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-

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-*