Journal of Statistical Physics, Vol. 71, Nos. 1/2, 1993

Adsorption of a Flexible Self-Avoiding Polymer Chain: Exact Results on Fractal Lattices

Vladimir Bubanja,[1] Milan Knežević,[2] and Jean Vannimenus[3]

Received September 3, 1992

The large-scale behavior of surface-interacting self-avoiding polymer chains placed on finitely ramified fractal lattices is studied using exact recursion relations. It is shown how to obtain surface susceptibility critical indices and how to modify a scaling relation for these indices in the case of fractal lattices. We present the exact results for critical exponents at the point of adsorption transition for polymer chains situated on a class of Sierpinski gasket-type fractals. We provide numerical evidence for a critical behavior of the type found recently in the case of bulk self-avoiding random walks at the fractal to Euclidean crossover.

KEY WORDS: Polymer adsorption; fractals; scaling relations.

1. INTRODUCTION

Configurational properties of polymer chains in the vicinity of an interface can be strongly modified relative to their bulk characteristics. A subtle competion between the gain of internal energy and a corresponding loss of configurational entropy when a portion of the chain is brought from the bulk to the attractive wall governs the large-scale behavior of the surface-interacting polymers. The subject has been in the focus of both experimental and theoretical activity.[1–3] This interest has been further enhanced by the possible application of polymer adsorption phenomena in numerous practical and technological problems.[4] The general picture that emerges from these studies reveals that, under certain conditions, polymer chains can form a self-similar adsorbed layer near the wall with a decreasing

[1] Department of Applied Physics, Delft University of Technology, 2628 CJ Delft, The Netherlands.
[2] Faculty of Physics, University of Belgrade, P.O. Box 550, 11001 Belgrade, Yugoslavia.
[3] Laboratoire de Physique Statistique de l'ENS, 75231 Paris, France.

0022-4715/93/0400-0001$07.00/0

density profile. Then the structure of the polymer chain can be sketched in a pictorial way as a collection of loops extending into solution and "trains" running along the wall (flat regions of the structure).

Most theoretical studies have focused on the case of surface-interacting polymers in dilute solutions, which corresponds to the single-chain models (see, however, refs. 1–3 for a review of the case of many-chain systems). The basic physics of a polymer chain in the vicinity of an attractive impenetrable surface can be captured by the self-avoiding random walk (SAW) model on a semi-infinite lattice with an energy contribution ε ($\varepsilon = -|\varepsilon|$) for each step along the lattice boundary. Thus, one assigns the energy $E = \varepsilon M < 0$ to each chain having M steps ("monomers") along the lattice boundary (attractive wall). This leads to an increased probability w of making a step along the wall, characterized by the Boltzmann factor

$$w = \exp(-\varepsilon/k_B T) > 1 \tag{1}$$

At high temperatures ($T \to \infty$) all chain configurations have the same weight and the polymer resides in the desorbed state. However, when the temperature is sufficiently lowered, the attractive interactions between the wall and the segments of the chain become important and the polymer prefers the adsorbed state. The polymer system undergoes a transition at a critical adsorption temperature T_a below which a finite fraction M/N of the monomers lie on the surface. Using the analogy between an adsorbed polymer chain and the magnetic $n \to 0$ vector model with a free surface, it has been shown that this point corresponds to a tricritical point[5] and in its proximity a crossover regime is observed. In particular, the mean number of monomers at the surface M is controlled by this point,

$$M \sim \begin{cases} N(T_a - T)^{1/\phi - 1}, & T < T_a \\ N^{\phi}, & T = T_a \\ (T - T_a)^{-1}, & T > T_a \end{cases} \tag{2}$$

where ϕ is the crossover exponent.

We recall the definitions of principal surface exponents. It is generally believed that the asymptotic behavior of the number of N-step SAWs in the bulk $C(N, T)$ and the number of N-step walks with one (both) end(s) attached to the surface $C_1(N, T)$ $[C_{11}(N, T)]$ is described by

$$C(N, T) \sim \mu^N N^{\gamma - 1} \tag{3}$$

$$C_1(N, T) \sim \mu^N N^{\gamma_1 - 1} \tag{4}$$

$$C_{11}(N, T) \sim \mu^N N^{\gamma_{11} - 1} \tag{5}$$

where $\mu = \mu(T)$ is the temperature-dependent connectivity constant and γ, γ_1, and γ_{11} are the associated critical exponents. It turns out that these exponents assume distinct values in different temperature regions: in the absorbed region ($T < T_a$) the chain is basically localized at the wall and one has $\gamma_1 = \gamma_{11} = \gamma(d-1)$ [where $\gamma(d-1)$ is the bulk value of the exponent in the space of dimension $d-1$], while right at the adsorption transition ($T = T_a$), as well as in the high-temperature region ($T > T_a$), the exponents γ_1 and γ_{11} take new values. It is useful to introduce the convenient generating functions for the above-defined numbers

$$C(x, T) = \sum_{N=1}^{\infty} x^N \sum_{M=1}^{N} C(N, M) w^M$$

$$= \sum_{N=1}^{\infty} C(N, T) x^N \sim (1 - x\mu)^{-\gamma} \tag{6}$$

$$C_1(x, T) = \sum_{N=1}^{\infty} x^N \sum_{M=1}^{N} C_1(N, M) w^M$$

$$= \sum_{N=1}^{\infty} C_1(N, T) x^N \sim (1 - x\mu)^{-\gamma_1} \tag{7}$$

$$C_{11}(x, T) = \sum_{N=1}^{\infty} x^N \sum_{M=1}^{N} C_{11}(N, M) w^M$$

$$= \sum_{N=1}^{\infty} C_{11}(N, T) x^N \sim (1 - x\mu)^{-\gamma_{11}} \tag{8}$$

where x is the fugacity per step of the walk. Here $C(N, M)$ is the number of N-step SAWs with M steps on the surface, while $C_1(N, M)$ [$C_{11}(N, M)$] represents the number of N-step SAWs with M steps on the surface provided one (both(and(s) of the walk is (are) attached to the wall. The leading singular behavior of corresponding generating functions that appears when x approaches $x_c = 1/\mu(T)$ from below is given on the right-hand sides of the above relations. Similarly, one can consider the number of N-step SAWs given that both endpoints of the walk lie in the bulk, $C_s(N, T) \sim \mu^N N^{\gamma_s - 1}$. The generating function for these numbers is

$$C_s(x, T) = \sum_{N=1}^{\infty} C_s(N, T) x^N \sim (1 - x\mu)^{-\gamma_s} \tag{9}$$

It is useful to note that, using the above-mentioned analogy between the polymer and magnetic systems, these generating functions can be related to

corresponding surface susceptibilities. Then a simple scaling argument leads to the scaling relations[6]

$$\gamma_s = 2\gamma_1 - \gamma_{11} = \gamma + \nu \tag{10}$$

where ν is the gyration radius (R) critical exponent. In the high-temperature region ($T \geqslant T_a$) one expects that both the parallel ($R_{||}$) and the perpendicular ($R_\perp$) to the surface components of the gyration radius ($R^2 = R_{||}^2 + R_\perp^2$) are governed by the same (bulk) exponent ν

$$\langle R_{||}^2 \rangle \sim N^{2\nu} \qquad \text{and} \qquad \langle R_\perp^2 \rangle \sim N^{2\nu} \tag{11}$$

However, in the low-temperature region $T < T_a$, due to the adsorption, one expects a different asymptotic behavior: $\langle R_{||}^2 \rangle \sim N^{2\nu_{||}}$, with $\nu_{||} = \nu(d-1)$ [$\nu(d-1)$ denotes the bulk gyration radius critical exponent in the space of dimension $(d-1)$], while $\langle R_\perp^2 \rangle$ becomes a constant independent of N (implying $\nu_\perp = 0$).[3]

The critical behavior of surface-interacting polymers has been studied in various ways, including computer simulations,[5,7,8] exact enumerations on lattices,[9,10] transfer-matrix methods,[11,12] renormalization group (RG) approaches,[13,14] and conformal-invariance techniques in two dimensions.[15,16] For a long time the exactly solvable models of the adsorption transition were limited to Gaussian random walks.[17] Recently, however, exact solutions have been found for a directed SAW model on regular lattices,[18] and for the case of a SAW on some fractal lattices.[19]

Interest in finitely ramified fractal lattices arises mainly from a belief that they may serve as crude models for real amorphous materials. On the other hand, many nontrivial physical models can be treated exactly on these lattices. Aside from being interesting in their own right, these results are often in qualitative (and sometimes even quantitative) agreement with their counterparts for standard Euclidean lattices.[20] One expects, therefore, that a study of fractal models may also yield some insight into the behavior of conventional homogeneous systems. The examples of surface-interacting SAWs (SISAWs) on finitely ramified deterministic fractals support this expectation. For this case Bouchaud and Vannimenus have developed a simple RG approach to study the two-point correlation functions.[19] These authors have presented a detailed study of the critical behavior for the case of 2D and 3D Sierpinski gaskets. In particular, they found the exact values of crossover and correlation length (i.e., gyration radius) critical exponents. In this paper we extend their approach to the case of open SISAWs. We show how to obtain the surface susceptibility critical exponents defined in (3)–(5) and how to modify the scaling relation (10) to the case of fractal lattices. Then, motivated by recent curious

findings for the bulk critical behavior of SAWs on a family of Sierpinski-type fractals,[21–23] we study the problem of SISAWs on the same class of lattices. The members of this family can be labeled by an integer b, $2 \leqslant b < \infty$, and for large values of b the underlying lattice structure becomes more and more similar to a triangular wedge, while its fractal and spectral dimension tend to their Euclidean value 2. Using the scaling method, Dhar argued that $\nu(b)$ should approach, for large b, its two-dimensional value ($\nu_{d=2} = 3/4$[24]) from below, whereas $\gamma(b)$ should tend to a non-Euclidean value $133/32$[22] (we recall $\gamma_{d=2} = 43/32$). We provide numerical evidence that a similar puzzle can take place in the case of SISAWs as well. More specifically, we find that the value of the crossover exponent ϕ monotonically decreases when the lattice parameter b increases, $2 \leqslant b \leqslant 9$. It turns out that the value of ϕ crosses its two-dimensional Euclidean value ($\phi_{d=2} = 1/2$[16]), while the specific heat critical exponent α becomes negative at $b \approx 6$. This means that ϕ and α (as well as ν) should become nonmonotonic functions of b, providing these exponents approach their Euclidean values in the limit $b \to \infty$.

In Section 2 we present the exact recursion relation for the corresponding set of restricted partition functions needed to obtain surface scaling exponents for a representative finitely ramified fractal, a 3-simplex lattice. Then we find corresponding expressions for the generating functions (7)–(9) which allow us to find the exact values of the critical exponents γ_1, γ_{11}, and γ_s. This approach can be easily generalized to the case of other finitely ramified fractal lattices. We provide also scaling arguments for the scaling relation between susceptibility critical exponents on fractal lattices. In Section 3 we describe the critical behavior of two-point correlation functions of the surface-interacting SAWs for the Sierpinski gasked family of fractals. Finally, in Section 4 we present an overall discussion of the results.

2. THE TRUNCATED 3-SIMPLEX LATTICE

Our model is very close to the one studied by Bouchaud and Vannimenus.[19] We assume that the surface-interacting polymer chain is situated on the truncated 3-simplex lattice, one boundary of which represents an attractive surface. This is a fractal lattice[25] with the fractal dimension $d_f = \log 3/\log 2$, while the fractal dimension of its "surface" in $d_s = 1$ (see Fig. 1). To each N-step walk having M steps along the wall and with P steps lying in the surface layer adjacent to the wall we associate the weight $x^N w^M t^P$, where w is given by (1). Here the Boltzmann factor $t = \exp(-\varepsilon_t/k_B T)$ is introduced to take into account the interaction between the surface and the polymer chain segments lying in the first

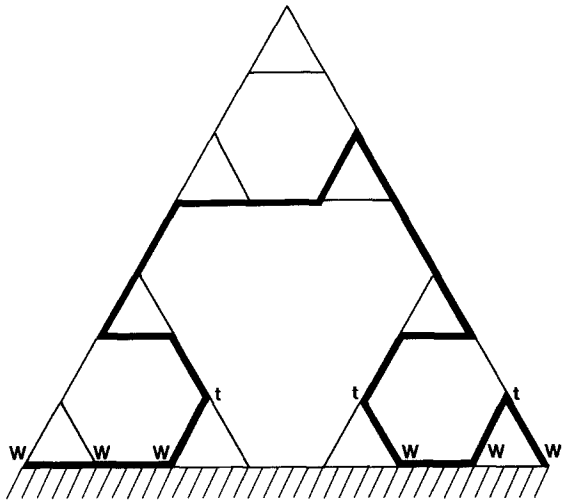

Fig. 1. Schematic sketch of a SISAW (thick line) on the truncated 3-simplex lattice at the third stage of iterative construction of the lattice. We assign the Boltzmann factor $w(t)$ to each vertex lying at the attractive wall (in the layer adjacent to the wall) through which the walk passes.

neighborhood of the wall (we attribute the energy ε_t for each such segment of the chain). It turns out that for an attractive surface an unbinding transition at a finite temperature exists only if $t < 1$ (i.e., for a repulsive interaction potential $\varepsilon_t > 0$).[19] As pointed out by Bouchaud and Vannimenus, the presence of such a repulsive part in the interaction potential, for a chain situated on the Sierpinski gasket, allows an entropic effect which causes the chain to prefer the desorbed state (for $t > 1$ the chain is always adsorbed).

We would like to determine the critical behavior of surface-interacting SAWs on the 3-simplex lattice. To achieve this, we extend the original approach of Dhar, who analyzed the bulk critical behavior of SAWs on finitely ramified fractals.[26] He showed that the relevant generating functions for SAWs can be expressed in terms of a finite number of restricted partition functions. These partition functions can be defined recursively as weighted sums over all internal configurations of SAWs for a given stage of iterative construction of the fractal lattice. To describe the bulk properties of SAWs on the 3-simplex lattice one needs only four variables in the recursion relations. In order to study the surface critical behavior of two-point correlation functions, Bouchaud and Vannimenus defined three restricted partition functions. However, the recursion relations required to obtain the generating function (7)–(9) involve, *a priori*, 20 restricted parti-

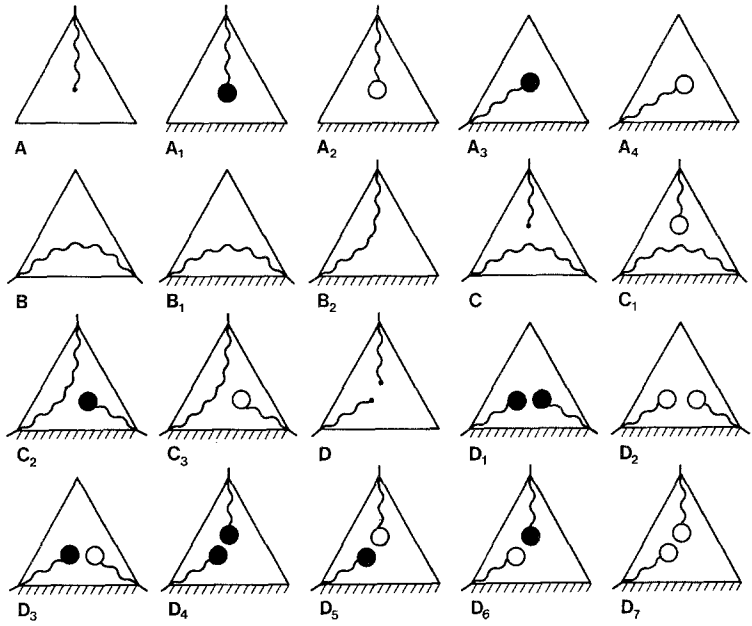

Fig. 2. Diagrams representing the 20 restricted generating functions for SISAWs on the truncated 3-simplex lattice. In order to describe open walks, one has to make a distinction between the walks ending at the attractive wall (black circles) and the walks that terminate somewhere in the bulk of the rth-order lattice (open circles). The endpoints of the bulk open walks lie, of course, in the bulk. In the case of the Sierpinski gasket family of fractals one has also to distinguish between the walks visiting only two vertices and those walks that pass through all three corner vertices.

tion functions. Their schematic representation is depicted in Fig. 2. Here the definitions of partition functions A, B, C, and D coincide with those of ref. 26, while for B_1 and B_2 we follow the corresponding definitions of ref. 19. Thus, for example,

$$A^{(r)}(x) = \sum_N \mathscr{A}^{(r)}(N) x^N$$

denotes the weighted sum over all $\mathscr{A}^{(r)}(N)$ N-step walk configurations of the rth-stage 3-simplex lattice provided one of the endpoints of the walk lies within the same rth-stage lattice. Similarly,

$$B_1^{(r)}(x, w, t) = \sum \mathscr{B}_1^{(r)}(N, M, P) x^N w^M t^P$$

is the generating function for the number $[\mathscr{B}_1^{(r)}(N, M, P)]$ of configurations of N-step SAWs with M steps along the attractive surface and with P steps lying in the layer adjacent to the surface, given that the SAW enters and leaves the rth-stage lattice at the vertices belonging to the wall. By analogy, the generating function $B_2^{(r)}(x, w, t)$ is related to the walks traversing the rth-order lattice fractal and passing through the corner vertices of the rth-order triangle, provided one of these vertices lies on the attractive wall and the other one belongs to the lattice bulk. It is useful to note that the restricted partition functions $B(x)$, $B_1(x, w, t)$, and $B_2(x, w, t)$ can be interpreted as two-point correlation functions for SISAWs on the 3-simplex lattice.

To describe open SISAWs, one has to make a distinction between walks with one (both) endpoints fixed on the attractive surface of the rth-order triangle and walks one (both) of whose extremities end(s) in the bulk of the rth-order lattice. Therefore, for example,

$$D_3^{(r)}(x, w, t) = \sum \mathscr{D}_3^{(r)}(N, M, P) x^N w^M t^P$$

refers to the SAWs with two open ends. The corresponding walks enter the rth-stage fractal at the corner vertices belonging to the atractive surface. We also suppose that one of the walk extremities lies on the surface (represented in Fig. 2 by a black circle), while the other one must end somewhere in the bulk of the rth-order lattice (open circle). The other restricted partition functions are defined similarly (Fig. 2).

To write down the recursion relation for different partition functions, one has to look for all possible ways in which a given configuration of the $(r+1)$th-stage fractal lattice may be constructed from the various configurations of the rth-stage lattice. In this way we obtain

$$A' = (1 + 2B + 2B^2)A + 2B^2C \tag{12}$$

$$A_1' = 2BA_1 + 2BB_2A_3 \tag{13}$$

$$A_2' = A + 2BA_2 + 2BB_2A_4 + 2B_2^2C \tag{14}$$

$$A_3' = (1 + B_1)A_3 + BB_2A_1 + BB_2C_2 \tag{15}$$

$$A_4' = B_2(1 + B_1)A + BB_2A_2 + (1 + B_1)A_4 + BB_2C_1 + BB_2C_3 \tag{16}$$

$$B' = B^2 + B^3 \tag{17}$$

$$B_1' = B_1^2 + BB_2^2 \tag{18}$$

$$B_2' = BB_2 + BB_1B_2 \tag{19}$$

$$C' = B^2 A + 3B^2 C \tag{20}$$

$$C_1' = B_1^2 A + B_2^2 C + 2BB_1 C_1 \tag{21}$$

$$C_2' = BB_2 A_3 + 2BB_1 C_2 \tag{22}$$

$$C_3' = B_2^2 C + BB_2 A_4 + 2BB_1 C_3 \tag{23}$$

$$D' = (1+2B)A^2 + 4BAC + 6BC^2 + (2B+3B^2)D \tag{24}$$

$$D_1' = A_3^2 + 2BC_2^2 + 2B_1 D_1 + 2BB_2 D_4 \tag{25}$$

$$D_2' = A_4^2 + 2B_2 AA_4 + 4B_1 AC_3 + 4BC_1 C_3 + 2BC_3^2 + B_2^2 D + 2B_1 D_2 + 2BB_2 D_7 \tag{26}$$

$$D_3' = A_3 A_4 + B_2 AA_3 + 2B_1 AC_2 + 2BC_1 C_2 + 2BC_2 C_3 + 2B_1 D_3 + BB_2 D_5 + BB_2 D_6 \tag{27}$$

$$D_4' = BA_1 A_3 + BA_3 C_2 + BB_2 D_1 + B(1+B_1)D_4 \tag{28}$$

$$D_5' = AA_3 + BA_2 A_3 + B_1 AA_3 + B_2 A_1 C + BA_3 C_1 + BA_4 C_2 + 3B_2 CC_2 + BB_2 D_3 + B(1+B_1)D_5 \tag{29}$$

$$D_6' = BA_1 A_4 + B_2 A_1 C + BA_3 C_3 + B_2 CC_2 + BB_2 D_3 + B(1+B_1)D_6 \tag{30}$$

$$D_7' = (1+B_1)AA_4 + BA_2 A_4 + 2B_2 A_2 C + BA_4 C_1 + BA_4 C_3 + 4B_2 CC_3 + 2B_2 CC_1 + B_2(1+B_1)D + BB_2 D_2 + B(1+B_1)D_7 \tag{31}$$

where on the left-hand sides of the above equations we have substituted the superscript $(r+1)$ with the superscript prime, and on the right-hand sides we have omitted the superscript r. It is useful to note that correlation function recursion relations do not involve the open-walk variables [see (17)–(19)]. Similarly, recursion relations for bulk variables do not depend on surface variables. To perform a numerical study of the above system of equations (12)–(31), one has to specify the initial conditions for all restricted partition functions. For this one can follow the conventions of ref. 26: One assigns a weight x to each bulk vertex that the walk passes through, and a weight $\sqrt{x}$ to each bulk vertex at which the walk ends (or, equivalently, at each vertex at which the walk starts). Then, if the relevant vertex lies on the attractive surface (in the layer adjacent to the surface), one should substitute the weight x with the weight $z(y)$, where $z = xw$ ($y = xt$). Thus, the initial conditions on the first-stage 3-simplex (the elementary triangle) are

$$
\begin{aligned}
A &= \sqrt{x}\,(1+2x+2x^2), & C_2 &= yz\sqrt{z} \\
A_1 &= 2y(1+z)\sqrt{z}, & C_3 &= 0 \\
A_2 &= \sqrt{y}, & D &= x(1+2x) \\
A_3 &= \sqrt{z}\,(1+z+zy), & D_1 &= z \\
A_4 &= z(1+z)\sqrt{y}, & D_2 &= 0 \\
B &= x^2+x^3, & D_3 &= z(yz)^{1/2} \\
B_1 &= z^2(1+y), & D_4 &= yz \\
B_2 &= zy(1+z), & D_5 &= (yz)^{1/2}(1+z) \\
C &= x^2\sqrt{x}, & D_6 &= 0 \\
C_1 &= z^2\sqrt{y}, & D_7 &= 0
\end{aligned}
\tag{32}
$$

where, for the sake of simplicity, we have omitted the superscript (1) on the left-hand sides of the above relations.

Now we are going to express the global generating functions (7)–(9) of the 3-simplex lattice in terms of 20 restricted partition functions. The global generating function $\Xi_{11}^{(r+1)}(x, w, t)$ [which corresponds to an unnormalized function (8)] for the whole $(r+1)$th-order fractal lattice can also be constructed recursively:

$$\Xi_{11}^{(r+1)} = 2\Xi_{11}^{(r)} + F_{11}^{(r)} \tag{33}$$

where

$$F_{11}^{(r)} = B^{(r)}(A_1^{(r)})^2 + (A_3^{(r)})^2 + 2B^{(r)}B_2^{(r)}D_4^{(r)} \tag{34}$$

and where we have taken into account that only two rth-order triangles of an $(r+1)$th-order triangle have the attractive surface for the boundary (see Fig. 1). Then, averaging over all possible starting points of the SAW and iterating the recursion relation (33), we obtain for the generating function per site

$$C_{11}(x, w, t) = \sum_{r=1}^{\infty} 2^{-(r+1)} F_{11}^{(r)} \tag{35}$$

Similarly, we find

$$C_1(x, w, t) = C_{11}(x, w, t) + \sum_{r=1}^{\infty} 2^{-r} F_1^{(r)} \tag{36}$$

and

$$C_s(x, w, t) = \sum_{r=1}^{\infty} 2^{-(r+1)} F_s^{(r)} \tag{37}$$

with

$$F_1^{(r)} = AA_1 + BA_1A_2 + A_3A_4 + B_2AA_3 + BB_2(D_5 + D_6) \tag{38}$$

$$F_s^{(r)} = 2A(A_2 + B_2A_4) + A_4^2 + BA_2^2 + B_2^2D + 2BB_2D_7 \tag{39}$$

where we have suppressed the superscript (r) on the right-hand sides of the relations (38) and (39). Now we turn to the scaling analysis of the critical behavior of SISAWs on the truncated 3-simplex lattice. As mentioned above, detailed study of the phase diagram of the system [including the critical behavior of the correlation functions (17)–(19)] has been performed in ref. 19. Our findings are in complete agreement with those of Bouchaud and Vannimenus. However, due to slightly different initial conditions, our numerical values for some "nonuniversal" quantities (in particular, for the critical fugacity $x_c = 1/\mu$) do not coincide with the corresponding values for the 2D Sierpinski gasket.[19] We will not repeat here the technical details which were given there, but we will quote the main results.

Three different temperature regions were identified:

(i) At high temperatures $w < w^*(t)$ ($t < 1$, being fixed), the critical fugacity x_c is constant and equal to its bulk critical value $x_c(w) = (\sqrt{5}-1)/2 \approx 0.61803$. For all these values of temperature the bulk SAW fixed fixed point is reached

$$(B^*, B_1^*, B_2^*) = \left(\frac{\sqrt{5}-1}{2}, 0, 0\right) \tag{40}$$

The fraction of SAW steps in contact with the surface,[18,19]

$$\frac{M}{N} = -\frac{w}{x_c}\frac{dx_c}{dw}$$

vanishes in this temperature region and therefore the polymer is in the desorbed state. Linearization about this fixed point leads to only one relevant eigenvalue

$$\lambda = 2B^* + 3(B^*)^2 = \frac{7-\sqrt{5}}{2} \approx 2.38197 \tag{41}$$

which yields the value of the gyration radius critical exponent $\nu = \log 2/\log \lambda \approx 0.79862$.

The leading singular behavior of the open walk restricted partition function at criticality $x = x_c$ can be easily deduced from the recursion delations (12)–(31). Taking into account (41), we find the following asymptotic behavior for large values of iteration index r:

$$\begin{aligned} &A^{(r)} \sim \lambda_1^r, \quad A_1^{(r)} \sim \lambda_2^r, \quad A_4^{(r)} \sim (B^*\lambda_1)^r, \quad D_5^{(r)} \sim \lambda_1^r \\ &C^{(r)} \sim \lambda_1^r, \quad A_2^{(r)} \sim \lambda_1^r, \quad B_2^{(r)} \sim (B^*)^r, \quad D_6^{(r)} \sim (B^*\lambda_1\lambda_2)^r \\ &D^{(r)} \sim \lambda_1^{2r}, \quad A_3^{(r)} \sim A_3^*, \quad D_4^{(r)} \sim \lambda_2^r, \quad D_7^{(r)} \sim (B^*\lambda_1^2)^r \end{aligned} \tag{42}$$

where

$$\lambda_1 = \frac{6 - 3B^* + (25 - 33B^*)^{1/2}}{2} \approx 3.14590, \qquad \lambda_2 = 2B^* \approx 1.23607 \tag{43}$$

A simple way to extract the leading critical behavior of global generating functions (35)–(37) relies on finite-size scaling arguments. Indeed, let $C_1^L(x_c)$ be the generating functions (36) of SISAWs on a lattice of length L at the critical fugacity $x_c = x_c(w, t)$. This function is expected to diverge as $L^{\gamma_1/\nu}$. On the other hand, taking into account (36), (38), and (42), we estimate that

$$C_1^L(x_c) \approx \sum_{r=0}^{K} \frac{F_1^{(r)}}{2^r} \sim \left(\frac{\lambda_1\lambda_2}{2}\right)^K$$

where $L = 2^K$. Therefore, we obtain

$$\gamma_1 = \frac{\log(\lambda_1\lambda_2/2)}{\log \lambda} \approx 0.76606 \tag{44}$$

Following the above scheme, we also find

$$\gamma_s = \frac{\log(\lambda_1^2/2)}{\log \lambda} \approx 1.84238 \tag{45}$$

However, some caution is necessary in the case of generating function C_{11}: It is easy to check that the sum (35) is not diverging at x_c (i.e., the exponent γ_{11} is negative in this temperature region). To avoid this difficulty, we consider the first derivative of C_{11}. An analysis of this derivative on the lattice of size $L = 2^K$ reveals that it follows the asymptotic law (for large K)

$$\left.\frac{dC_{11}^L}{dx}\right|_{x=x_c} \sim 2^{-K}(A_1^{(K)})^2 \left.\frac{dB^{(K)}}{dx}\right|_{x=x_c} \sim \left(\frac{\lambda\lambda_2^2}{2}\right)^K$$

where we also have taken into account that

$$\left.\frac{dB^{(K)}}{dx}\right|_{x=x_c} = \lambda^K$$

Finally, comparing the above behavior and the behavior that follows from finite-size scaling arguments,

$$\left.\frac{dC_{11}^L}{dx}\right|_{x=x_c} \sim L^{(1+\gamma_{11})/\nu}$$

we have

$$\gamma_{11} = \frac{\log(\lambda_2^2/2)}{\log \lambda} \approx -0.31025 \tag{46}$$

We note also that a direct numerical approach leads to the same values of the above critical exponents. These exponents are in qualitative agreement with corresponding, presumably exact, values in $d=2$: $\gamma_1(d=2)=61/64$, $\gamma_{11}(d=2)=-3/16$ (see, for example, ref. 27).

(ii) When the temperature is lowered, an adsorption transition occurs for $w=w^*(t)$. This transition is controlled by a tricitical fixed point ("special" fixed point in the terminology of surface physics)

$$(B^*, B_1^*, B_2^*) = \left(\frac{\sqrt{5}-1}{2}, \frac{\sqrt{5}-1}{2}, \frac{\sqrt{5}-1}{2}\right) \tag{47}$$

The fact that all three correlation functions assume the same value at this point is in agreement with a generally accepted picture: At this point a balance between the attractive polymer-surface potential and an effective repulsion (due to the loss of configurational entropy) sets in, which makes polymer correlation functions isotropic. In particular, the gyration radius scaling relation (11) is satisfied, i.e., $\nu_{||}=\nu_{\perp}=\nu$, where ν is the bulk value of this exponent. Indeed, the above fixed point (47) has two relevant eigenvalues, $\lambda_> = \lambda$ [see (41)] and

$$\lambda_< = \frac{1+2B^*+(21-32B^*)^{1/2}}{2} \approx 1.67096 \tag{48}$$

The gyration radius critical exponent ν is determined by the larger eigenvalue ($\lambda_>$), while the crossover exponent (2) involves both of them[19]

$$\phi = \frac{\log \lambda_<}{\log \lambda_>} \approx 0.59152 \tag{49}$$

Note that the values of the crossover exponent (49) is not far from the value $\phi = 1/2$ for the standard 2D lattice.[16]

To determine the susceptibility critical exponents (3)–(5), we proceed along the lines of the discussion of region (i). Specifically, an analysis reveals the following limiting behavior of surface open-walk generating functions at the special fixed point (47) [note that $A^{(r)}$, $C^{(r)}$, and $D^{(r)}$ still follow the asymptotic law (42)]

$$\begin{aligned} &A_1^{(r)} \sim A_3^{(r)} \sim \lambda_3^r, \qquad C_2^{(r)} \sim \lambda_3^r, \qquad D_4^{(r)} \sim \lambda_3^{2r}, \qquad D_6^{(r)} \sim (\lambda_1 \lambda_3)^r \\ &A_2^{(r)} \sim \lambda_1^r, \qquad A_4^{(r)} \sim \lambda_1^r, \qquad D_5^{(r)} \sim (\lambda_1 \lambda_3)^r, \qquad D_7^{(r)} \sim \lambda_1^{2r} \end{aligned} \tag{50}$$

where

$$\lambda_3 = \frac{B^* + 2 + (45 - 69B^*)^{1/2}}{2} \approx 2.07642 \tag{51}$$

is the largest eigenvalue of the corresponding 3×3 matrix for the set of recursion relations involving the variables A_1, A_3, and C_2 [note that recursion relations (13), (15), and (22) become linear at the fixed point]. Then, using the approach described above, we find

$$\begin{aligned} \gamma_1 &= \frac{\log(\lambda_1 \lambda_3/2)}{\log \lambda} \approx 1.36371 \\ \gamma_{11} &= \frac{\log(\lambda_3^2/2)}{\log \lambda} \approx 0.88504 \\ \gamma_s &= \frac{\log(\lambda_1^2/2)}{\log \lambda} \approx 1.84238 \end{aligned} \tag{52}$$

(iii) In the low-temperature region $[w > w^*(t)]$, due to the localization of the polymer chain, the polymer system should display the features of a one-dimensional system. In this case, the critical fugacity $x_c(w)$ is a decreasing function of w, while the correlation function recursion relations iterate toward the fixed point

$$(B^*, B_1^*, B_2^*) = (0, 1, 0) \tag{53}$$

Linearization about this fixed point gives only one relevant eigenvalue, $\lambda_4 = 2$, which yields $\nu_{\|} = 1$ and $\nu_{\perp} = 0$, as one could expect. The leading singular behavior of the generating functions C_1 and C_{11} comes from the term $A_3^{(r)} \sim \lambda_4^r$ [note that in this temperature region $C_1 \approx C_{11}$, (36)]. It is

easy to check that all susceptibility critical indices coalesce, assuming the value for a 1D system

$$\gamma_1 = \gamma_{11} = \gamma_s = \gamma = 1 \tag{54}$$

Before leaving the case of adsorption on the truncated 3-simplex lattice it would be interesting to consider the scaling relations (10). These relations are generally expected to hold in the case of standard homogeneous lattices. A simple substitution of the above critical exponents supports the first of these relations, $\gamma_s = 2\gamma_1 - \gamma_{11}$. However, after taking the values of bulk exponents ν and γ ($\gamma = 1.37522$[26]), one sees that the second scaling relation ($2\gamma_1 - \gamma_{11} = \gamma + \nu$) is not satisfied. It would be tempting, therefore, to modify this scaling relation in order for it to hold for the case of fractals. To achieve this goal, we consider the scaling ansatz for the singular parts of the bulk (f_B) and surface (f_S) free-energy densities of an appropriate magnetic model on a fractal lattice. By analogy with the relevant case for regular lattices,[6] we can write

$$f_B(t, h) = t^{d_f/y_T} \mathscr{F}_B(h t^{-y_H/y_T})$$
$$f_S(t, h, h_1) = t^{d_s/y_T} \mathscr{F}_S(h t^{-y_H/y_T}, h_1 t^{-y_{H_1}/y_T})$$

where t, h, and h_1 are (reduced) temperature, bulk field, and surface field variables. The "temperature eigenvalue" y_T can be related to the correlation length critical exponent ν ($\nu = 1/y_T$), and the scaling indices y_H and y_{H_1} are known as bulk and surface magnetic eigenvalues, in the terminology of the RG approach. Then, using the definitions

$$\frac{\partial^2 f_B}{\partial^2 h} \sim t^{\gamma}, \qquad \frac{\partial^2 f_S}{\partial^2 h} \sim t^{\gamma_s}, \qquad \frac{\partial^2 f_S}{\partial^2 h_1} \sim t^{\gamma_{11}}, \qquad \frac{\partial^2 f_S}{\partial h_1 \, \partial h} \sim t^{\gamma_1}$$

we express the magnetic susceptibility exponents in terms of thermal and magnetic eigenvalues:

$$\gamma = \frac{2y_H - d_f}{y_T}, \qquad \gamma_s = \frac{2y_H - d_s}{y_T}, \qquad \gamma_{11} = \frac{2y_{H_1} - d_s}{y_T}, \qquad \gamma_1 = \frac{y_H + y_{H_1} - d_s}{y_T}$$

These relations imply

$$\gamma_s = 2\gamma_1 - \gamma_{11} = \gamma + \nu(d_f - d_s) \tag{55}$$

It is easy to check that the above values of the susceptibility exponents (which have been obtained without referring to any magnetic model) satisfy the scaling relation (55). It is worth noticing that our findings for

other studied models of polymer adsorption on fractals[28] also support this relation. Note also that we recover the scaling relation (10) when d_f is equal to $d_s + 1$, in particular, in the case of standard homogeneous lattices (in which case one has $d_f = d$, $d_s = d - 1$).

3. SIERPINSKI GASKET FAMILY OF FRACTAL LATTICES

In Section 2 we described an approach that can be used in order to obtain all surface exponents of surface-interacting SAWs on finitely ramified fractal lattices. Now, motivated by the intricate findings for the case of bulk SAWs,[21–23] we study the problem of polymer adsorption on a family of Sierpinski-type fractals introduced by Given and Mandelbrot.[29] Different members of this family can be characterized by an integer b, which takes all values from 2 to ∞. We recall that each lattice of this family (labeled by b) can be constructed recursively. Thus, to construct the fractal lattice with spatial scaling factor b, one starts with an equilateral triangle (generator) that contains b^2 smaller equilateral triangles. Then one replaces each of the $b(b+1)/2$ upward-oriented small triangles of the initial generator by a new generator (see, for example, Fig. 1 of ref. 21). To obtain the rth-stage fractal lattice, this process of construction has to be repeated $r-1$ times in a self-similar way.

The fractal dimension of the lattices obtained in the above way is given by $d_f = \log[b(b+1))/2]/\log b$. When the lattice parameter b tends to infinity, the resulting lattice structure resembles a triangular lattice and one would expect that SAW critical exponents converge toward their values for homogeneous lattices in $d = 2$. However, the available exact results for $2 \leqslant b \leqslant 8$ show that the susceptibility critical exponent γ systematically increases and moves away from its two-dimensional value.[21] Using the finite-size scaling approach, Dhar argued that the limiting value $\gamma(b \to \infty)$ is completely different from $\gamma(d=2)$, while $\nu(b)$ must approach $\nu(d=2)$ from below. The latter prediction then implies that $\nu(b)$ should be a non-monotonic function of b, which would seem in contrast with the short sequence of the exact results.[21] The results of a recent RG Monte Carlo study[23] support, however, Dhar's prediction.

In the present paper we confine ourselves to a study of the critical behavior of two-point correlation functions of the SISAWs on the class of Sierpinski gasket lattices. For this we use the approach described in the preceding section. To have a closed set of recursion relations one needs six restricted partition functions. Namely, one has to introduce three generating functions $B^{(r)}$, $B_1^{(r)}$, $B_2^{(r)}$ for the walks passing through only two vertices of an rth-order fractal lattice (compare Fig. 2), and three corresponding

functions $\tilde{B}^{(r)}$, $\tilde{B}_1^{(r)}$, $\tilde{B}_2^{(r)}$ for the walks visiting all three corner vertices. Here, for example, $\tilde{B}_1^{(r)}$ refers to the walks that enter and leave an rth-order fractal at the vertices that lie on the attractive wall, having visited the third bulk vertex as well (compare Fig. 2). The recursion relations for low values of the lattice parameter b can be obtained straightforwardly. In the simplest case $b=2$, i.e., for the Sierpinski gasket lattice, the recursion relations for B, B_1, B_2, $\tilde{B}$, $\tilde{B}_1$, and $\tilde{B}_2$ are given by

$$B' = B^2 + B^3 + 2B^2\tilde{B} + \tilde{B}_2 + 2B\tilde{B}$$

$$B_1' = B_1^2 + \tilde{B}_1^2 + 2BB_2\tilde{B}_2 + 2B_1\tilde{B}_1 + BB_2^2$$

$$B_2' = (B+\tilde{B})(B_2+\tilde{B}_2) + B_2(BB_1 + B\tilde{B}_1 + \tilde{B}B_1)$$

$$\tilde{B}' = B^2\tilde{B} + 2B\tilde{B}^2$$

$$\tilde{B}_1' = \tilde{B}B_2^2 + 2\tilde{B}B_2\tilde{B}_2$$

$$\tilde{B}_2' = \tilde{B}_2(BB_1 + B\tilde{B}_1 + \tilde{B}B_1)$$

An examination of the above system of recursion relations shows that all three generating functions $\tilde{B}$, $\tilde{B}_1$, and $\tilde{B}_2$ vanish at the relevant fixed point and that these functions do not affect any of the above-defined critical exponents. This allows us to reduce the above system of recursion relations to the simpler one (17)–(19). The same conclusion can be reached for an arbitrary value of the spatial scaling factor b of the lattice. This reduction is very useful, in particular, for large values of b, in which case the number of polymer configurations to be considered is so large that one has to use a computer to sort them out. In what follows we will discuss the critical behavior of SISAWs in terms of B, B_1, and B_2.

We have been able to obtain the exact recursion relations of the polymer correlation functions for eight values of lattice parameter, $2 \leqslant b \leqslant 9$. The resulting systems of recurrence equations are rather complex and take up too much space to be given here (a listing of corresponding results is available on request). Instead, we report here only the main results, which are qualitatively similar to the case of the 3-simplex lattice. As in that case, three different temperature regions were identified. The high-temperature region associated with the desorbed phase of the polymer system has been discussed in some detail in the context of the bulk SAW behavior on the same class of lattices.[21–23] Here we only add one new member to the existing sequence of eight exact values[21] of the correlation length critical exponent: $\nu(b=9) \approx 0.77196$. The low-temperature behavior of the system is basically that described in detail in ref. 19 and outlined in Section 2 of this paper.

We focus our attention on the point of adsorption transition, i.e.,

Table I. The Eigenvalues $\lambda_>$ and $\lambda_<$ of the Renormalization Group Transformations for SISAWs on the Sierpinski Gasket Family of Fractals at the Special Fixed Point[a]

b	B^*	$\lambda_>$	$\lambda_<$	ν	ϕ	α
2	0.61803	2.38196	1.67096	0.79862	0.59152	0.30945
3	0.55115	3.99193	2.16286	0.79364	0.55728	0.20557
4	0.50634	5.80290	2.54182	0.78840	0.53054	0.11512
5	0.47449	7.78985	2.84261	0.78401	0.50892	0.03504
6	0.45074	9.93601	3.08642	0.78033	0.49082	−0.03739
7	0.43237	12.22951	3.28727	0.77717	0.47529	−0.10397
8	0.41773	14.66122	3.45488	0.77441	0.46171	−0.16585
9	0.40580	17.22367	3.59634	0.77196	0.44968	−0.22380

symmetric fixed point $B = B_1 = B_2 = B^*$ (see Table I). Here the exponent α refers to the leading singular behavior of the polymer free energy density

$$f(T) = -k_B T \log \mu(T) \sim (T_a - T)^{2-\alpha}$$

It is known[31] that, at a tricritical point, the "specific heat" critical exponent α can be related to the above-defined crossover exponent ϕ: $\alpha = 2 - 1/\phi = 2 - \log \lambda_> / \log \lambda_<$. Our results for the critical exponents ν, ϕ, and α are given in Table I. It is seen (Fig. 3) that ϕ is a decreasing function

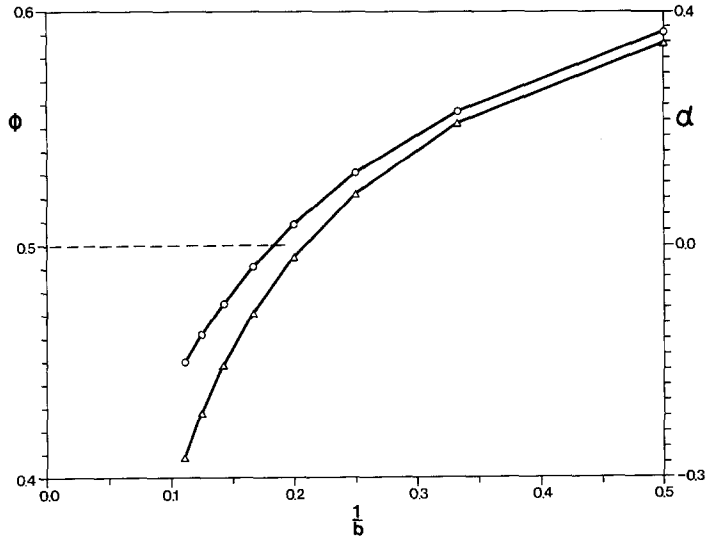

Fig. 3. The crossover critical exponent ϕ as a function of $1/b$ (circles). The horizontal broken line represents the 2D Euclidean value $\phi = 1/2$. We also present the thermal critical exponent α as a function of $1/b$ (triangles). Note that ϕ and α have different vertical axes.

of b in the studied region $2 \leqslant b \leqslant 9$ and that it crosses the exact 2D Euclidean value $\phi = 1/2$ at $b \approx 6$. The thermal critical exponent α has a similar behavior and becomes negative for $b \geqslant 6$. It seems plausible, on the other hand, that ϕ and α should approach their 2D Euclidean values in the asymptotic region $b \to \infty$. This implies that ϕ and α should be some nonmonotonic functions of b—as in the case of the gyration radius critical exponent ν.

It is interesting to note that our exact values of the crossover exponent satisfy the upper and lower bounds for this exponent derived by Bouchaud and Vannimenus[19]: $1 - \nu(d_f - d_s) \leqslant \phi \leqslant d_s/d_f$. Unfortunately, being quite narrow for small values of b, these bounds are rather wide in the region of the fractal to the homogeneous system crossover ($b \to \infty$):

$$\frac{1}{4} + \frac{3}{16}\frac{\log(\log b)}{\log b} \leqslant \phi \leqslant \frac{1}{2} + \frac{\log 2}{4 \log b}$$

where we have used Dhar's prediction[22]:

$$\nu(b) \sim \frac{3}{4} - \frac{3}{16}\frac{\log(\log b)}{\log b}$$

4. DISCUSSION

We have presented results for SISAWs on the truncated 3-simplex lattice and on a family of Sierpinski gasket-type fractals. By extending the real-space RG approach to the case of open SISAWs, we showed how to obtain the surface susceptibility exponents. It is demonstrated that these exponents obey a scaling relation that we derived using the analogy between polymer adsorption and surface magnetism on fractals. Our approach can be generalized to the case of other finitely ramified fractals. The number of parameters needed to describe the properties of open walks increases very quickly with lattice complexity (by increasing, for instance, the ramification of the lattice). It is useful to note, however, that the number of parameters can be reduced considerably in the case when one wants to study only the critical behavior.

We found that many critical properties in the case of fractal lattices are similar to those of SISAWs on homogeneous lattices. Our study of SAWs on the family of Sierpinski gasket lattice reveals, however, that the critical behavior is not always as would be expected. Namely, our numerical data for critical exponents ϕ and α show that these exponents must be some nonmonotonic functions of the lattice parameter b if they approach the corresponding Euclidean values in the limit $b \to \infty$. It seems likely that

a puzzle remains in the case of surface susceptibility exponents as well. Indeed, Dhar's predictions[22] and our scaling relation (55) imply

$$\gamma_s(b) \sim \frac{157}{32} - \frac{345}{128} \frac{\log(\log b)}{\log b} \qquad \text{as} \quad b \to \infty$$

which means that $\gamma_s(\infty) = 157/32 \approx 4.90625$ is completely different from its Euclidean counterpart $\gamma_{s,d=2} = \gamma_{d=2} + \nu_{d=2} = 67/32 \approx 2.09375$. This is in contrast with recent arguments that critical exponents on fractals should be the analytical continuation of their counterparts on Euclidean lattices, providing both the fractal and the spectral dimension of the fractal lattice coalesce (see, for example, ref. 31).

It is difficult to get a proper explanation for these somewhat surprising findings. As pointed out by Dhar, short SAWs do not feel the lattice boundary, for large, finite b, whereas very long chains go through the lattice constrictions.[22] The large-scale behavior of SAWs on fractals therefore can be strongly modified relative to their comportment on standard Euclidean lattices. One may expect that the fractal structure makes the SISAW behavior yet more sensitive to the details of the underlying lattice (for example, in order to stabilize the desorbed phase of a polymer system one has to choose the Boltzmann factor $t < 1$, which is quite different from the corresponding case on Euclidean lattices). Our findings for various surface scaling indices reveal, however, that a critical behavior of the type predicted for bulk SAWs (as $b \to \infty$) might occur in the case of SISAWs as well. Further investigation in this direction, using finite size-scaling or Monte Carlo approaches, would be very desirable in order to achieve a better understanding of the region of the fractal to Euclidean system crossover.

ACKNOWLEDGMENT

One of us (M.K.) is grateful to Prof. Sava Milošević for a critical reading of the manuscript.

REFERENCES

1. E. Bouchaud, L. Auvray, J. Cotton, M. Daoud, B. Farnoux, and G. Jannink, *Prog. Surf. Sci.* **27**:5 (1988).
2. P. G. de Gennes, *Adv. Colloid Interface Sci.* **27**:189 (1987).
3. K. Binder and K. Kremer, in *Scaling Phenomena in Disordered Systems*, R. Pynn and A. Skjeltrop, eds. (Plenum Press, New York, 1985), p. 525.
4. D. Napper, *Polymeric Stabilization of Colloidal Dispersions* (Academic Press, New York, 1983).

5. E. Eisenriegler, K. Kremer, and K. Binder, *J. Chem. Phys.* **77**:6296 (1982).
6. K. Binder, in *Phase Transitions and Critical Phenomena*, Vol. 8, C. Domb and J. L. Lebowitz, eds. (Academic Press, New York, 1983).
7. H. Meirovitch and S. Livne, *J. Chem. Phys.* **88**:4507 (1988).
8. F. Seno and A. L. Stella, *Europhys. Lett.* 7:605 (1989).
9. T. Ishinabe, *J. Chem. Phys.* **76**:5589 (1982).
10. K. De'Bell, T. Lookman, and S. G. Whittington, *Phys. Rev. A* **41**:682 (1990).
11. I. Guim and T. Burkhardt, *J. Phys. A* **22**:1131 (1989).
12. A. R. Veal, J. M. Yeomans, and G. J. Jug, *J. Phys. A* **24**:827 (1991).
13. K. Kremer, *J. Phys. A* **16**:4333 (1983).
14. M. Benhamou and G. Mahoux, *J. Phys.* (Paris) **49**:577 (1988), and references therein.
15. B. Duplantier and H. Saleur, *Phys. Rev. Lett.* **57**:3179 (1986).
16. T. W. Burkhardt, E. Eisenriegler, and I. Guim, *Nucl. Phys. B* **316**:559 (1989).
17. G. H. Weiss and R. J. Rubin, *Adv. Chem. Phys.* **52**:363 (1983).
18. V. Privman, G. Forgacs, and H. L. Frisch, *Phys. Rev. B* **37**:9897 (1988).
19. E. Bouchaud and J. Vannimenus, *J. Phys.* (Paris) **50**:2931 (1989).
20. J. Vannimenus, *Physica D* **38**:351 (1989).
21. S. Elezović, M. Knežević, and S. Milošević, *J. Phys. A* **20**:1215 (1987).
22. D. Dhar, *J. Phys.* (Paris) **49**:397 (1988).
23. S. Milošević and I. Živić, *J. Phys. A* **24**:L833 (1991).
24. B. Nienhuis, *Phys. Rev. Lett.* **49**:1062 (1982).
25. D. Dhar, *J. Math. Phys.* **18**:577 (1977).
26. D. Dhar, *J. Math. Phys.* **19**:5 (1978).
27. B. Duplantier, *J. Stat. Phys.* **54**:581 (1989).
28. M. Knežević, unpublished.
29. J. A. Given and B. B. Mandelbrot, *J. Phys. A* **16**:L56 (1983).
30. B. Derrida and H. Herrmann, *J. Phys.* (Paris) **44**:1365 (1984).
31. B. Bonnier, Y. Leroyer, and C. J. Meyers, *J. Phys.* (Paris) **48**:533 (1987).