

Exact study of surface critical exponents of polymer chains grafted to adsorbing boundary of fractal lattices embedded in three-dimensional space

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Abstract.

We study the adsorption problem of linear polymers, when the container of the polymer–solvent system is taken to be a member of the three dimensional Sierpinski gasket (SG) family of fractals. Members of the SG family are enumerated by an integer b ($2 \leq b \leq \infty$), and it is assumed that one side of each SG fractal is impenetrable adsorbing boundary. We calculate the critical exponents γ_1 , γ_{11} , and γ_s which, within the self-avoiding walk model (SAW) of polymer chain, are associated with the numbers of all possible SAWs with one, both, and no ends grafted on the adsorbing impenetrable boundary, respectively. By applying the exact renormalization group (RG) method, for $2 \leq b \leq 4$, we have obtained specific values for these exponents, for various type of polymer conformations. We discuss their mutual relations and their relations with other critical exponents pertinent to SAWs on the SG fractals.

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1. Introduction

The statistical properties of linear polymers near an impenetrable short-range attractive boundary have been extensively studied for a long time. The most frequently applied model for a polymer chain has been the self-avoiding walk (SAW) model (that is, the walk without self-intersections), so that steps of the walk have been identified with monomers that comprise the polymer, while the solvent surrounding has been represented by a lattice. Here we assume that polymer is immersed in a good solvent, and interacts only with an adsorbing surface bounding the polymer container, so that for strong enough monomer-surface interaction the polymer undergoes phase transition from desorbed to adsorbed phase.

Since the polymer adsorption is a surface critical phenomenon, it has been possible to describe various polymer quantities in terms of power laws described by concomitant critical exponents. Early investigations of polymer behavior near attractive surfaces dealt with polymer chains immersed in homogeneous spaces with planar adsorbing boundaries (see [1] for a review). These studies have been subsequently extended to polymers immersed in porous (inhomogeneous) media, modeled by fractal lattices embedded in two-dimensional [2–4] and three-dimensional [5,6] space. In these studies, almost exclusively, only two critical exponents have been studied, that is, the end-to-end distance critical exponent ν and the crossover exponent ϕ (that governs the number of contacts between the polymer and the surface). However, a complete picture about the adsorption problem requires knowledge of surface critical exponents that describe numbers of polymer configurations grouped according to the different ways of anchoring to the adsorbing boundary. In terms of the self-avoiding random walk (SAW) model of linear polymers, these exponents are defined by the following formulas for numbers of possible different configurations averaged over the number of sites on the impenetrable surface

$$C_{11}(N, T) \sim \mu^N N^{\gamma_{11}-1}, \quad C_1(N, T) \sim \mu^N N^{\gamma_1-1}, \quad C_s(N, T) \sim \mu^N N^{\gamma_s-1}, \quad (1.1)$$

valid for large number N of SAW steps. Here C_{11} , C_1 , and C_s , are numbers of all possible SAWs with both, one, and no ends grafted on the boundary respectively, $\mu = \mu(T)$ is temperature dependent connectivity constant and γ_{11} , γ_1 , and γ_s , are concomitant surface critical exponents that take different values in various polymer phases. So far, surface critical exponents have been studied mostly for SAWs near the boundary surfaces of two and tree-dimensional Euclidean spaces. These studies were performed using various techniques including series enumeration [7–9], conformal invariance theory [10, 11], Coulomb gas method [12], field theoretical approach [13, 14], and Monte Carlo simulations [15, 16]. On fractals, the surface critical exponents were studied only for SAWs immersed in a good solvent on two-dimensional fractal lattices [17, 18]. In this paper we study the surface critical exponents for the polymer chain situated on fractals that belong to the three-dimensional (3d) Sierpinski gasket (SG) family. Each member of the SG family is labeled by an integer b ($2 \leq b \leq \infty$), and it is assumed that one side of each SG fractal is impenetrable adsorbing wall. By applying an exact renormalization

group (RG) method for the SAW model that includes monomer-surface interactions we have calculated critical exponents γ_{11} , γ_1 , and γ_s , for $b = 2, 3$ and 4 fractals.

This paper is organized as follows. In section 2 we describe the 3d SG fractals for general scaling parameter b , and introduce the self-avoiding walk model in the case when a boundary of 3d SG fractal is an adsorbing surface. Then, we present the framework of the general RG method for studying the polymer adsorption problem on these fractals. In section 3 we display the exact results for the studied critical exponents γ_1, γ_{11} , and γ_s for $b = 2, 3$ and 4 fractals, in different polymer regimes. All obtained results are summarized, discussed and compared with related previous results in section 4. Finally, some technical details are given in the Appendix.

2. Framework of the renormalization group approach

In this section we are going to expound on the renormalization group (RG) approach of calculating the critical exponents γ_1, γ_{11} , and γ_s for the adsorption problem of SAWs immersed in a solvent modeled by fractals belonging to the 3d SG family of fractals. Here we give a brief summary of their basic properties. We start with recalling the fact that each member of 3d SG fractal family is labeled by an integer $b \geq 2$ and can be constructed in stages. At the first stage ($r = 1$) of the construction there is a tetrahedron of base b containing $b(b+1)(b+2)/6$ upward oriented unit tetrahedrons. The subsequent fractal stages are constructed recursively, so that the complete self-similar fractal lattice can be obtained as the result of an infinite iterative process of successive ($r \rightarrow r + 1$) enlarging the fractal structure b times, and replacing the smallest parts of enlarged structure with the initial ($r = 1$) structure. In the case under study, we take that one of the four boundaries of the 3d SG fractal is impenetrable adsorbing surface (wall), which is itself a 2d SG fractal with the fractal dimension $d_s = \ln[b(b+1)/2]/\ln b$, whereas the fractal dimension of the complete 3d SG fractal is $d_f = \ln[b(b+1)(b+2)/6]/\ln b$.

In order to describe the effect of attractive (adsorbing) surface, one should introduce two Boltzmann factors: $w = e^{-\varepsilon_w/k_B T}$, and $t = e^{-\varepsilon_t/k_B T}$, where ε_w is the energy of a monomer lying on the adsorbing surface, and ε_t is the energy of a monomer in the layer adjacent to the surface. If we assign the weight x to a single step of the SAW walker, then the weight of a walk having N steps, with M steps on the surface, and K steps in the layer adjacent to the surface, is $x^N w^M t^K$ (see figure 1).

The weighting factors defined in the foregoing paragraph allow us to introduce the following global generating functions

$$G_{11}(x, T) = \sum_{N=1}^{\infty} x^N \sum_{M,K} \mathcal{G}_{11}(N, M, K) w^M t^K = \sum_{N=1}^{\infty} C_{11}(N, T) x^N, \quad (2.1)$$

$$G_1(x, T) = \sum_{N=1}^{\infty} x^N \sum_{M,K} \mathcal{G}_1(N, M, K) w^M t^K = \sum_{N=1}^{\infty} C_1(N, T) x^N, \quad (2.2)$$

$$G_s(x, T) = \sum_{N=1}^{\infty} x^N \sum_{M,K} \mathcal{G}_s(N, M, K) w^M t^K = \sum_{N=1}^{\infty} C_s(N, T) x^N, \quad (2.3)$$

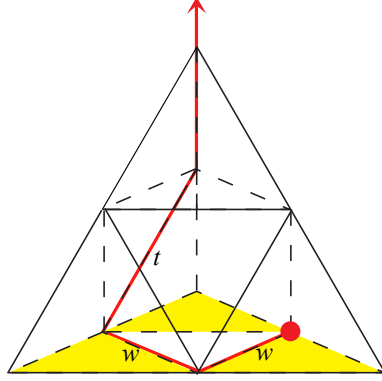


Figure 1. The fractal structure of the $b = 2$ 3d SG fractal at the first stage of construction, with an example of the SAW path starting from the adsorbing surface depicted by the yellow area. The steps on the adsorbing surface and in the adjacent layer are weighted by the factors $w = e^{-\epsilon_w/k_B T}$ and $t = e^{-\epsilon_t/k_B T}$, respectively. Here ϵ_w is the energy of a monomer lying on the adsorbing wall ($\epsilon_w < 0$), and $\epsilon_t > 0$ is the energy of a monomer that appears in the layer adjacent to the wall. The depicted SAW path corresponds to a polymer configuration with one end (red point) grafted on the adsorbing surface and has the weight $x^4 w^2 t$.

where $\mathcal{G}_1(N, M, K)$ ($\mathcal{G}_{11}(N, M, K)$) represents the average number (over all sites of adsorbing wall) of N -step SAWs with M steps on the surface and K steps in the layer adjacent to the wall provided one (both) end(s) of the walk is (are) anchored to the wall, while $\mathcal{G}_s(N, M, K)$ is the number of SAWs with no ends anchored to the wall. If we assume that, for large N , the numbers $C_{11}(N, T)$, $C_1(N, T)$ and $C_s(N, T)$ behave in accordance with the laws defined in (1.1), then the leading singular behavior of the generating functions are of the form

$$G_{11}(x, T) \sim (1 - x\mu)^{-\gamma_{11}}, \quad G_1(x, T) \sim (1 - x\mu)^{-\gamma_1}, \quad G_s(x, T) \sim (1 - x\mu)^{-\gamma_s}, \quad (2.4)$$

in the vicinity of the critical value $x_c = 1/\mu$, *i.e.* when x approaches x_c from below.

To calculate the surface critical exponents γ_1, γ_{11} , and γ_s , we have found that it is helpful to define three kinds of restricted generating functions that provide a complete description of the generating functions G_{11} , G_1 and G_s . These functions are: the traversing SAW generating functions $A^{(r)}$, $B^{(r)}$, $A_1^{(r)}$, $A_2^{(r)}$ and $B_1^{(r)}$; one-leg SAW functions $C^{(r)}$, $D^{(r)}$, $C_i^{(r)}$ ($i = 1, \dots, 4$) and $D_i^{(r)}$ ($i = 1, \dots, 6$) (which are depicted in figure 2); and, the two-leg SAW functions $E_m^{(r)}$ (which are not presented in figure 2, because they are not relevant for the critical exponent calculation [19]). Using these restricted generating functions, one can express each global generating function in the following manner. We start with the function G_{11} , that can be written in the form

$$G_{11}(x, T) = \sum_{r=0}^{\infty} \frac{1}{\left[\frac{b(b+1)}{2}\right]^{r+1}} \left(\sum_{i=1}^2 \sum_{j=1}^2 f_{ij} C_i^{(r)} C_j^{(r)} + \sum_{i=1}^2 \sum_{j=1}^3 g_{ij} C_i^{(r)} D_j^{(r)} + \sum_{i=1}^3 \sum_{j=1}^3 h_{ij} D_i^{(r)} D_j^{(r)} + \sum_m e_m E_m^{(r)} \right), \quad (2.5)$$

where the coefficients f_{ij} , g_{ij} , h_{ij} and e_m are polynomials in $A^{(r)}$, $B^{(r)}$, $A_1^{(r)}$, $A_2^{(r)}$ and $B_1^{(r)}$. Similarly, the generating functions $G_1(x, T)$ and $G_s(x, T)$ can be written as

$$\begin{aligned}
G_1(x, T) = & G_{11}(x, T) + \sum_{r=0}^{\infty} \frac{1}{\left[\frac{b(b+1)}{2}\right]^{r+1}} \left[\sum_{i=1}^2 \sum_{j=3}^4 p_{ij} C_i^{(r)} C_j^{(r)} + \sum_{i=1}^2 \sum_{j=4}^6 q_{ij} C_i^{(r)} D_j^{(r)} \right. \\
& + \sum_{i=3}^4 \sum_{j=1}^3 r_{ij} C_i^{(r)} D_j^{(r)} + \sum_{i=1}^3 \sum_{j=4}^6 s_{ij} D_i^{(r)} D_j^{(r)} + \sum_{i=1}^2 C_i^{(r)} (p_i C^{(r)} + q_i D^{(r)}) \\
& \left. + \sum_{i=1}^3 D_i^{(r)} (r_i C^{(r)} + s_i D^{(r)}) + \sum_m t_m E_m^{(r)} \right], \tag{2.6}
\end{aligned}$$

and

$$\begin{aligned}
G_s(x, T) = & \sum_{r=0}^{\infty} \frac{1}{\left[\frac{b(b+1)}{2}\right]^{r+1}} \left[\sum_{i=3}^4 \sum_{j=3}^4 p'_{ij} C_i^{(r)} C_j^{(r)} + \sum_{i=3}^4 \sum_{j=4}^6 q'_{ij} C_i^{(r)} D_j^{(r)} \right. \\
& + \sum_{i=4}^6 \sum_{j=4}^6 s'_{ij} D_i^{(r)} D_j^{(r)} + \sum_{i=3}^4 C_i^{(r)} (p'_i C^{(r)} + q'_i D^{(r)}) + \sum_{i=4}^6 D_i^{(r)} (r'_i C^{(r)} + s'_i D^{(r)}) \\
& \left. + p'(C^{(r)})^2 + q' C^{(r)} D^{(r)} + s'(D^{(r)})^2 + \sum_m t'_m E_m^{(r)} \right], \tag{2.7}
\end{aligned}$$

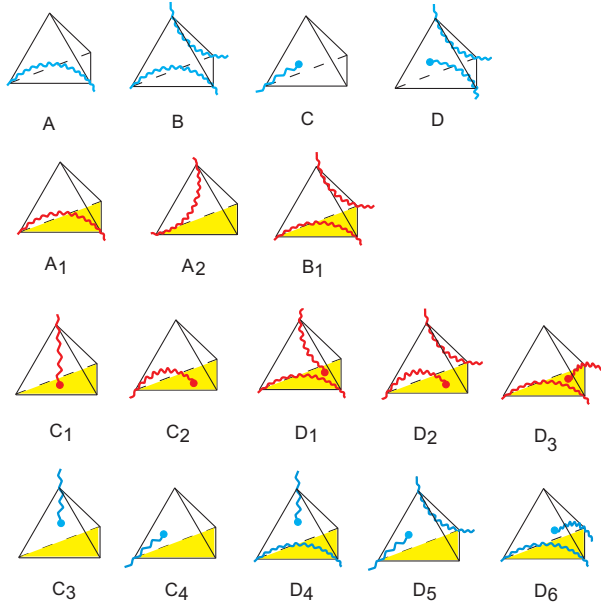


Figure 2. Schematic representation of traversing and one-leg restricted generating functions used to describe all possible configurations of SAW (needed to construct the global generating functions G_{11} , G_1 and G_s), within the r th stage of 3d SG fractal structure. Thus, for example, the $C_1^{(r)}$ represents the situation when SAW starts from the impenetrable surface and leaves the r th stage fractal lattice at its vertex which does not lie in the surface. The interior details of the r th stage fractal structure, as well as details of the chains, are not shown. Small red circles depict the SAW starting points from the attaching surface, while the blue ones denote the SAW starting points that are in the bulk part of tetrahedron lying on the surface.

where, again, the coefficients standing with one- and two-leg generating functions on the right-hand side, are polynomials in traversing functions $A^{(r)}$, $B^{(r)}$, $A_1^{(r)}$, $A_2^{(r)}$ and $B_1^{(r)}$.

Due to the self-similarity of fractals, restricted generating functions obey recursive relations, which can be interpreted as RG equations [19]. For arbitrary r , these equations for the bulk restricted partition functions (for any $b \geq 2$) have the form

$$A^{(r+1)} = \sum_{i,j} a(i,j) \left(A^{(r)}\right)^i \left(B^{(r)}\right)^j, \quad (2.8)$$

$$B^{(r+1)} = \sum_{i,j} b(i,j) \left(A^{(r)}\right)^i \left(B^{(r)}\right)^j, \quad (2.9)$$

$$C^{(r+1)} = c_1(A^{(r)}, B^{(r)})C^{(r)} + c_2(A^{(r)}, B^{(r)})D^{(r)}, \quad (2.10)$$

$$D^{(r+1)} = d_1(A^{(r)}, B^{(r)})C^{(r)} + d_2(A^{(r)}, B^{(r)})D^{(r)}, \quad (2.11)$$

where $a(i,j)$ and $b(i,j)$ are non-negative integers, whereas coefficients $c_1(A,B)$, $c_2(A,B)$, $d_1(A,B)$ and $d_2(A,B)$ are polynomials in A and B , neither of them depending on r [6, 20, 21]. For surface traversing functions, $A_1^{(r)}$, $A_2^{(r)}$ and $B_1^{(r)}$, RG equations have the form

$$A'_1 = \sum_{i,j,i_1,i_2,j_1} a_1(i,j,i_1,i_2,j_1) A^i B^j A_1^{i_1} A_2^{i_2} B_1^{j_1}, \quad (2.12)$$

$$A'_2 = \sum_{i,j,i_1,i_2,j_1} a_2(i,j,i_1,i_2,j_1) A^i B^j A_1^{i_1} A_2^{i_2} B_1^{j_1}, \quad (2.13)$$

$$B'_1 = \sum_{i,j,i_1,i_2,j_1} b_1(i,j,i_1,i_2,j_1) A^i B^j A_1^{i_1} A_2^{i_2} B_1^{j_1}, \quad (2.14)$$

where on the left-hand side we have used the prime symbol as a superscript for the $(r+1)$ -th order generating functions, and no indices on the right-hand side for the r -th order functions. The numbers a_1 , a_2 , and b_1 do not depend on r [5, 6]. Analogously, we can construct additional recursion relations for surface one-leg generating functions

$$\begin{bmatrix} C'_1 \\ C'_2 \\ D'_1 \\ D'_2 \\ D'_3 \end{bmatrix} = \mathcal{M}_S \begin{bmatrix} C_1 \\ C_2 \\ D_1 \\ D_2 \\ D_3 \end{bmatrix}, \quad \begin{bmatrix} C'_3 \\ C'_4 \\ D'_4 \\ D'_5 \\ D'_6 \end{bmatrix} = \mathcal{M}_S \begin{bmatrix} C_3 \\ C_4 \\ D_4 \\ D_5 \\ D_6 \end{bmatrix} + \mathcal{M}_B \begin{bmatrix} C \\ D \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad (2.15)$$

where elements of matrices \mathcal{M}_S and \mathcal{M}_B (S denotes the surface functions, while B the bulk ones) are polynomials in A , B , A_1 , A_2 and B_1 functions. Starting with the initial conditions

$$A^{(0)} = x, \quad A_1^{(0)} = wx, \quad A_2^{(0)} = tx, \quad B^{(0)} = x^2, \quad B_1^{(0)} = wtx^2, \quad (2.16)$$

which correspond to the elementary tetrahedron ($r=0$)[‡] one can iterate RG relations (2.8), (2.9), and (2.12)-(2.14) for traversing SAW function in order to establish the phase

[‡] Here we note that in the approach applied in the present paper the SAW is forced to leave the unit tetrahedron after completing one step. Such restriction simplifies the model, but is not expected to alter the critical behavior [20].

diagram of the polymer system. In addition, we define the initial condition for one-leg generating functions

$$\begin{aligned}
C^{(0)} &= 1 + 3x, & D^{(0)} &= x + x^2, \\
C_1^{(0)} &= 3xt, & C_2^{(0)} &= 1 + 2xw, & C_3^{(0)} &= 1, & C_4^{(0)} &= xt, \\
D_1^{(0)} &= x^2wt, & D_2^{(0)} &= xt + x^2wt, & D_3^{(0)} &= xw, \\
D_4^{(0)} &= xw, & D_5^{(0)} &= 0, & D_6^{(0)} &= x^2wt,
\end{aligned} \tag{2.17}$$

that are needed for studying large r behavior of these functions (through relations (2.10), (2.11) and (2.15)), and consequently to determine the surface critical exponents γ_{11} , γ_1 and γ_s , from the singular parts of functions G_{11} , G_1 and G_s . To perform described procedure we need to know all RG equations for a specific fractal. We have been able to complete the exact form of required RG transformations and carry out a comprehensive analysis for the first three members ($b = 2, 3$ and 4) of the 3d SG family of fractals. The RG equations (2.8)-(2.14) were found in previous studies [5, 6, 19–22], and in this work we have determined the additional RG transformation (2.15) by applying an exact enumeration method. For $b = 2$ fractal these are given in the Appendix, while for $b = 3$ and 4 fractals they can be obtained upon request to the authors (to be more precise, for the critical exponents calculation only transformations defined with \mathcal{M}_S were needed, and consequently only that transformations are quoted). We note that computer enumeration and classification of all SAW configurations required to build RG transformations for one-leg generating functions, was done in a few seconds for $b = 2$ and $b = 3$ fractals, while in $b = 4$ case it took 7 hours on a PC with i5 Intel microprocessor. Details of the performed RG analysis together with the specific results for $b = 2, 3$ and 4 fractals are presented in the next section.

3. Results for $b = 2, 3$ and 4 fractals

Numerical analysis of RG equations for traversing SAW functions showed that for each value of t (between 0 and 1) there exists a critical value of $w = w_c(t)$, such that for values of w smaller than $w_c(t)$ polymer is in desorbed state, whereas for $w > w_c(t)$ it is adsorbed at the surface. Precisely at the critical value $w = w_c(t)$ the transition from adsorbed to desorbed phase occurs. In the following subsections all established polymer regimes will be reviewed separately and for each of them the surface critical exponents will be evaluated.

3.1. Desorbed phase ($w < w_c(t)$)

For weak monomer-surface interactions $w < w_c(t)$, and critical value of the fugacity $x = x_c$ (which does not depend on the values of w and t) the parameters $(A^{(r)}, B^{(r)}, A_1^{(r)}, A_2^{(r)}, B_1^{(r)})$ tend to $(A^*, B^*, 0, 0, 0)$, when $r \rightarrow \infty$, which indicates that polymer, stays away from the attractive surface [5, 6]. This state is referred to as

desorbed phase, determined by the RG fixed point

$$(A, B, A_1, A_2, B_1)^* = (A^*, B^*, 0, 0, 0). \quad (3.1)$$

The mean squared end-to-end distance $\langle R_N^2 \rangle$ of the polymer chain scales with its length N as $N^{2\nu}$, where the critical exponent ν is equal to

$$\nu = \frac{\ln b}{\ln \lambda_\nu}, \quad (3.2)$$

and λ_ν is the largest eigenvalue of the RG transformation (2.8) and (2.9) linearized in the vicinity of the corresponding fixed point (A^*, B^*) [6, 19, 21].

In order to calculate surface critical exponents γ_{11} , γ_1 and γ_s , one should investigate singular behavior of the generating functions (2.1)–(2.3), for which it is first necessary to analyze RG transformations (2.12)–(2.15) in the vicinity of the bulk fixed point (3.1). After large number of RG iterations, the traversing functions behave as

$$A^{(r)} \approx A^*, \quad B^{(r)} \approx B^*, \quad A_1^{(r)} \approx 0, \quad A_2^{(r)} \sim q^r \rightarrow 0, \quad B_1^{(r)} \approx 0, \quad (3.3)$$

where $q = \left(\frac{\partial A_2}{\partial A_2}\right)^*$ is irrelevant eigenvalue of (2.12)–(2.14) calculated at the fixed point (3.1). Also, one-leg generating functions have the following large r behavior

$$C^{(r)} \sim D^{(r)} \sim \lambda_B^r, \quad (3.4)$$

$$C_1^{(r)} \sim \lambda_S^r, \quad C_2^{(r)} \sim \text{const} + (q\lambda_S)^r, \quad D_1^{(r)} \sim D_2^{(r)} \sim (q^2\lambda_S)^r, \quad D_3^{(r)} \sim (q^3\lambda_S)^r, \quad (3.5)$$

$$C_3^{(r)} \sim \lambda_B^r, \quad C_4^{(r)} \sim \text{const} + (q\lambda_B)^r, \quad D_4^{(r)} \sim D_5^{(r)} \sim (q^2\lambda_B)^r, \quad D_6^{(r)} \sim (q^3\lambda_B)^r, \quad (3.6)$$

where λ_B is the relevant eigenvalue of the matrix

$$\mathcal{M}_\gamma = \begin{bmatrix} c_1(A^*, B^*) & c_2(A^*, B^*) \\ d_1(A^*, B^*) & d_2(A^*, B^*) \end{bmatrix}, \quad (3.7)$$

made out of the coefficients c_i and d_i appearing in RG equations (2.10) and (2.11) for the pure bulk functions $C^{(r)}$ and $D^{(r)}$, and

$$\lambda_S = [\mathcal{M}_S]_{11}^*, \quad (3.8)$$

asterisk denoting that the value of the polynomial $[\mathcal{M}_S]_{11}$ (appearing in RG equations (2.15)) is evaluated in the fixed point (3.1). We remind here that the eigenvalue λ_B determines the bulk critical exponent

$$\gamma = \frac{\nu}{\ln b} \ln \frac{\lambda_B^2}{b(b+1)(b+2)/6}, \quad (3.9)$$

which governs the singular behavior $G_{sing} \sim (1 - x\mu)^{-\gamma}$ of the generating function

$$G(x, T) = \sum_{N=1}^{\infty} C(N, T) x^N \quad (3.10)$$

for all possible SAWs in the bulk (away from adsorbing boundary), where $C(N, T) \sim \mu^N N^{\gamma-1}$ is the average number (over all starting points) of such N -step SAWs [22].

From (3.5) and (3.6), we perceive that, for large r , behavior of $C_2^{(r)}$, $C_4^{(r)}$ and $D_i^{(r)}$ ($i = \overline{1, 6}$), depends on mutual relation between the specific values of λ_S , λ_B and q . Calculated values of λ_S and λ_B , for $b = 2, 3$ and 4 fractals, are given in table 1, while the

particular values for q are: $q(b=2) = 0.4294$, $q(b=3) = 0.2285$ and $q(b=4) = 0.1440$. Since for each studied fractal $\lambda_B > \lambda_S > 1$ and $q^2 < 1/\lambda_B < q < 1/\lambda_S$ one finds that $C_2^{(r)} \rightarrow \text{const}$, $C_3^{(r)} \gg C_1^{(r)} \rightarrow \infty$, $C_3^{(r)} \gg C_4^{(r)} \rightarrow \infty$, and $D_i^{(r)} \rightarrow 0$ ($i = \overline{1,6}$). Then, from (2.7) it follows that on the large scale $L = b^r$ behavior of the generating function G_s^L is determined by the term containing $[C_3^{(r)}]^2$, and consequently

$$G_s^L \sim \left(\frac{\lambda_B^2}{\frac{b(b+1)}{2}} \right)^r. \quad (3.11)$$

Since $L \sim \langle N \rangle^\nu$, and $\langle N \rangle \sim (x_c - x)^{-1}$, the critical behavior $G_s \sim (1 - \mu x)^{-\gamma_s}$ follows, with

$$\gamma_s = \frac{\nu}{\ln b} \ln \frac{\lambda_B^2}{b(b+1)/2}. \quad (3.12)$$

By examining the large r behavior of the terms in the sum (2.5), representing the generating function G_{11} , one concludes that the term containing $[C_1^{(r)}]^2$ dominates, so that the largest term in the sum behaves as $[\lambda_S^2/(b(b+1)/2)]^r$. However, λ_S^2 is smaller than $b(b+1)/2$ in each studied b case, implying that G_{11} remains finite at the critical point. Therefore, one should inspect the large scale behavior of the derivative $\frac{dG_{11}}{dx}$. By finding this derivative from (2.5), one finds that it can be expressed as an infinite sum, similar to the sum on right-hand side of (2.5), but with terms that, apart from RG parameters, also contain their derivatives with respect to x . On the other hand, by finding derivative of the RG equations (2.8)–(2.15), one can find recurrence relations for the RG parameters derivatives, and analyze their large r behavior. From such an analysis, it follows that derivatives of the traversing RG parameters behave as λ_ν^r , as well as $\frac{dD_2^{(r)}}{dx}$, whereas $\frac{dC_{1,2}^{(r)}}{dx} \sim (\lambda_S \lambda_\nu)^r$, $\frac{dD_1^{(r)}}{dx} \sim (q^2 \lambda_S \lambda_\nu)^r$, and $\frac{dD_3^{(r)}}{dx} \rightarrow 0$. These findings, together with the established behavior of the RG parameters, imply that

$$\frac{dG_{11}^L}{dx} \sim \left(\frac{\lambda_S^2 \lambda_\nu}{\frac{b(b+1)}{2}} \right)^r, \quad (3.13)$$

with $\lambda_S^2 \lambda_\nu > \frac{b(b+1)}{2}$ in all cases, meaning that the function $\frac{dG_{11}}{dx}$ diverges on the large scale $L = b^r$. On the other hand, in the vicinity of the critical point, the following relation [17] is satisfied

$$\frac{dG_{11}}{dx} \sim (1 - \mu x)^{-(\gamma_{11}+1)}, \quad (3.14)$$

whereupon follows

$$\gamma_{11} = \frac{\nu}{\ln b} \ln \frac{\lambda_S^2}{b(b+1)/2}. \quad (3.15)$$

Finally, using the established behavior of the RG parameters and G_{11} , from (2.6) one can, in a similar way, find that on large scale the generating function G_1 behaves as

$$G_1^L \sim \left(\frac{\lambda_S \lambda_B}{\frac{b(b+1)}{2}} \right)^r, \quad (3.16)$$

Table 1. Values of the critical exponents γ_{11} , γ_1 and γ_s for desorbed ($w < w_c$), attached ($w = w_c$) and adsorbed ($w > w_c$) phases, for $b = 2, 3$, and 4 3d SG fractals. For the sake of completeness and comparison, here we also give coordinates of the corresponding fixed points (f.p.), the values of the end-to-end distance critical exponent ν [6, 19, 21] for desorbed phase ($w < w_c$) and crossover region ($w = w_c$), together with the corresponding eigenvalues λ_B and λ_S , as well as the values of γ exponent found previously in [22]. For adsorbed SAW ($w > w_c$) critical exponents γ_{11} , γ_1 and γ_s are all equal to the value of γ for the corresponding 2d SG fractal, calculated in [23].

Desorbed SAW ($w < w_c$) [f.p. ($A^*, B^*, 0, 0, 0$)]									
b	A^*	B^*	ν	λ_B	λ_S	γ	γ_{11}	γ_1	γ_s
2	0.4294	0.0500	0.6740	4.2069	1.2883	1.4461	-0.5756	0.5751	1.7259
3	0.3420	0.0239	0.6542	11.477	1.7206	1.5352	-0.4206	0.7094	1.8394
4	0.2899	0.0122	0.6411	25.679	2.3381	1.6165	-0.2793	0.8289	1.9370
Surface attached SAW ($w = w_c$) [f.p. (A^*, B^*, A^*, A^*, B^*)]									
b	A^*	B^*	ν	λ_B	λ_S		γ_{11}	γ_1	γ_s
2	0.4294	0.0500	0.6740	4.2069	3.1441		1.1596	1.4427	1.7259
3	0.3420	0.0239	0.6542	11.477	6.7759		1.2118	1.5256	1.8394
4	0.2899	0.0122	0.6411	25.679	12.4404		1.2668	1.6019	1.9370
Adsorbed SAW ($w > w_c$) [f.p. ($0, 0, A^{2d}, 0, 0$)]									
b	A^{2d}		ν_{SAW}^{2d}	λ_B^{2d}		$\gamma = \gamma_{11} = \gamma_1 = \gamma_s$			
2	0.6180		0.7986	3.1456		1.3752			
3	0.5511		0.7936	6.6395		1.4407			
4	0.5063		0.7884	11.645		1.4832			

implying that

$$G_1 \sim (1 - \mu x)^{-\gamma_1}, \quad (3.17)$$

with

$$\gamma_1 = \frac{\nu}{\ln b} \ln \frac{\lambda_S \lambda_B}{b(b+1)/2}. \quad (3.18)$$

For all studied fractals, the obtained specific results of these critical exponents, in desorbed polymer phase, are listed in table 1.

3.2. Adsorbed phase ($w > w_c(t)$)

When w is increased beyond $w_c(t)$, and for $x = x_c(w, t)$ [5, 6] RG parameters flow towards the new fixed point that describes the adsorbed polymer chain

$$(A, B, A_1, A_2, B_1)^* = (0, 0, A^{2d}, 0, 0), \quad (3.19)$$

where A^{2d} is the fixed point for the corresponding two-dimensional SG fractal [23]. In this fixed point polymer chain displays the features of a polymer system situated on two-dimensional SG fractal, and consequently all surface critical exponents are equal to

the corresponding value of γ for 2d SG fractals (*i.e.* $\gamma_1 = \gamma_{11} = \gamma_s = \gamma(2d \text{ SG})$), whose values were found in [23], and are quoted in table 1.

3.3. Surface attached chain ($w = w_c(t)$)

Precisely at $w = w_c(t)$ behavior of the polymer abruptly changes. For this value of w , and $x = x_c$ (the same as for the desorbed phase), the symmetric special fixed point is reached

$$(A, B, A_1, A_2, B_1)^* = (A^*, B^*, A^*, A^*, B^*), \quad (3.20)$$

which corresponds to the surface attached chain, when a balance between the attractive polymer–surface interaction and an effective “entropic” repulsion sets in. In this case, we have found the following large r behavior for traversing functions

$$A^{(r)} \approx A_1^{(r)} \approx A_2^{(r)} \approx A^*, \quad B^{(r)} \approx B_1^{(r)} \approx B^*, \quad (3.21)$$

whereas the one-leg functions behave as

$$C^{(r)} \sim D^{(r)} \sim \lambda_B^r \quad (3.22)$$

$$C_1^{(r)} \sim C_2^{(r)} \sim D_1^{(r)} \sim D_2^{(r)} \sim D_3^{(r)} \sim \lambda_S^r, \quad (3.23)$$

$$C_3^{(r)} \sim C_4^{(r)} \sim D_4^{(r)} \sim D_5^{(r)} \sim D_6^{(r)} \sim \lambda_B^r, \quad (3.24)$$

where λ_B has the same value as in desorbed SAW phase (*i.e.* it is the eigenvalue of (3.7)), and λ_S is the largest eigenvalue of the matrix \mathcal{M}_S , evaluated at the symmetric fixed point (3.20). Using already described approach, one can establish the same singular behavior of the generating functions with the relations (3.12), (3.15), and (3.18), for the surface critical exponents γ_s , γ_{11} , and γ_1 , respectively, as in the case of the desorbed chain. The obtained specific results for surface critical exponents, together with related eigenvalues needed for their evaluation, are given in table 1.

4. Summary and discussion

In this paper we have studied the configurational properties of linear polymers in the vicinity of adsorbing wall of fractal containers modeled by self-avoiding walks on 3d SG family of fractals. Each member of the 3d SG fractal family has a fractal impenetrable 2d adsorbing boundary (which is, in fact, 2d SG fractal surface) and can be labeled by an integer b ($2 \leq b \leq \infty$). In this model interactions between monomers and adsorbing wall are described by parameters $w = e^{-\varepsilon_w/k_B T}$, and $t = e^{-\varepsilon_t/k_B T}$, where ε_w is the energy of a monomer lying on the adsorbing surface, and ε_t is the energy of a monomer in the layer adjacent to the surface. Depending of the values of w and t the polymer chain can exist in one of three possible states: adsorbed, desorbed and surface attached [5, 6].

For the first three members ($b = 2, 3$ and 4) of the 3d SG fractal family we have performed the exact RG analysis to evaluate the surface critical exponents γ_{11} , γ_1 , and γ_s that govern the numbers of all possible polymer configurations with both, one, and no ends grafted on the adsorbing boundary, respectively. To evaluate specific values

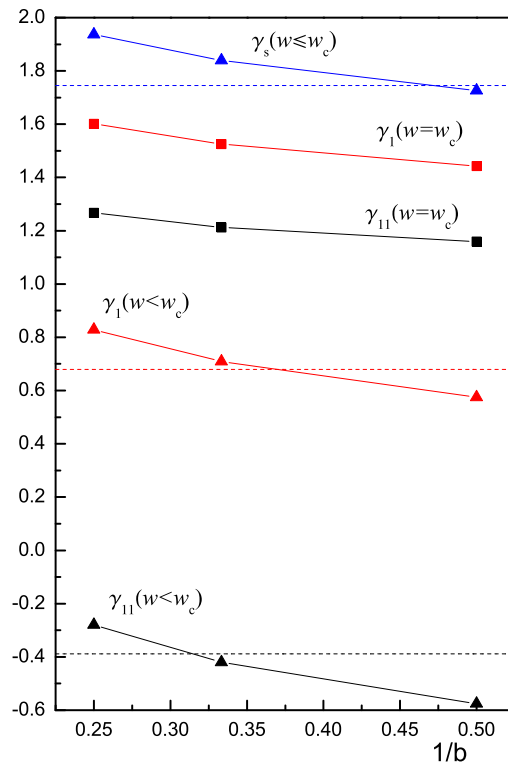


Figure 3. Values of the critical exponents γ_{11} , γ_1 and γ_s , for desorbed ($w < w_c$) and surface attached polymer ($w = w_c$) as functions of $1/b$ ($b = 2, 3$ and 4). Full lines only serve as guides for the eyes. The $d = 3$ Euclidean values $\gamma_{11} \approx -0.389$, and $\gamma_1 \approx 0.679$, for desorbed polymer phase ($w < w_c$), that spring from two findings [14,16], are depicted by dashed horizontal lines, black for γ_{11} and red for γ_1 . The dashed horizontal blue line corresponds to the $d = 3$ Euclidean value of $\gamma_s \approx 1.7449(2)$.

of γ_1, γ_{11} , and γ_s , one needs to know the values of the end-to-end distance critical exponent ν and eigenvalues λ_B and λ_S of matrices \mathcal{M}_S and \mathcal{M}_γ defined by (2.15) and (3.7) respectively. The exact values for ν and λ_B have been already found [6, 19–22], for fractals with $b = 2, 3$ and 4 , and it has remained to calculate the values of λ_S , which requires knowledge of the elements of the matrix \mathcal{M}_S . The required elements are polynomials, that can be formed by enumeration and classification of SAWs, described by restricted partition functions C_1, C_2, D_1, D_2 and D_3 (see figure 2), and we have found that this is feasible for $2 \leq b \leq 4$. The obtained specific results for studied surface critical exponents γ_{11}, γ_1 , and γ_s are given in table 1.

For the sake of a better assessment of the global behavior of the surface critical exponents as functions of the scaling parameter b , we present our results in figure 3. It can be seen that the following chain of inequalities is satisfied

$$\gamma_{11}(w < w_c) < \gamma_1(w < w_c) < \gamma_{11}(w = w_c) < \gamma_1(w = w_c) < \gamma_s(w \leq w_c). \quad (4.1)$$

This is a quite plausible result since the generating function G_{11} describes SAWs with a

stronger constraint than those described by the generating function G_1 , which implies the inequality $\gamma_{11} < \gamma_1$, for both desorbed and surface attached chain. Also, we see that for each b the inequalities $\gamma_{11}(w < w_c) < \gamma_{11}(w = w_c)$, and $\gamma_1(w < w_c) < \gamma_1(w = w_c)$ are valid, implying that the number of SAW configurations with one or two ends anchored to the wall are larger in the surface attached regime than in the desorbed one. Here we note that the inequality $\gamma_{11} < \gamma_1$, for both desorbed and surface attached chain, were established for SAWs grafted on one edge of fractals belonging to 2d SG fractal family, whereas for $b > 3$ it was obtained that $\gamma_1(w < w_c) > \gamma_{11}(w = w_c)$ [18]. Furthermore, for $w < w_c$, we see that γ_{11} and γ_1 are monotonically increasing functions of b , and can be compared with their Euclidean counterparts. In desorbed phase the exponent γ_{11} for $b = 4$ is larger than the corresponding three-dimensional Euclidean value $\gamma_{11}^{3d} \approx -0.389$ that springs from the field-theory approach result $\gamma_{11}^{3d} = -0.388$ [14] and Monte Carlo simulations finding $\gamma_{11}^{3d} = -0.390(2)$ [16] (black dashed line in figure 3), whereas γ_1 surpasses the Euclidean value $\gamma_1^{3d} = 0.679$ (evaluated from $\gamma_1^{3d} = 0.680$ [14] and $\gamma_1^{3d} = 0.6786(12)$ [16]), for $b > 2$. In the case of the surface attached extended chain ($w = w_c$), both critical exponents, γ_1 and γ_{11} are also monotonically increasing functions of b , being always larger than the corresponding Euclidean values for $\gamma_{11}^{3d} \approx 0.686$ (obtained as an average of $\gamma_{11}^{3d} = 0.666$ [14], and $\gamma_{11}^{3d} = 0.707(5)$ [16]) and $\gamma_1^{3d} \approx 1.216$ (average of $\gamma_1^{3d} = 1.207$ [14] and $\gamma_1^{3d} = 1.226(2)$ [16]). The behavior of the critical exponent γ_s (whose values are the same in both the desorbed chain phase and the surface attached chain region), is similar to the behavior of γ_1 and γ_{11} , that is, γ_s is monotonically increasing function of b , which for $b > 2$ surpasses its Euclidean counterpart $\gamma_s^{3d} \approx 1.7449(2)$ (calculated from scaling relation $\gamma_s = \gamma + \nu$ [24], where we have put the last estimates for three dimensional Euclidean values of $\gamma = 1.1573(2)$ [25] and $\nu_E = 0.587597(7)$ [26]).

Finally, we have tested the scaling relation

$$\gamma_s = 2\gamma_1 - \gamma_{11} = \gamma + \nu(d_f - d_s), \quad (4.2)$$

which was proposed in [17] as a modification of the scaling relation $2\gamma_1 - \gamma_{11} = \gamma + \nu$, obtained for Euclidean containers [24,27]. Here d_f is the fractal dimension of the solvent and d_s is the fractal dimension of the attracting surface. Putting the data from table 1 into (4.2), one can see that this scaling relation is exactly satisfied for both desorbed and surface attached polymers.

At the end, one may pose the question about the possible behavior of the surface critical exponents γ_1 , γ_{11} , and γ_s for larger b (when the SG fractal dimension approaches the Euclidean value 3). To answer this question one have to apply some other method, such as Monte Carlo renormalization group method which appeared to be very precise and quite efficient method for critical exponents calculation on finitely ramified fractals, which will be the matter of an independent study.

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Appendix A. RG equations for the surface one-leg parameters for $b = 2$ 3d SG fractal

In this Appendix we give the exact RG equations (2.15) for the surface one-leg parameters C_1 , C_2 , D_1 , D_2 and D_3 in the case of the $b = 2$ 3d SG fractal. We have found that these equations have the following form:

$$\begin{aligned}
C'_1 &= (3A + 6A_2^2 B)C_1 + (6AA_2 + 6AA_1 A_2)C_2 + 6A_2^2 B D_1 + (6AA_1^2 + 12A_2^2 B)D_2, \\
C'_2 &= (2AA_2 + 2AA_1 A_2)C_1 + (1 + 2A_1 + 2A_1^2 + 2AA_2^2 + 4AA_2 B_1)C_2 + \\
&\quad (2AA_2 + 4AA_1 A_2 + 4AA_1 B_1)D_1 + (2AA_2 + 4AA_1 A_2 + 8AA_1 B_1)D_2 + \\
&\quad (2A_1^2 + 2AA_2^2)D_3, \\
D'_1 &= (AA_1^2 + A_2^2 B)C_1 + 2AA_1 B_1 C_2 + (2AA_1 + 3AA_1^2 + 2A_2^2 B + 8A_2 B B_1 + 10BB_1^2)D_1 + \\
&\quad (2A_2^2 B + 4A_2 B B_1 + 12BB_1^2)D_2 + (2AA_1 A_2 + 4AA_1 B_1)D_3, \\
D'_2 &= A_2^2 B C_1 + (AA_2 + 2AA_1 A_2 + 2AA_1 B_1)C_2 + (2A_2^2 B + 4A_2 B B_1 + 6BB_1^2)D_1 + \\
&\quad (2AA_1 + 3AA_1^2 + 4A_2^2 B + 12A_2 B B_1 + 16BB_1^2)D_2 + (2AA_1 A_2 + 6AA_1 B_1)D_3, \\
D'_3 &= (A_1^2 + AA_2^2)C_2 + (2AA_1 A_2 + 6AA_1 B_1)D_1 + (4AA_1 A_2 + 10AA_1 B_1)D_2 + \\
&\quad (3A_1^2 + 22AB_1^2)D_3.
\end{aligned}$$

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