

## Continuously varying crossover exponent for adsorption of linear polymers on fractals

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In this work we study the problem of physical (reversible) adsorption of a linear polymer in a good solvent in the case when the container of the polymer-solvent system is taken to be the Mandelbrot-Given (MG) model of a percolation cluster and the plane-filling (PF) fractal lattice. We accept the self-avoiding random walk as a model of the linear polymer, and, in addition, we assume that the adsorption energy pertaining to the bonds that lie in the layer next to the adsorbing boundary depends on their directions and is different from the adsorption energy for the bonds that belong to the boundary. Under these conditions we have found, in the case of both fractals (MG and PF), that the crossover exponent  $\phi$  (associated with the number of adsorbed monomers) continuously varies with the parameter that measures the monomer-surface interaction along the bonds that are perpendicular to the adsorbing boundary. We discuss this result and its relevance to the understanding of the validity (violation) of the universality hypothesis in the case of critical phenomena on fractals.

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### I. INTRODUCTION

Polymer adsorption on a rigid impenetrable adsorbent has been widely studied because of its practical importance, such as in the domain of oil recovery, chromatography, stabilization of colloids, and surface protection. The statistical mechanics approach to this problem has been successfully applied, in particular in the case of a good solvent that contains only one linear polymer interacting with the impenetrable wall. Broadly speaking, the success consists in the recognition of the polymer adsorption problem as a surface critical phenomenon. Motivated by the relevant works done in the case of Euclidean lattices, several studies have appeared recently [1–5] in which it has been assumed that the adsorbate is immersed in a fractal container, which, on the other hand, should have its own practical relevance. In this work we have studied the same problem in the case when the fractal container is taken to be the Mandelbrot-Given model of a percolation cluster and the plane-filling fractal lattice and assuming the presence of appropriate interactions between the polymer and the adsorbing boundary of the fractal lattices. In the case of both fractals, we have found that the crossover exponent  $\phi$  (associated with the number of adsorbed monomers) continuously depends on a parameter that measures the monomer-surface interaction in the layer contiguous with the impenetrable boundary. This appears to be a different result that should be relevant to the understanding of the validity (violation) of the universality hypothesis in the case of critical phenomena on fractals and hence we are going to elaborate on the way this result has been obtained and discuss its significance in the framework of the present knowledge about continuously varying critical exponents for various model systems.

This paper is organized as follows. In Sec. II we present a general approach to the calculation of the criti-

cal exponent  $\phi$  starting from properties of the corresponding partition functions (generating functions) that describe the polymer adsorption statistics. Then, the same section is divided in two subsections, in which we provide separate exact renormalization-group calculations of  $\phi$  for the Mandelbrot-Given fractal and for the plane-filling fractal. Finally, in Sec. III we give an overall discussion of the obtained results and pertinent conclusions.

### II. CALCULATION OF THE CROSSOVER EXPONENT

We describe equilibrium properties of a linear polymer in a good solvent by the self-avoiding walk (SAW) model, which is a random walk that must not contain self-intersections. We assume that the walk is performed on a lattice and make a correspondence between a step of the walk and a monomer of the polymer chain. In the terminology that applies to the SAW, we assign the weight  $x$  (fugacity) to each step in the bulk (away from the adsorbing boundary) and the weight  $xw$  to each step performed on the boundary. Here  $w$  is the Boltzmann factor  $w = e^{-\epsilon_w/kT}$ , where  $\epsilon_w$  is the energy of a monomer lying on the adsorbing wall and  $kT$  is the product of the Boltzmann constant and the temperature of the solvent. In order to promote competition between the adsorbed and desorbed polymer phases, it is necessary [1] to introduce one additional factor  $t = e^{-\epsilon_t/kT}$  in such a way that  $xt$  is the weight of those steps that are performed in the layer adjacent to the wall, while  $\epsilon_t$  is the energy of the corresponding monomer-wall interaction. Of course, one can introduce additional weighting factors (which may describe different steps of the walk), but it would not substantially change the discussion that follows.

The grand partition function (generating function) of the problem under study can be written in the form

$$C(x, w, t) = \sum_{N=1}^{\infty} Z_N(w, t) x^N, \quad (2.1)$$

where the partition function  $Z_N$  for a given number of steps  $N$  is given by

$$Z_N(w, t) = \sum_{M, L} C_N(M, L) w^{M_t L}, \quad (2.2)$$

with  $C_N(M, L)$  being the total number of all possible SAWs of  $N$  steps, out of which  $M$  are performed on the adsorbing boundary and  $L$  are made in the layer next to the boundary. The statistics of SAWs displays critical behavior when (2.1) becomes singular, that is, when  $x$  reaches from below the value  $x_c$  that, for large  $N$ , satisfies

$$Z_N(w, t) x_c^N = 1, \quad (2.3)$$

whereupon one can write [6] the corresponding free energy per step (per monomer)

$$f_{\text{sing}} = kT \ln x_c(w, t). \quad (2.4)$$

In addition, we can establish a relation between  $x_c$  and the average number of the adsorbed monomers  $\langle M \rangle$ . Indeed, by definition  $\langle M \rangle$  is given by

$$\langle M \rangle = \frac{\sum_{M, L} M C_N(M, L) w^{M_t L}}{Z_N(w, t)} = w \frac{\partial \ln Z_N}{\partial w}. \quad (2.5)$$

For the critical fugacity  $x_c$ , the average number  $\langle N \rangle$  of the monomers that comprise the polymer chain is very large and consequently we can insert (2.3) in (2.5)

$$\frac{\langle M \rangle}{\langle N \rangle} = - \frac{\partial \ln x_c}{\partial \ln w}. \quad (2.6)$$

In the high-temperature region, at the critical fugacity  $x_c$  and small  $w$  (for given  $t$ ), the polymer is in a bulk state and  $\langle M \rangle$  is vanishingly small, while in the low-temperature region, for large  $w$ , the adsorption takes place and  $\langle M \rangle$  is proportional to  $\langle N \rangle$ . Between the high- and low-temperature regions, there is a crossover temperature  $T_a$  such that the number of adsorbed monomers is given by the power law

$$\langle M \rangle \sim \langle N \rangle^\phi, \quad (2.7)$$

where  $\phi$  is the crossover exponent [7]. Now we would like to establish a relation between the crossover exponent  $\phi$  and the properties of the critical manifold  $x_c(w, t)$ , for the polymer adsorption problem, in the space  $(x, w, t)$ . To this end, we first denote by  $w^*$  the value of  $w$  for  $T = T_a$ . In the neighborhood of a point on the line  $x_c^* = x_c(w^*, t)$ , which is expected to be a tricritical point, we substitute  $(x_c^* - x_c)^{-1}$  for the conjugate variable  $\langle N \rangle$ , so that (2.6) and (2.7) give

$$(x_c^* - x_c)^{1-\phi} \sim - \frac{w^*}{x_c^*} \frac{\partial x_c}{\partial w}. \quad (2.8)$$

Taking into account that  $w^*/x_c^*$  appears here as a constant, we find

$$(x_c^* - x_c) \sim (w - w^*)^{1/\phi}. \quad (2.9)$$

This simple relation, together with (2.4), will be useful in analyzing phase diagrams of the problem under study and, in particular, it will be helpful in cases of numerical corroboration of results obtained through the renormalization-group approach to the problem.

### A. The Mandelbrot-Given fractal

In this subsection we apply the exact renormalization-group (RG) method to study the problem of polymer adsorption in the case of the Mandelbrot-Given (MG) fractal, which was proposed as a model for the percolation cluster [8,9]. More precisely, we will study the backbone of the MG fractal (see Fig. 1) as we expect that the removed dangling bonds do not affect the critical behavior of the accepted SAW model. In this case the impenetrable adsorbing boundary appears to be the one-dimensional edge of the fractal backbone and in order to calculate the critical exponent  $\phi$  we need to introduce the three restricted partition functions  $B^{(n)}$ ,  $C^{(n)}$ , and  $D^{(n)}$ , which are relevant to the  $n$ th stage of the fractal construction (see Fig. 2). For arbitrary  $n$ , the self-similarity of the fractal under study implies the recursion relations

$$B' = B^3 + B^5, \quad (2.10)$$

$$C' = C^3 + C^2 D^2 B, \quad (2.11)$$

$$D' = D B^2 + D B^4, \quad (2.12)$$

where we have used the prime for the  $n$ th-order partition functions and no indices for the  $(n-1)$ th-order partition functions. In fact, Eqs. (2.10)–(2.12) are the RG transformations and  $B$ ,  $C$ , and  $D$  can be thought of as the RG parameters. In accord with the physical picture described at the beginning of this section, we assume the initial conditions

$$B^{(0)} = x, \quad C^{(0)} = xw, \quad D^{(0)} = xt, \quad (2.13)$$

which are pertinent to the corresponding bonds of the MG fractal lattice. The set of the RG transformations has three nontrivial fixed points  $(b_{\text{MG}}^*, 0, b_{\text{MG}}^* t)$ ,

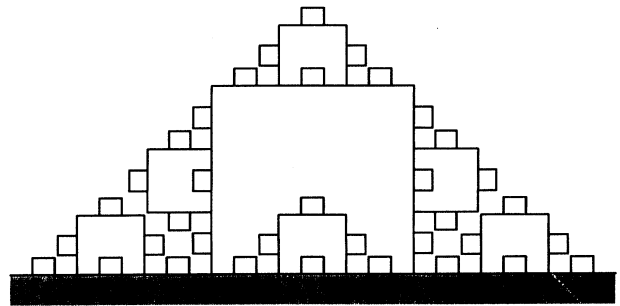


FIG. 1. Backbone of the Mandelbrot-Given (MG) fractal model of the percolation cluster [8,9], at the  $n=3$  stage of the fractal construction. The shaded region depicts the impenetrable wall, with the adsorbing boundary whose fractal dimension  $d_s$  is equal to one. The fractal dimension  $d_f$  of the MG fractal is equal to  $\ln 6 / \ln 3$ .

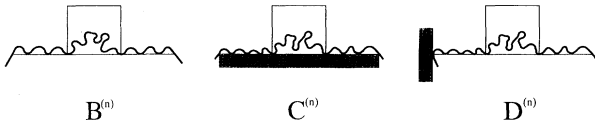


FIG. 2. Diagrammatic representation of the three restricted partition functions for an  $n$ th stage construction of the MG fractal. The fractal interior structure is not shown (it is manifested by wiggles of the SAW paths).

$[b_{MG}^*, C_{MG}^*(t), b_{MG}^*t]$ , and  $(0,1,0)$ , which we shall term, respectively, the bulk, crossover, and adsorption fixed point. Here we have introduced the notation

$$b_{MG}^* = \left[ \frac{\sqrt{5}-1}{2} \right]^{1/2} \quad (2.14)$$

for the fixed point value of (2.10). On the other hand,

$$C_{MG}^*(t) = \frac{1}{2} [\sqrt{(b_{MG}^*)^6 t^4 + 4 - (b_{MG}^*)^3 t^2}] \quad (2.15)$$

is the parameter-dependent solution of (2.11) for the fixed point values  $B^* = b_{MG}^*$  and  $D^* = b_{MG}^*t$ .

Knowing the fixed points of the RG equations (2.10)–(2.12) and starting with the initial conditions (2.13), we can perform an analysis of the domains of attraction of particular fixed points in the space of the interaction parameters  $w$  and  $t$ . Our results of this analysis are depicted in Fig. 3, where there is one main curve  $w^*(t) = C_{MG}^*(t)/b_{MG}^*$ , which divides the entire space in two parts: the bulk region (below the curve) and the adsorption region (above the curve). The bulk region is in fact the domain of attraction of the bulk fixed point  $(b_{MG}^*, 0, b_{MG}^*t)$  that is characterized by only one relevant eigenvalue  $\lambda_B = 3(b_{MG}^*)^2 + 5(b_{MG}^*)^4 = 3.76393$ , which

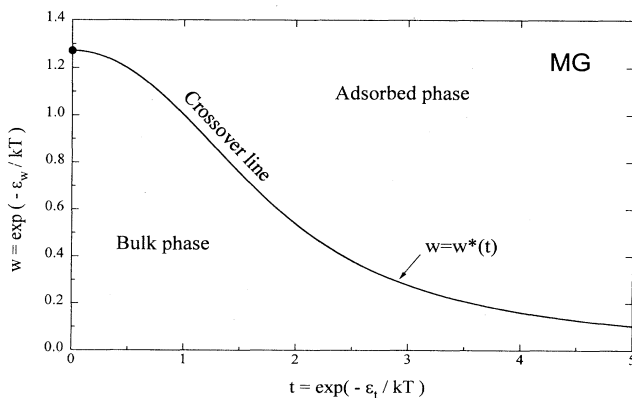


FIG. 3. “Phase diagram” for the MG polymer adsorption problem in the space of the interaction parameters  $w$  and  $t$ . One should note that there are two phases (the bulk phase and the adsorbed phase), which are separated by the crossover line  $w = w^*(t)$ . The solid circle (located at  $t=0$  and  $w=1/b_{MG}^*$ ) corresponds to the repulsive fixed point  $(b_{MG}^*, 1, 0)$  and can be associated with the first-order phase transition. The latter fact has been confirmed by the numerical analysis of  $f_{\text{sing}}$  that is given by (2.4).

gives the end-to-end distance critical exponent  $\nu_B = \ln 3 / \ln \lambda_B = 0.82885$ . On the other hand, the adsorption region is the domain of attraction of the adsorption fixed point  $(0,1,0)$ , where the end-to-end distance critical exponent  $\nu_A$  is equal to 1, implying that the polymer is entirely adsorbed. Finally, if the iteration of the RG transformations starts with a point on the line  $w = w^*(t)$ , the crossover fixed point  $[b_{MG}^*, C_{MG}^*(t), b_{MG}^*t]$  is reached, which has two relevant eigenvalues  $\lambda_B$  and  $\lambda_\phi(t)$  with the distinctive property that the second one depends on the interaction parameter  $t$ , that is,  $\lambda_\phi(t) = 3[C_{MG}^*(t)]^2 + 2(b_{MG}^*)^3 C_{MG}^*(t)t^2$ . Within the RG approach, the two eigenvalues  $\lambda_B$  and  $\lambda_\phi(t)$  determine the crossover exponent  $\phi$  through the relation [1]

$$\phi = \frac{\ln \lambda_\phi}{\ln \lambda_B}, \quad (2.16)$$

which in the case under study gives

$$\phi(t) = \frac{\ln \{ 3[C_{MG}^*(t)]^2 + 2(b_{MG}^*)^3 C_{MG}^*(t)t^2 \}}{\ln [3(b_{MG}^*)^2 + 5(b_{MG}^*)^4]}. \quad (2.17)$$

Hence one can notice that in the case of the MG fractal the crossover exponent  $\phi$  continuously depends on the interaction parameter  $t$  that measures the monomer-surface interaction in the layer contiguous with the impenetrable boundary. The relation (2.17) is plotted in Fig. 4, where one can see that  $\phi(t)$  is a *continuously varying* (monotonically decreasing) function of  $t$ . We would like to emphasize here that we have confirmed this finding by obtaining the same graph through the complementary approach presented at the beginning of this section, that is, using directly the formula (2.9) for numerical evaluation of the exponent  $\phi$ .

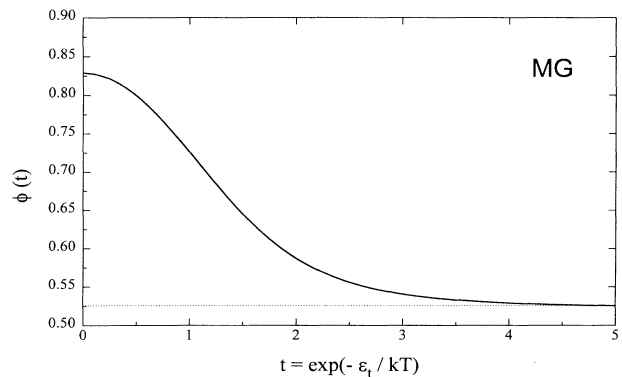


FIG. 4. Crossover exponent  $\phi$  for the adsorption problem on the MG fractal. The solid curve is given by Eq. (2.17), whereas the dotted line represents the asymptotic value of  $\phi$  when  $t \rightarrow \infty$ , i.e.  $\phi_\infty = \ln 2 / \ln(6 - \sqrt{5})$ . In the opposite limit, that is, when  $t \rightarrow 0$ , the crossover exponent approaches  $\phi_0 = \ln 3 / \ln(6 - \sqrt{5})$ . The limiting values  $\phi_0$  and  $\phi_\infty$  may be compared with the specific lower limit  $\phi_l = \ln(\lambda_B/2) / \ln \lambda_B = 0.47705$  and the upper limit  $\phi_u = \ln 3 / \ln 6 = 0.61315$ , which follow from the phenomenological proposal of Bouchaud and Vannimenus [1].

**B. The plane-filing fractal**

The plane-filing (PF) fractal lattice has two distinctive properties in comparison with the MG fractal and the Sierpinski gaskets (SG's) that were studied in the preceding subsection and in previous papers [1,2,4,5], respectively. In the first place, the fractal dimension of the PF fractal is equal to the dimension of the Euclidean space in which PF is embedded in, that is,  $d_f = 2$ . Second, the impenetrable adsorbing boundary of PF is a fractal with  $d_s = \ln 5 / \ln 3$  (see Fig. 5), whereas both the MG and SG fractals have  $d_s = 1$ . The fractal structure of the adsorbing boundary of the PF fractal makes it necessary to introduce one weighting factor  $u = e^{-\epsilon_u / kT}$ , where  $\epsilon_u$  is the corresponding monomer-wall interaction (see Fig. 6). Accordingly,  $xu$  is the weight of the steps along the bonds that appear as bridges over unit holes on the adsorbing wall.

In order to study the adsorption problem in the case of the PF fractal, we follow the RG approach applied for the MG fractal. Thus, for arbitrary  $n$ th stage fractal construction, we introduce four restricted partition functions  $B^{(n)}$ ,  $C^{(n)}$ ,  $D^{(n)}$ , and  $E^{(n)}$  (see Fig. 7), which satisfy the recursion relations

$$B' = B^3 + 2B^5, \tag{2.18}$$

$$C' = C^2(C^3 + E + D^2B), \tag{2.19}$$

$$D' = D(B^2 + 2B^4), \tag{2.20}$$

$$E' = D^2(B + 2B^3). \tag{2.21}$$

Here we have used the prime for the  $n$ th-order partition functions and no indices for the  $(n-1)$ th-order partition functions. Now taking into account the arrangement of

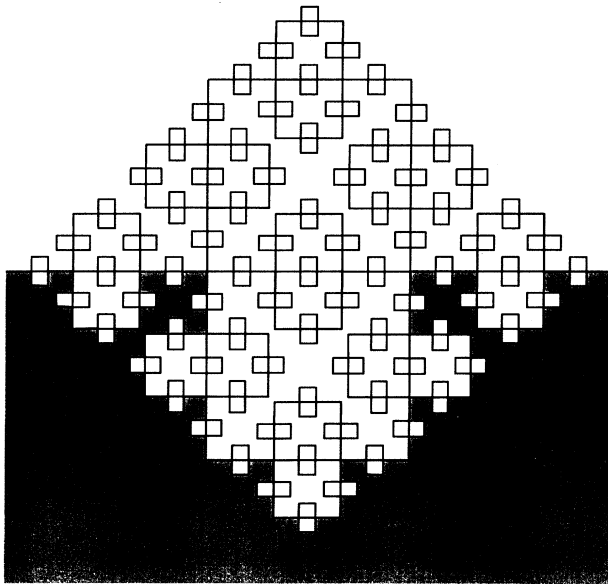


FIG. 5. Plane-filing (PF) fractal at the  $n = 3$  stage of construction. The shaded region depicts the impenetrable wall, with the adsorbing boundary whose fractal dimension  $d_s$  is equal to  $\ln 5 / \ln 3$ . It should be noticed that the fractal dimension  $d_f$  of the entire PF lattice is equal to 2.

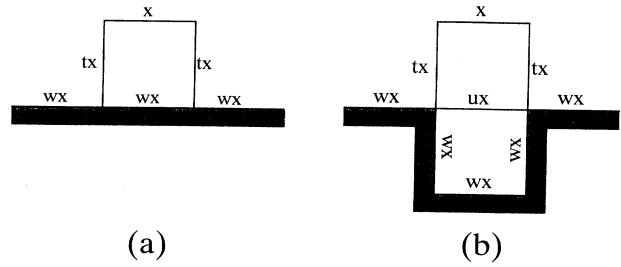


FIG. 6. Weight factors of the SAW steps (monomers) on the various bonds of the impenetrable boundaries of the (a) MG and (b) PF fractal. Thus, for instance, the weight factor  $xw$  corresponds to each step (adsorbed monomer) performed directly on the boundary, where  $w$  is the Boltzmann factor  $w = e^{-\epsilon_w / kT}$  and  $\epsilon_w$  is the pertinent energy of the monomer-wall interaction.

bonds at the adsorbing wall (see Fig. 6), we assume the initial conditions

$$B^{(0)} = x, \quad C^{(0)} = xw, \quad D^{(0)} = xt, \quad E^{(0)} = xu. \tag{2.22}$$

Accepting the above recursion relations as a set of RG transformations, we find the three nontrivial fixed points  $(b_{PF}^*, 0, b_{PF}^*t, b_{PF}^*t^2)$ ,  $[b_{PF}^*, C_{PF}^*(t), b_{PF}^*t, b_{PF}^*t^2]$ , and  $(0, 1, 0, 0)$ , which we shall call the bulk, crossover, and adsorption fixed point, respectively. Here  $b_{PF}^* = \sqrt{2}/2$ , whereas  $C_{PF}^*(t)$  should satisfy the equation

$$C_{PF}^*(t) \left[ [C_{PF}^*(t)]^3 + \frac{3\sqrt{2}}{4}t^2 \right] = 1, \tag{2.23}$$

that is,  $C_{PF}^*(t)$  is given by

$$C_{PF}^*(t) = \frac{(9t^2\sqrt{2Q} - \sqrt{P^3})^{1/2} - (P^3)^{1/4}}{(48)^{1/3}(Q)^{1/6}(P)^{1/4}}, \tag{2.24}$$

where

$$P = -8(3)^{1/3} + (2Q^2)^{1/3}, \tag{2.25}$$

$$Q = \frac{8}{4}t^2 + [3(256 + \frac{2187}{64}t^8)]^{1/2}.$$

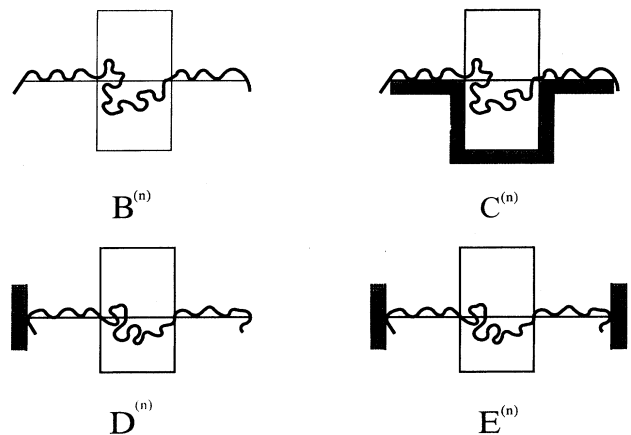


FIG. 7. Diagrammatic representation of the four restricted partition functions for an  $n$ th stage construction of the PF fractal. The fractal interior structure is not shown (it is indicated by wiggles of the SAW paths).

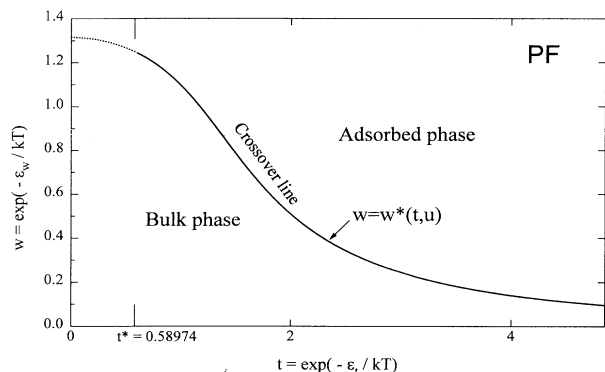


FIG. 8. Phase diagram for the PF polymer adsorption problem is the space of the interaction parameters  $w$  and  $t$ , for a given value of  $u = 0.5$ . The crossover line (solid line) merges with the dotted line of the first-order phase transitions (which appear in the region  $0 \leq t < t^*$ ). The bulk phase exists only for  $x_c = b_{PF}^*$ , where  $b_{PF}^* = \sqrt{1/2}$ , while the adsorbed phase exists for  $x_c < b_{PF}^*$ .

The RG analysis of the transformations (2.18)–(2.21), together with the initial conditions (2.22), reveals different features, such as the appearance of a crossover surface (instead of the crossover line), together with a domain of the first-order phase transitions (see Fig. 8). In Fig. 8 one can see that there are two regions: the bulk phase region, which is the domain of attraction of the bulk fixed point  $(b_{PF}^*, 0, b_{PF}^*t, b_{PF}^*t^2)$  that is characterized by only one relevant eigenvalue  $\lambda_B = 3(b_{PF}^*)^2 + 10(b_{PF}^*)^4 = 4$ , and the adsorbed phase region, which is domain of attraction of the adsorption fixed point  $(0, 1, 0, 0)$  whose relevant eigenvalue  $\lambda_A$  is equal to 5. The eigenvalues  $\lambda_B$  and  $\lambda_A$  give the corresponding end-to-end distance critical exponents  $\nu_B = 0.79248$  and  $\nu_A = 0.68261$ , which are both smaller than the respective values for the MG fractal. For given  $u$ , the line  $w = w^*(t, u)$  that separates the bulk phase region from the adsorbed phase region (see Fig. 8) is given by the implicit equation

$$(b_{PF}^*w^*)^2[(b_{PF}^*w^*)^3 + b_{PF}^*u + (b_{PF}^*)^3t^2] - C_{PF}^*(t) = 0. \quad (2.26)$$

If we start the iteration of the RG transformations (2.18)–(2.21) with a point on the line  $w = w^*(t, u)$ , the crossover fixed point  $[b_{PF}^*, C_{PF}^*(t), b_{PF}^*t, b_{PF}^*t^2]$  is reached. The latter has two relevant eigenvalues  $\lambda_B = 4$  and  $\lambda_\phi(t) = 2 + 3[C_{PF}^*(t)]^2$ , which gives the following formula for the crossover exponent:

$$\phi(t) = \frac{\ln\{2 + 3[C_{PF}^*(t)]^2\}}{\ln 4}. \quad (2.27)$$

Here we see again (as in the case of the MG fractal) that  $\phi$  is continuous function of the monomer-wall interaction parameter  $t$ . However, it appears that the values of the function (2.27) in the region  $0 < t < t^*$ , where  $t^* = \frac{2}{3}(\frac{3}{8})^{1/8}$ , are larger than one, which is physically untenable, judging according to the formula (2.7). For this reason, we have analyzed the first derivative of the singu-

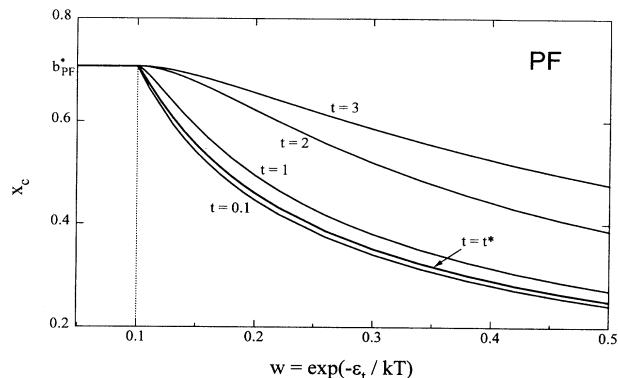


FIG. 9 Critical fugacity curves for the PF fractal problem as a function of the parameter  $w$ , for various values of  $t$  and the corresponding values of  $u$  that follow from (2.26) with  $w^* = 0.1$ . One can notice the difference in behavior of these curves, for  $t > t^*$  and  $t < t^*$ , in the vicinity of the point  $(b_{PF}^*, 0.1)$ . Indeed, precise numerical investigations revealed that the critical fugacity function  $x_c(w)$ , at the point  $(b_{PF}^*, 0.1)$ , has a continuous first-order derivative for  $t > t^*$  and a discontinuous first-order derivative for  $t < t^*$ , which confirms that for  $t < t^*$  the polymer system undergoes the first-order phase transitions. The vertical dotted line serves merely to facilitate location of the point  $(b_{PF}^*, 0.1)$ .

lar part of the free energy using the formula (2.4) (see Fig. 9). Thus, performing very accurate numerical investigations, we have found that the region  $0 < t < t^*$  corresponds to the first-order phase transitions between the bulk and the adsorbed polymer phases. On the other hand, for  $t^* < t < \infty$  we find that the singular part of the free energy (2.4) has characteristics that are pertinent to the critical behavior of the polymer system, with the plausible values for the crossover exponent  $\phi$  (see Fig. 10) ranging between the extreme value  $\phi = 1$ , for  $t^* = 0.58974$ , and the Euclidean value  $\phi = \frac{1}{2}$  [10], which appears in the limit  $t \rightarrow \infty$ .

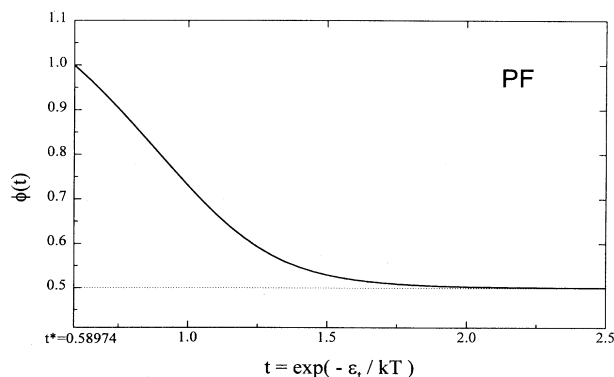


FIG. 10. Crossover exponent  $\phi$  for the adsorption problem on the PF fractal. The dotted line represents the Euclidean value of  $\phi = \frac{1}{2}$ . The range  $(0.5, 1)$  of possible values of  $\phi$  can be compared with the specific lower limit  $\phi_l = \ln(\frac{20}{9})/\ln 4 = 0.57600$  and the upper limit  $\phi_u = \ln 5/\ln 9 = 0.73249$  which follow from the phenomenological proposal of Bouchaud and Vannimenus [1].

### III. DISCUSSION AND SUMMARY

In the modern theory of critical phenomena, there are notable examples of systems on the Euclidean lattices, such as the two-dimensional  $XY$  model and the Ashkin-Teller model, which have exponents that change continuously as an interaction parameter varies. Recently, the continuous dependence of a critical exponent on a parameter has been found in the case of oriented polymers (oriented SAWs) in which the short-range repulsive interactions between two segments depend on their relative orientations [11]. Moreover, continuous variation of a critical exponent has been reported [12] in the case of a dynamical two-dimensional  $XY$  model described in accordance with the concept of the self-organized criticality [13]. Within the framework of the RG theory, it has been understood that continuously varying critical exponents with a parameter are related to the existence of continuous manifolds of fixed points in the interaction parameter space. Indeed, in the cases under study in this paper, we have found that the continuous variation of the crossover exponent  $\phi$  is associated with existence of continuous lines of fixed points, which is, to our knowledge, the first such example for systems situated on fractals.

The specific variation of the crossover exponent  $\phi$  for the MG and PF fractals is shown in Figs. 4 and 10, respectively. Looking at these figures, one might be puzzled by the fact that  $\phi$  decreases as the monomer-wall interaction  $\epsilon_t$  becomes more and more attractive ( $t \rightarrow \infty$ ). However, one should keep in mind that the crossover phenomenon (see Figs. 3 and 8) for increasing  $t$  occurs only if  $w$  decreases, that is, only if the monomer-wall interaction  $\epsilon_w$  becomes increasingly repulsive, which altogether makes the region close to the adsorbing wall more and more neutral and, consequently,  $\phi$  should decrease. It is appropriate to compare here our findings with the general upper  $\phi_u = d_s/d_f$  and lower  $\phi_l = 1 - (d_f - d_s)v_B$  limits proposed by Bouchaud and Vannimenus [1] for the crossover exponent  $\phi$ . Inserting the relevant values for  $d_s$ ,  $d_f$ , and  $v_B$  in the latter expressions, one can see that in the case of the MG fractal  $\phi$  goes beyond the upper limit ( $\phi_u = 0.61315$ ), while in the case of the PF fractal both limits ( $\phi_u = 0.73249$  and  $\phi_l = 0.57600$ ) are violated. The reason for the violation of the lower bound in the case of the PF fractal can be found in the assumption [1] that the number of accessible sites  $\rho(z)$ , as a function of distance  $z$  from the adsorbing wall, should be a monotonically decreasing function. This assumption is plausible in

the case of the MG fractal (see Fig. 1); however, it is hardly tenable in the case of the PF fractal, in which case  $\rho$ , instead of being a decreasing function of  $z$ , is a constant (because the lattice above the adsorbing wall is compact; see Fig. 5). Next we note that the reason for the violation of the phenomenological prediction for the upper bound of the crossover exponent  $\phi$  in both cases (MG and PF) lies in the presumption [1] that, for a polymer that stays in equilibrium, the self-repelling energy is homogeneously distributed in the adsorbed layer. This presumption is conceivable in situations characterized by small values of  $\phi$ , but not in those marked by larger values of  $\phi$  (which is exactly what happens in the cases under study). Then a large number of monomers can be found in close proximity of the adsorbing wall and consequently the large part of the self-repelling energy becomes concentrated very close to the wall, bringing about an inhomogeneous distribution of the self-repelling energy within the entire adsorbed layer, which in turn violates the assumed requirement for polymer equilibrium. The observed violations, together with the previously found cases [5,14–16], call for a work on augmenting the only known limits for the crossover exponent  $\phi$  [1].

In summary, we may point out that in this work we have found, for the fractal MG and PF lattices, that the crossover exponent  $\phi$  continuously varies with the parameter  $t = e^{-\epsilon_t/kT}$  that measures the monomer-surface interaction in the layer adjacent to the impenetrable adsorbing wall. The same interaction was included in the model of polymer adsorption in the case of the SG fractals, but it was found [1,2,4,5] that the relevant crossover exponents  $\phi$  are independent of the interaction parameter  $t$ . This distinction in the behavior of the crossover exponent in the two cases (MG and PF versus SG) can be related to the distinction between the corresponding eigenvalues at the crossover fixed point. In the case of the SG fractals, the variation of  $t$  is dominated by the irrelevant eigenvalue ( $\lambda_t < 1$ ) [1], whereas in the case of the MG and PF fractals  $t$  is invariant under the RG transformations, that is, variation of  $t$  at the crossover fixed point is controlled by the marginal eigenvalue  $\lambda_t = 1$ . In addition, we may note that the dependence of  $\phi$  on  $t$  appears in the case of fractals in which the bonds that are weighted by  $xt$  (see Fig. 6) are not mutually connected (in contrast to the case of the SG fractals). Finally, this observation can be corroborated by studying the adsorption problem on the Koch curve type of fractals.

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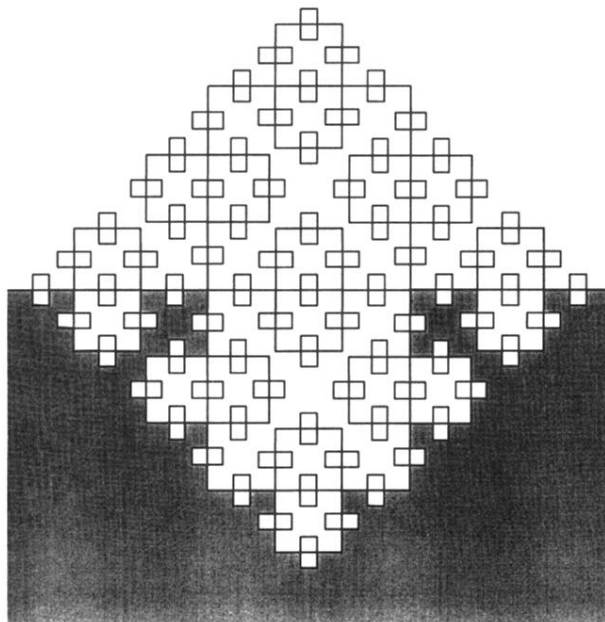


FIG. 5. Plane-filling (PF) fractal at the  $n=3$  stage of construction. The shaded region depicts the impenetrable wall, with the absorbing boundary whose fractal dimension  $d_s$  is equal to  $\ln 5 / \ln 3$ . It should be noticed that the fractal dimension  $d_f$  of the entire PF lattice is equal to 2.