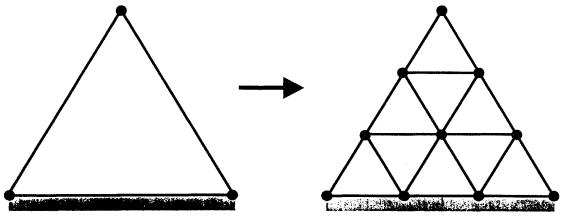

FIG. 4. Iterative construction of a two-dimensional modified Sierpinski gasket with a one-dimensional boundary.

$$\begin{aligned}\Gamma&=(1-6A)(1-4A)^2(1-4A-2B)A\\&\quad+(1-4A)(1-17A+54A^2)B^2\\&\quad-(1-6A)^2B^3-(5-28A)B^4-2B^5\ ,\\\Delta&=(1-10A+24A^2-2B+12AB-6B^2)\\&\quad\times(1-8A+16A^2-B^2)\ ,\\\Lambda&=B^3(1-10A+24A^2+4B-16AB+2B^2)\ .\end{aligned}\tag{35}$$

One can also show that the two-corner bulk correlation function takes the form

$$G^{(r)}=\frac{B^{(r)}}{(1-2A^{(r)})^2-B^{(r)}(1-2A^{(r)})-2B^{(r)^2}}\ .\tag{36}$$

Here we shall briefly describe the bulk critical behavior of an ideal polymer chain governed by the above relations. It turns out that at the critical value of fugacity, $K_c=0.227\,148\,225\ldots$, the recursion relations (34) become singular under iterations [initial conditions still retain the form (9)]. An analysis, similar to that of Sec. II, reveals the existence of an invariant line qualitatively similar to the one presented in Fig. 2. The asymptotic equation of this line can be written in the form

$$A=\tfrac{1}{6}-(3+\sqrt{3})B^2-\frac{27+4\sqrt{27}}{2}B^3+O(B^4)\ ,\tag{37}$$

which is valid for low values of B (as in previously studied examples, after a large number of iteration at $K=K_c$, $B\to 0$, and $A\to\frac{1}{6}$). Along this line, parameter B follows the law $B'=2\sqrt{3}B^2+O(B^3)$, implying

$$B^{(r)}\sim\frac{1}{2\sqrt{3}}\kappa^{2^r}\qquad\text{with }\kappa=\lim_{r\to\infty}\left[\frac{B^{(r+1)}}{B^{(r)}}\right]^{2^{-r}}=0.802\,178\,548\ldots\ .\tag{38}$$

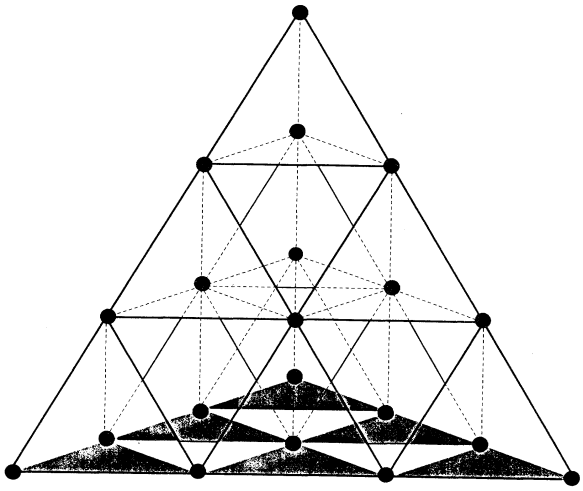

FIG. 5. Schematic representation of a three-dimensional modified Sierpinski gasket having a spatial scaling factor equal to 3. An rth stage fractal unit consists of ten $(r-1)$th stage units, which means that the final fractal object has the fractal dimension $D=\ln 10/\ln 3$. The adsorbing boundary (shadow region) is represented by the two-dimensional modified gasket from Fig. 4.

One can also show that $\partial A^{(r)}/\partial K\sim\partial B^{(r)}/\partial K\sim 2^r$ at $K=K_c$, which leads to the asymptotic law $N^{(r)}\sim(1/B^{(r)})(\partial B^{(r)}/\partial K)\sim 2^r\kappa^{-2^r}$. Consequently, instead of a standard power law, the average end-to-end distance $R\sim 3^r$ follows a logarithmic law

$$R\sim(\ln N)^{\ln(3)/\ln 2}\left[1-\frac{\ln 3}{\ln 2}\frac{\ln(\ln N)}{\ln N}\right]\ .\tag{39}$$

In comparison with the previous examples, the polymer chain is much less swollen in this case. The effect has been first described in Ref. [13], and termed localization of the chain. The localization effect has been explained in terms of an entropic trapping: In order to maximize the entropy it is profitable for an ideal chain to visit the sites of the highest coordination number. These sites act, therefore, as entropic traps preventing the swelling of the chain [13].

It is interesting to see how the above mentioned lattice structure affects the asymptotic behavior of the other quantities of interest. Here we give some details concerning the singular behavior of the generating function $\chi(K)$ for the numbers $\Omega(N)$ of all N-step paths. The singular behavior of this function can be deduced from recursion relations (34), and corresponding recursions involving field variables,

$$\begin{aligned}C'&=\frac{(1-6A)(1-4A+2B)C+2B(1-6A+B)H}{1-10A+24A^2-2B+12AB-6B^2}\ ,\\E'&=6E+\frac{(33-180A+54B)C^2+(30-168A+48B)CH+(7-40A+10B)H^2}{2(1-10A+24A^2-2B+12AB-6B^2)}\ .\end{aligned}\tag{40}$$

Using the first of these relations one can establish the asymptotic behavior $\partial C^{(r)}/\partial H|_{H=0} \sim (1+\sqrt{3})^r$, which is valid along the invariant line (37). An analysis of the second relation (40) allows us to estimate the most divergent term of $\mathcal{N}^{(r)}\chi^{(r)}$. ($\mathcal{N}^{(r)}$ denotes the number of sites of an rth order lattice, $\mathcal{N}^{(r)} \sim 6^r$.) In this way we found $\chi^{(r)} \sim (1/\mathcal{N}^{(r)}B^{(r)})(\partial C^{(r)}/\partial H)^2$, which yields to the following confluent logarithmic singularity:

$$\chi \sim \frac{1}{K_c - K}|\ln(K_c - K)|^{\varphi}$$

$$\text{with } \varphi = \frac{\ln\frac{2+\sqrt{3}}{6}}{\ln 2} = -0.684\,99\ . \quad (41)$$

On the other hand, it is widely accepted that the numbers of all N-step walks per lattice sites follow the asymptotic law: $\Omega(N) \sim K_c^{-N} N^{-\gamma}$, which entails an usual power law type of singularity. It is clear, however, that the singular form (41) is not compatible with the power law form $N^{\gamma-1}$ of the subdominant term of $\Omega(N)$. Indeed, it is rather a logarithmic subdominant term in the asymptotic form of $\Omega(N)$ (see, for example, [21]),

$$\Omega(N) \sim K_c^{-N}\left|\ln\frac{K_c}{N}\right|^{\varphi} \quad \text{as } N \to \infty\ , \quad (42)$$

which leads to the singular behavior (41). It is interesting to note here that, even though an anomalous behavior is observed neither for a nonideal linear chain nor for a kinetic random walk, an unusual critical comportment indeed has been noticed in a model of lattice animals on the same lattice [16]. Here we would like to stress that the above established behavior for an ideal polymer chain is rather a rule than an exception. For example, an analysis show that the singular behavior of type (41) occurs in the generating function $P(K)$ for the number of loops, with the exponent $\varphi = -\ln 6/\ln 2$. As we shall describe in what follows, a similar critical behavior appears in the surface generating functions as well.

To study the surface critical behavior of the chain, one has to consider the complete system of recursion relations for surface variables A_1, A_2, B_1, B_2, C_1, C_2, D_1, and E_1. The starting values of these variables can be taken in the form $A_1^{(1)} = A_2^{(1)} = C_1^{(1)} = C_2^{(1)} = E_1^{(1)} = 0$, $D_1^{(1)} = 1$, $B_1^{(1)} = Kw$, and $B_2^{(1)} = Kt$, with t being the fugacity for those monomers which lie in the layer adjacent to the boundary (in this paper we confine ourselves to the simplest case $t = 1$). In addition, one should examine the surface correlation function $G_{\parallel}$ for two corner spins lying on the adsorbing boundary. This function has the form

$$G_{\parallel} = \frac{B_1 - 2A_2B_1 + B_2^2}{(1-2A_1+B_1)(1-2A_1-2A_2+4A_1A_2-B_1+2A_2B_1-2B_2^2)}\ , \quad (43)$$

where we have omitted the iteration index (r). Alternatively, one may study the correlation function $G_{\perp}$ for two corner spins, one of which lies on the adsorbing surface, while the other is situated on the bulk corner vertex from Fig. 4. Although $G_{\perp}$ has a somewhat different form from that of $G_{\parallel}$, it is possible to show that, at the point of adsorption transition, these two functions and their corresponding derivatives have the same asymptotic behavior. Thus we shall focus our attention here on $G_{\parallel}$ only.

An analysis shows that a general picture of the adsorption transition, described in Sec. II, holds in this case as well. In particular, a critical adsorption transition takes place for $w = 1$. At this point the successive values of corresponding surface variables satisfy the recursion relation (34) for bulk variables. The critical behavior of the chain is still determined by the invariant line (37), along which we find: $\partial B_1^{(r)}/\partial w \sim \partial B_2^{(r)}/\partial w \sim 3^{-r}$, yielding to the following law:

$$\frac{M}{N} \sim (\ln N)^{-\ln(6)/\ln 2} \quad \text{as } N \to \infty\ . \quad (44)$$

This result is in contrast with the expectation that the fraction of monomers on the adsorbing boundary vanishes according to the power law $M/N \sim N^{\phi-1}$.

The singular behavior of the surface generating functions can be extracted in a similar way. At the point of adsorption transition ($w = 1$) we have found $\partial C^{(r)}/\partial H \sim \partial C_1^{(r)}/\partial H \sim \partial C_2^{(r)}/\partial H \sim (1+\sqrt{3})^r$, $\partial C_2^{(r)}/\partial H_s \sim (\sqrt{3})^{-r}$, while $\partial C_1^{(r)}/\partial H_s$ remains unchanged under iterations along the line (37). On the other hand, an analysis of $\partial^2 E_1/\partial H \partial H_s$ shows that the leading singular behavior of $\chi_1^{(r)}$ at criticality can be represented by a term of the type $\sim 3^{-r}(1/B^{(r)})(\partial C^{(r)}/\partial H)(\partial C_2^{(r)}/\partial H_s)$, which leads to an asymptotic behavior of the same kind as that found for bulk generating function (41),

$$\chi_1(K) \sim \frac{1}{K_c - K}|\ln(K_c - K)|^{\varphi_1}$$

$$\text{with } \varphi_1 = \frac{\ln\frac{3+\sqrt{3}}{18}}{\ln 2} = -1.927\,46\ . \quad (45)$$

In an analogous way one can show that the generating function χ_{11} displays a similar behavior with a slightly weaker singularity,

$$\chi_{11}(K) \sim \frac{1}{K_c - K}|\ln(K_c - K)|^{\varphi_{11}}$$

$$\text{where } \varphi_{11} = -\frac{\ln 18}{\ln 2} = -4.169\,93\ . \quad (46)$$

In order to deduce the asymptotic behavior of the above generating functions in the regime of the desorbed phase, some caution is necessary. A careful analysis reveals that in the region $0 < w < 1$, there is another invariant manifold, in addition to (37), which controls the criti-

cal behavior of the chain. To lowest order in B the equation of that manifold can be written in the form $A_2=\frac{1}{6}-B/2$. Using this equation and (37), one can show that, at criticality, parameters B_1 and B_2 renormalize according to the laws $B_1'\approx 9BB_2^2$ and $B_2'\approx 27B^2B_2$, which leads to

$$B_1^{(r)}\sim K_1\kappa^{(5/2)2^r}\left[\frac{4}{9}\right]^{2r} \quad \text{and} \quad B_2^{(r)}\sim K_2\kappa^{2\,2^r}\left[\frac{4}{9}\right]^{r}, \tag{47}$$

where κ is given in (38), while K_1 and K_2 represent two slowly varying functions of w [it is interesting, however, that there exists a simple universal combination of these functions $K_1/K_2^2=8\sqrt{3}/27$; let us also mention that $A_1^{(r)}\to A_1^*(w)$ for large r, with $A_1^*(w)$ being a slowly varying function of w]. In this regime we also found the asymptotic law $\partial C_2^{(r)}/\partial H_s\sim(\sqrt{3})^r B^{(r)}$, whereas derivatives $\partial C^{(r)}/\partial H$ and $\partial C_1^{(r)}/\partial H_s$ follow the asymptotic laws established earlier for the case $w=1$. Using the above results, one can show that generating function $\chi_1^{(r)}$ grows up relatively slowly under iterations

$$\chi_1^{(r)}\sim 3^{-r}(\partial^2 E_1^{(r)}/\partial C^{(r-1)}\partial C_1^{(r-1)})(\partial C^{(r-1)}/\partial H)(\partial C_1^{(r-1)}/\partial H_s)\sim[(3+\sqrt{3})/3]^r ,$$

which results in a logarithmic critical behavior

$$\chi_1(K)\sim|\ln(K_c-K)|^{\varphi_1}$$
$$\text{with } \varphi_1=\frac{\ln\frac{3+\sqrt{3}}{3}}{\ln 2}=0.657\,50 . \tag{48}$$

A similar analysis shows that χ_{11} vanishes as $K\to K_c$ from below in a logarithmic way,

$$\chi_{11}(K)\sim|\ln(K_c-K)|^{\varphi_{11}}$$
$$\text{with } \varphi_{11}=-\frac{\ln 3}{\ln 2}=-1.584\,96 . \tag{49}$$

B. Ideal chain on a three-dimensional modified Sierpinski gasket

We shall only briefly consider the adsorption of an ideal polymer chain on a three-dimensional modified Sierpinski gasket depicted in Fig. 5. The fractal dimension of this lattice is equal to $D=\ln 10/\ln 3=2.095\,90$, while its adsorbing boundary is represented by a two-dimensional modified gasket from Fig. 4 (i.e., $D_s=\ln 6/\ln 3$). A set of renormalization parameters entering the appropriate partition functions can be taken in any way similar to that described in Sec. III A. The recursion relations for bulk variables A and B can be written in the form $A'=\Gamma/(2\Delta)$ and $B'=\Lambda/\Delta$, with

$$\begin{aligned}\Gamma=&2A(1-4A)^3(1-6A)^2-4A(3-16A)(1-4A)^2(1-6A)B\\&+(1-4A)(3-68A+436A^2-840A^3)B^2-4(3-65A+416A^2-828A^3)B^3\\&-3(13-150A+416A^2)B^4+6(5-22A)B^5+18B^6 ,\\ \Delta=&(1-14A+64A^2-96A^3+2AB-8A^2B-7B^2+32AB^2-2B^3)(1-10A+24A^2-6B+30AB-3B^2) ,\\ \Lambda=&(1-4A)(1-6A+3B)^2B^3 ,\end{aligned} \tag{50}$$

while the correlation function takes the form

$$G^{(r)}=\frac{B^{(r)}}{(1-2A^{(r)})^2-2B^{(r)}(1-2A^{(r)})-3B^{(r)2}} . \tag{51}$$

We find that for a critical value of the fugacity K_c, $K_c=0.142\,512\,703\ldots$, there is an invariant line

$$A=\tfrac{1}{6}-\tfrac{1}{2}B-6B^2-45B^3+216B^4+O(B^5) , \tag{52}$$

along which parameter B renormalizes according to the law $B'=B/2+O(B^3)$ [note that there is no terms of the order $O(B^2)$ in this relation; it is also useful to note that one has to retain at least the terms of the order $O(B^3)$ in (52), in order to obtain the form of renormalization equation correct to lowest order for B]. Using these results, one can show that the elements of corresponding 2×2 matrix, appearing in recursion relations for derivatives of $A^{(r)}$ and $B^{(r)}$ with respect to K [see (13)], *depend on the iteration index r*. It turns out that these elements follow the asymptotic law $\sim 4^r$, so that one finds $\partial A^{(r)}/\partial K\sim\partial B^{(r)}/\partial K\sim 2^{r^2}$. Taking into account this result and (51), it is not difficult to see that the leading asymptotic behavior of the average number of steps at $K=K_c$ has the same form, $N^{(r)}\sim 2^{r^2}$, leading to

$$R\sim\exp\left[\frac{\ln 3}{\sqrt{\ln 2}}\sqrt{\ln N}\right] , \tag{53}$$

which means that the average end-to-end distance of the chain grows up more slowly than any power of the number of steps. We can, therefore, speak of a localization of the ideal polymer chain on a three-dimensional modified Sierpinski gasket (it is obvious, however, that this localization is weaker than in the case of a two-dimensional modified gasket).

Requisite recursion relations for surface variables are very cumbersome, so here we are going to report only a few results concerning critical adsorption of the chain ($w=1$). An analysis of an appropriate surface correlation function and of a matrix which enters into recursion relations for derivatives of the variables A_1, A_2, B_1, and B_2 with respect to the fugacity w, reveals the following asymptotic behavior $M^{(r)}/N^{(r)} \sim 2^{-r}$, which yields further to

$$\frac{M}{N} \sim \exp[-\sqrt{\ln N^{\ln 2}}] \ . \tag{54}$$

As in the case of Sec. III A, we find that the average fraction of the polymer chain steps along the fractal adsorbing boundary vanishes more slowly than any power of its length N, providing, once again, a manifestation of the effect of localization of the chain. In this paper we did not study other surface generating functions. It seems likely, however, that the singular behavior of these functions could be similar to the one described above.

IV. CONCLUSION

In this paper we have studied the adsorption of an ideal polymer chain model on a variety of fractal lattices. Using a suitable Gaussian model, we have described a quite general approach to treat the statistics of an ideal chain in the vicinity of an adsorbing boundary. The obtained exact results on fractal lattices with nonuniform coordination show that critical adsorption in this case can be rather different from the corresponding case on fractals with a constant coordination number.

In particular, if a localization of the chain takes place, the average fraction of adsorbed monomers near the point of adsorption transition does not follow a simple power law [see (44) and (54)]. We also demonstrated that various bulk and surface generating functions can display rather complex leading singular behaviors. For example, in some cases we have been able to extract multiplicative logarithmic corrections to the leading power law [see, e.g., (41)]. Such a form of the leading singularity is in very good qualitative agreement with the results of our numerical analysis of relevant generating functions in the critical region. Due to the above mentioned singular structure of pertinent recursion relations, it is very difficult, however, to reach a satisfactory quantitative agreement between analytical and numerical findings [22]. It is also clear from our approach that we cannot *a priori* exclude the presence of some still weaker multiplicative singular terms [for example, the terms of the type $\ln^{\psi}|\ln(K_c-K)|$ in (41)]. This possibility makes every numerical approach yet more delicate, and we think that this point deserve some further investigation.

Note added: After this paper was submitted, we learned that some results presented here, concerning bulk properties of an ideal chain on fractal space, have been derived earlier in Ref. [23].

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[18] We can note here that, for $w \gg 1$, (21) can be approximated by the expressions $A_1' = A_1 + B_1^2/[2(1-4A_1)]$ and $B_1' = B_1^2/(1-4A_1)$, which represent the exact recursion relations for the simple Gaussian model on an one-dimensional lattice. It is easy to see that a functional equation of the invariant line, $A_1 = f(B_1)$, can be written in the form $f(B_1^2/[1-4f(B_1)]) - \frac{1}{2}B_1^2/[1-4f(B_1)] = f(B_1)$. It is interesting to note that this equation allows a simple closed form solution $f(B_1) = \frac{1}{4} - \frac{1}{2}B_1$, which provides the exact equation of the invariant line. Along this line we obtain $B_1' = \frac{1}{2}B_1$, yielding, once again, to $\nu = \frac{1}{2}$.

[19] In other words, a polymer chain in the vicinity of an *at-*

tractive wall is adsorbed for any finite temperature. A similar effect has been noted in all previous studies of various models of polymer adsorption on fractal spaces [3]–[8], and has been attributed to an insufficient loss of conformational entropy of the chain lying near an impenetrable attractive fractal boundary [due to the presence of impenetrable walls (holes) of all sizes in the fractal bulk]. One way to promote a finite-temperature desorbed phase is to add a repulsive part in the interaction potential between monomers and the fractal boundary. We can readily incorporate this type of potential into our models as well. One does not expect, however, that such a modification could change the critical behavior established in this paper, and therefore it will not be considered here.

[20] See Refs. [13,14]. It is worth mentioning here that there is no analogous effect in the case of a *nonideal* polymer chain on the Koch curve in the presence of the adsorbing boundaries depicted in Figs. 3(b) and 3(c). Indeed, for the self-avoiding random-walk model we have found $\phi^{(b)}=0.765\,73<\phi^{(c)}=0.852\,61$, as could be expected.

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[22] This is related to the fact that in the case of localization we have a very narrow critical region. Thus even a huge precision—$K_c-K<10^{-1000}$, in the example of Sec. III A—does not allow us to make more than ten iterations along the invariant line. Let us also mention the presence of small oscillations in the values of the correlation length, and relevant generating functions in the critical region. As a consequence, it is rather difficult to check numerically the above reported values of exponents entering leading singularities.

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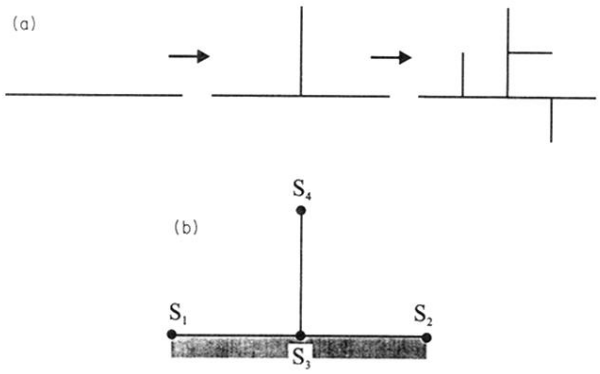

FIG. 1. (a) First two stages in the iterative construction of the T-fractal lattice. The final object has a fractal dimension $D=\ln 3/\ln 2$. (b) Schematic representation of an rth stage T fractal with the adsorbing boundary (shadow region). To obtain the partition function $Z^{(r)}(S_1,S_2)$, one has to perform integration over two internal spins S_3 and S_4 [see relation (6)].

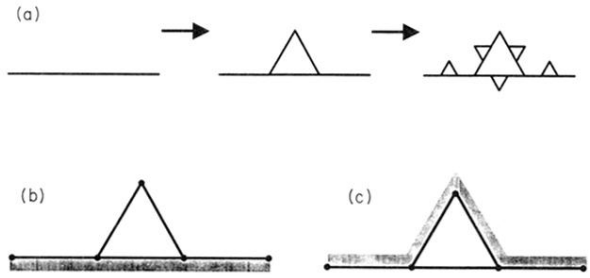

FIG. 3. (a) First two stages in the iterative construction of the branching Koch curve. We consider two cases of adsorbing boundaries—the one-dimensional line (b) and the nonbranching Koch curve (c).

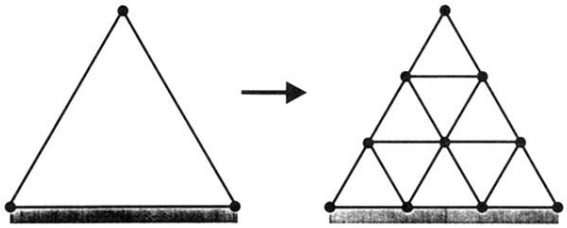

FIG. 4. Iterative construction of a two-dimensional modified Sierpinski gasket with a one-dimensional boundary.

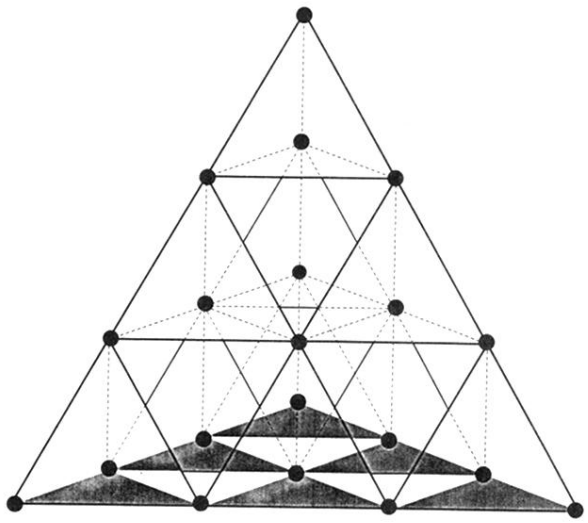

FIG. 5. Schematic representation of a three-dimensional modified Sierpinski gasket having a spatial scaling factor equal to 3. An rth stage fractal unit consists of ten $(r-1)$th stage units, which means that the final fractal object has the fractal dimension $D=\ln 10/\ln 3$. The adsorbing boundary (shadow region) is represented by the two-dimensional modified gasket from Fig. 4.