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Test of the bounds on the crossover exponent for polymer adsorption on fractals

Ivan Živić,[1] Sava Milošević,[2,3] and H. Eugene Stanley[2]
[1]*Faculty of Natural Sciences and Mathematics, University of Kragujevac, 34000 Kragujevac, Serbia*
[2]*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215*
[3]*Faculty of Physics, University of Belgrade, P.O. Box 550, 11001 Belgrade, Serbia*
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We study the problem of adsorption of linear chain polymers situated on fractal substrates that belong to the 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 an impenetrable adsorbing wall. By applying the Monte Carlo renormalization-group (MCRG) method, we calculate the critical exponent ϕ, associated with the number of adsorbed monomers, for a sequence of SG fractals with $2 \leq b \leq 100$. We find that our MCRG results deviate at most 0.12% from the available ($2 \leq b \leq 9$) exact renormalization-group results. In addition, we test the bounds for ϕ, proposed recently on heuristic grounds by Bouchaud and Vannimenus [J. Phys. (Paris) **50**, 2931 (1989)]. We demonstrate that their lower bound is violated for $b \geq 12$. Finally, we discuss a possible behavior of ϕ for large b, including the limit $b \to \infty$.

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I. INTRODUCTION

Adsorption of linear polymer chains at surfaces has been extensively studied because of its practical and theoretical importance. In almost all theoretical studies it has been assumed that polymers are present in a homogeneous container that has one adsorbing impenetrable boundary [1]. Recently, a few studies have appeared in which a fractal container of polymers was assumed [2,3] (this assumption may have its own technological relevance). In these studies, it has been assumed that in the container there is a single-chain polymer immersed in a good solvent, which means that the interaction between the contiguous monomers in the bulk are not taken into account. On the other hand, the interaction with the adsorbing surface is taken into account by assigning an energy $\varepsilon_w < 0$ to each monomer that is found at the surface. The number of the adsorbed monomers M is a function of temperature T and its relation to the total number of monomers N is assumed to be

$$M \sim \begin{cases} N(T_a - T)^{1/\phi - 1}, & T < T_a, \\ N^{\phi}, & T = T_a, \\ (T - T_a)^{-1}, & T > T_a, \end{cases} \tag{1.1}$$

where T_a is the critical temperature of the adsorption, and ϕ is the crossover exponent [1]. It follows that, for temperatures higher than T_a, one should expect a vanishingly small fraction of monomers adsorbed at the surface, whereas for $T < T_a$ there should appear a finite fraction of adsorbed monomers.

In the case of a two-dimensional Euclidean container of polymers, it is known [4] that 1/2 is the exact value for the critical exponent ϕ. Bouchaud and Vannimenus [2] studied the adsorption problem for the two-dimensional and three-dimensional Sierpinski gaskets (SG) by modeling polymers as self-avoiding walks (SAW's). In addition to some other results, they found $\phi = 0.5915$ for the two-dimensional SG and $\phi = 0.7481$ for the three-dimensional SG. Furthermore, the same authors [2] established the following bounds for ϕ:

$$1 - (d_f - d_s)\nu \leq \phi \leq \frac{d_s}{d_f}, \tag{1.2}$$

where d_f is the fractal dimension of the polymer container, d_s is the fractal dimension of the adsorbing surface, and ν is the critical exponent of the end-to-end distance of polymer in the bulk. The above bounds were obeyed for the results found in Ref. [2]. The same bounds have been also confirmed in the exact renormalization group (RG) study [3] of the adsorption problem for the first eight members, enumerated by the integer b ($2 \leq b \leq 9$), of the infinite two-dimensional SG family of fractals.

In this paper we introduce the Monte Carlo renormalization-group (MCRG) method to calculate the critical exponent ϕ for linear chain polymers on the two-dimensional SG family of fractals. We have obtained ϕ for a long sequence of the SG fractals, that is, for $2 \leq b \leq 100$. Comparing our results for $2 \leq b \leq 9$ with the exact RG results [3] we find that there is no deviation larger than 0.12%, and, for this reason, we can accept the MCRG results as reliable. As regards the proposed bounds (1.2), the MCRG results demonstrate that the lowered bound is not valid for all $b \geq 12$. Details of the present MCRG calculations are explained in Sec. II. In Sec. III we present an overall discussion of our findings and related results obtained by other authors.

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II. THE MCRG APPROACH

In this section we are going to apply the MCRG method to the SAW adsorption problem on the SG family of fractals. These fractals have been studied in numerous papers so far, and consequently we shall give here only a brief summary of their basic properties. It starts with recalling the fact that each member of the SG fractal family can be constructed in stages. At the initial stage ($r = 1$) of the construction there is an equilateral triangle (generator) that contains b^2 identical smaller triangles of unit side length, out of which only the upper oriented are physically present. The subsequent fractal stages are constructed self-similarly, so that the complete fractal is obtained in the limit $r \to \infty$. In the case under study, it is assumed that one side, of each fractal, is an impenetrable attractive wall, and, for the sake of convenience, we assume that it is the basis of the corresponding triangle. Thus it follows that the fractal dimension of the adsorbing wall (surface) is $d_s = 1$, whereas the fractal dimension of the complete SG fractal is known to be $d_f = \ln[b(b+1)/2]/\ln b$.

In order to explore effects of the adsorbing wall, we introduce the two Boltzmann factors $w = e^{-\varepsilon_w/T}$ and $t = e^{-\varepsilon_t/T}$, where ε_w is the energy of a monomer lying on the adsorbing wall, and ε_t is the energy of a monomer that appears in the layer adjacent to the wall. Here we set the Boltzmann constant k_B equal to unity. Besides, we should set $\varepsilon_t > 0$ so as to prevent the tendency of polymer chain towards being always adsorbed [2]. In the terminology that applies to the SAW, we assign the weight x to each step in the bulk (away from the wall), the weight wx to each step on the wall, and the weight tx to each step in the layer adjacent to the wall (see Fig. 1).

Important aspects of the statistics of chain polymers can be learned by studying never-starting and never-ending SAW's, which can be described by the three restricted partition functions $B^{(r)}, C^{(r)}$, and $D^{(r)}$, that are depicted in Fig. 2. The recursive nature of the fractal construction implies the following recursion relations for the restricted partition functions:

$$B^{(r+1)} = \sum_{N_B} \mathrm{B}_{N_B} \left(B^{(r)}\right)^{N_B}, \tag{2.1}$$

$$C^{(r+1)} = \sum_{N_B,N_C,N_D} \mathrm{C}_{N_B,N_C,N_D} \left(B^{(r)}\right)^{N_B} \times \left(C^{(r)}\right)^{N_C} \left(D^{(r)}\right)^{N_D}, \tag{2.2}$$

$$D^{(r+1)} = \sum_{N_B,N_C,N_D} \mathrm{D}_{N_B,N_C,N_D} \left(B^{(r)}\right)^{N_B} \times \left(C^{(r)}\right)^{N_C} \left(D^{(r)}\right)^{N_D}, \tag{2.3}$$

where the coefficients B_{N_B}, C_{N_B,N_C,N_D}, and D_{N_B,N_C,N_D} are not functions of r, and each of them represents the number of ways in which the corresponding part of the SAW path, within the $(r+1)$th stage fractal structure, can be comprised of the SAW paths within the fractal structures of the next lower order (see, for instance, Fig. 1). Because of the independence of r, these coefficients can be calculated by studying all possible SAW's within the fractal generator only.

The above set of relations (2.1), (2.2), and (2.3), can be considered as the RG equations. One can argue that these RG equations should have three relevant fixed points (B^*, C^*, D^*) of the type $(B^*, 0, 0)$, (B^*, B^*, B^*), and $(0, 1, 0)$ [2]. The first fixed point with $C^* = 0$ and $D^* = 0$, due to the meaning of these quantities (see Fig. 2), describes desorbed phase of the chain polymer (with vanishingly small number of adsorbed monomers). Conversely, the third fixed point with $B^* = 0$ and $D^* = 0$ describes the adsorbed polymer state. Finally, the second symmetric fixed point, with all three RG parameters being mutually equal, describes the critical state of the polymer chain which occurs at temperature $T = T_a$, when adsorbed and desorbed polymer phases become

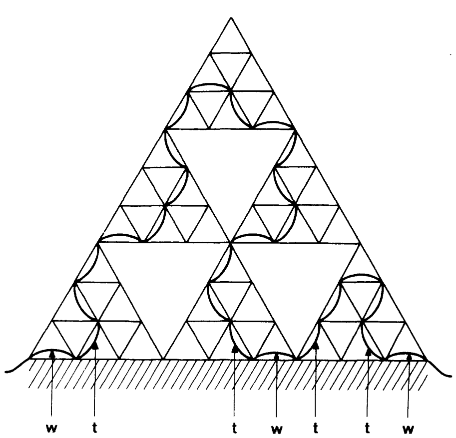

FIG. 1. The fractal structure of the $b = 3$ SG fractal at the second stage of construction, with an example of the SAW path. The crosshatched area at the basis of the triangle represents the adsorption wall. The steps on the adsorbing wall and in the adjacent layer are weighted by the factors $w = e^{-\varepsilon_w/T}$ and $t = e^{-\varepsilon_t/T}$, respectively. Here ε_w is the energy of a monomer lying on the adsorbing wall ($\varepsilon_w < 0$), and $\varepsilon_t > 0$ is the energy of a monomer that appears in the layer adjacent to the wall. The depicted SAW path represent one term in Eq. (2.2) for $r = 1$ with $N_B = 3$, $N_C = 1$, and $N_D = 2$.

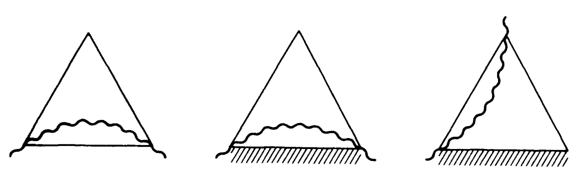

FIG. 2. Schematic representation of the three restricted partition functions (for an rth stage fractal structure) used in the calculation of the SAW critical exponent ϕ. Thus, for example, $C^{(r)}$ represents the SAW path that starts at the triangle left vertex that lies on the adsorption wall, and exits the triangle at the right vertex that also lies on the adsorption wall. The interior details of the rth order fractal structure is not shown (it is manifested by the wiggles of the SAW paths).

identical. In what follows we focus our attention on the symmetric fixed point in order to calculate the critical exponent ϕ [2,3]. It should be observed that Eq. (2.1), for each b, has only one nontrivial fixed point value B^* [5,6], which thereby completely determines the symmetric fixed point.

Calculation of the critical exponent ϕ begins with solving the eigenvalue equation

$$\begin{vmatrix} \left(\dfrac{\partial B'}{\partial B}-\lambda\right) & 0 & 0 \\ \dfrac{\partial C'}{\partial B} & \left(\dfrac{\partial C'}{\partial C}-\lambda\right) & \dfrac{\partial C'}{\partial D} \\ \dfrac{\partial D'}{\partial B} & \dfrac{\partial D'}{\partial C} & \left(\dfrac{\partial D'}{\partial D}-\lambda\right) \end{vmatrix}^{*} = 0 , \tag{2.4}$$

where we have used the prime symbol as a superscript for the $(r+1)$th order parameters and no indices for the rth order parameters, and the asterisk means that all derivatives should be taken at the *symmetric* fixed point. The above eigenvalue problem can be separated into two parts, so that the first part

$$\lambda_\nu = \left.\frac{\partial B'}{\partial B}\right|_{B^*} , \tag{2.5}$$

appears to be pertinent to the bulk critical exponent $\nu = \ln b/\ln \lambda_\nu$ [5,6], while the second part

$$\begin{vmatrix} \left(\dfrac{\partial C'}{\partial C}-\lambda\right) & \dfrac{\partial C'}{\partial D} \\ \dfrac{\partial D'}{\partial C} & \left(\dfrac{\partial D'}{\partial D}-\lambda\right) \end{vmatrix}^{*} = 0 , \tag{2.6}$$

gives, in general, two additional eigenvalues for each b, but in practice it turns out that only one of them (to be henceforth denoted by λ_ϕ) is relevant ($\lambda_\phi > 1$). Knowing λ_ϕ we can determine the critical exponent ϕ [2] through the formula

$$\phi = \frac{\ln \lambda_\phi}{\ln \lambda_\nu} . \tag{2.7}$$

Hence in an exact RG evaluation of ϕ one needs to calculate partial derivatives of sums (2.1), (2.2), and (2.3), and thereby one should find the coefficients B_{N_B}, C_{N_B,N_C,N_D}, and D_{N_B,N_C,N_D} by an exact enumeration of all possible SAW's for each particular b, which has been accomplished in Ref. [3] for the SG fractals with $b \leq 9$. However, for $b \geq 10$ the exact enumeration turns out to be a formidable task. We have circumvented this problem by applying the MCRG method. Within this method, the first step would be to locate the interesting fixed point, but the results obtained in [6] provide information for both B^* and λ_ν for a sequence with $2 \leq b \leq 80$. In this paper, among other things, we supplement these data by making larger number of the Monte Carlo (MC) simulations and by treating the additional case of $b = 100$ (see Table I). The next step in the MCRG method consists of finding λ_ϕ without explicit calculation of the RG equation coefficients.

To solve the partial eigenvalue problem (2.6), so as to learn λ_ϕ, we need to find the requisite partial derivatives. These derivatives can be related to various averages of the numbers N_B, N_C, and N_D of different steps (monomers) within a SAW path. For instance, starting with (2.2) (in the notation that does not use the superscripts $(r+1)$ and r) and by differentiating it with respect to C we get

$$\frac{\partial C'}{\partial C} = \sum_{N_B,N_C,N_D} N_C\, \mathrm{C}_{N_B,N_C,N_D} (B)^{N_B} (C)^{N_C-1} (D)^{N_D} . \tag{2.8}$$

Now, it is convenient to conceive C' as the grand canonical partition function for the ensemble of all possible SAW's that start at the lower left vertex of the generator (lying on the adsorbing wall) and exit at the lower right vertex. With this concept in mind, we can write the corresponding ensemble average

$$\langle N_C(B,C,D)\rangle_{C'} = \frac{1}{C'} \sum_{N_B,N_C,N_D} N_C\, \mathrm{C}_{N_B,N_C,N_D} (B)^{N_B} \times (C)^{N_C} (D)^{N_D} , \tag{2.9}$$

which can be directly measured in a MC simulation. Combining (2.8) and (2.9) we can express the requisite partial derivative in terms of the measurable quantity

$$\frac{\partial C'}{\partial C} = \frac{C'}{C} \langle N_C(B,C,D)\rangle_{C'} . \tag{2.10}$$

In a similar way we can get the additional three derivatives

$$\frac{\partial C'}{\partial D} = \frac{C'}{D} \langle N_D(B,C,D)\rangle_{C'} , \tag{2.11}$$

$$\frac{\partial D'}{\partial C} = \frac{D'}{C} \langle N_C(B,C,D)\rangle_{D'} , \tag{2.12}$$

$$\frac{\partial D'}{\partial D} = \frac{D'}{D} \langle N_D(B,C,D)\rangle_{D'} . \tag{2.13}$$

Consequently, calculating the above derivatives at the symmetric fixed point and solving the eigenvalue equation (2.6) we obtain

$$\lambda_\phi = \frac{\langle N_C\rangle^*_{C'} + \langle N_D\rangle^*_{D'}}{2} + \sqrt{\left(\frac{\langle N_C\rangle^*_{C'} - \langle N_D\rangle^*_{D'}}{2}\right)^2 + \langle N_C\rangle^*_{D'} \langle N_D\rangle^*_{C'}} , \tag{2.14}$$

TABLE I. The MCRG ($2 \leq b \leq 100$) results obtained in this work for the fixed point value parameter B^*, the eigenvalues λ_ν and λ_ϕ, and the corresponding critical exponent ϕ for the SG family of fractals. For the sake of comparison, we give also the corresponding exact RG results [3], for $2 \leq b \leq 9$.

b	No. of MC realizations	B^*	λ_ν	λ_ϕ	ϕ
2	Exact				0.5915
	5×10^5	0.61773 ± 0.00038	2.3819 ± 0.0009	1.671 ± 0.005	0.5915 ± 0.0040
3	Exact				0.5573
	5×10^5	0.55165 ± 0.00028	3.994 ± 0.002	2.163 ± 0.007	0.5573 ± 0.0025
4	Exact				0.5305
	5×10^5	0.50650 ± 0.00022	5.802 ± 0.003	2.541 ± 0.008	0.5304 ± 0.0019
5	Exact				0.5089
	5×10^5	0.47437 ± 0.00018	7.793 ± 0.004	2.844 ± 0.009	0.5090 ± 0.0016
6	Exact				0.4908
	5×10^5	0.45059 ± 0.00015	9.936 ± 0.005	3.09 ± 0.01	0.4908 ± 0.0015
7	Exact				0.4753
	5×10^5	0.43223 ± 0.00013	12.237 ± 0.006	3.28 ± 0.01	0.4746 ± 0.0014
8	Exact				0.4617
	5×10^5	0.41749 ± 0.00012	14.661 ± 0.008	3.46 ± 0.01	0.4618 ± 0.0013
9	Exact				0.4497
	5×10^5	0.40573 ± 0.00011	17.211 ± 0.009	3.60 ± 0.01	0.4499 ± 0.0012
10	5×10^5	0.39587 ± 0.00010	19.91 ± 0.01	3.72 ± 0.01	0.4388 ± 0.0012
11	5×10^5	0.38755 ± 0.00009	22.72 ± 0.01	3.82 ± 0.01	0.4293 ± 0.0012
12	5×10^5	0.38043 ± 0.00008	25.64 ± 0.01	3.92 ± 0.01	0.4211 ± 0.0011
13	5×10^5	0.37426 ± 0.00008	28.68 ± 0.02	3.99 ± 0.01	0.4123 ± 0.0011
15	5×10^5	0.36418 ± 0.00007	35.09 ± 0.02	4.11 ± 0.01	0.3976 ± 0.0011
17	5×10^5	0.35610 ± 0.00006	41.84 ± 0.02	4.21 ± 0.02	0.3848 ± 0.0010
20	5×10^5	0.34693 ± 0.00006	52.75 ± 0.03	4.33 ± 0.02	0.3693 ± 0.0010
22	5×10^5	0.34193 ± 0.00005	60.25 ± 0.03	4.39 ± 0.02	0.3611 ± 0.0010
26	5×10^5	0.33452 ± 0.00005	76.63 ± 0.04	4.45 ± 0.02	0.3440 ± 0.0009
30	5×10^5	0.32886 ± 0.00004	94.05 ± 0.05	4.52 ± 0.02	0.3319 ± 0.0009
35	5×10^5	0.32347 ± 0.00004	117.83 ± 0.06	4.56 ± 0.02	0.3181 ± 0.0009
40	5×10^5	0.31956 ± 0.00004	142.92 ± 0.08	4.59 ± 0.02	0.3072 ± 0.0008
50	5×10^5	0.31379 ± 0.00003	197.2 ± 0.1	4.65 ± 0.02	0.2910 ± 0.0008
60	5×10^5	0.31012 ± 0.00003	257.0 ± 0.1	4.68 ± 0.02	0.2782 ± 0.0008
70	3×10^5	0.30743 ± 0.00004	322.3 ± 0.2	4.62 ± 0.02	0.2650 ± 0.0009
80	3×10^5	0.30538 ± 0.00003	389.4 ± 0.2	4.74 ± 0.02	0.2608 ± 0.0008
100	3×10^5	0.30264 ± 0.00003	537.6 ± 0.4	4.65 ± 0.03	0.2444 ± 0.0009

which means that λ_ϕ has been expressed in terms of quantities that all are measurable through MC simulations. Indeed, the quantities $\langle N_C\rangle^*_{C'}$, $\langle N_D\rangle^*_{D'}$, $\langle N_C\rangle^*_{D'}$, and $\langle N_D\rangle^*_{C'}$ can be directly measured via MC simulations. Details of the requisite MC technique have been extensively explained in recent Refs. [6] and [7], and we would not like to elaborate on them in this paper.

III. RESULTS AND DISCUSSION

The MCRG results for B^* and λ_ν are given in Table I. These results are somewhat improved in comparison with the results of Ref. [6] (the improvement has been achieved by enlarging numbers of the MC simulations). Besides, we have studied here the $b = 100$ fractal that was not reached in Ref. [6]. Hence we can offer a new bit of information relevant to the SAW bulk critical exponent ν, that is, we have found $\nu = 0.73248 \pm 0.00008$ for $b = 100$.

In Table I we present our MCRG results for λ_ϕ, which together with λ_ν gives, according to (9), specific values for the critical exponent ϕ for $2 \leq b \leq 100$. For $2 \leq b \leq 9$, we quote, for the sake of comparison, the values of ϕ obtained by the exact RG approach [3]. Thus one can see that the MCRG results deviate at most 0.12% from the exact RG findings, which is an unusually good agreement between the two (MC and exact) different approaches of solving the problem.

In Fig. 3 we depict the critical exponent ϕ, for the SG family of fractals, as the function of $1/b$. In the same figure, we have graphically presented (using our data) the lower and upper bounds (1.2) for the critical exponent ϕ, established in a heuristic way in Ref. [2]. Thus one can observe that ϕ, being a monotonically decreasing function of b (in the region under study), violates the lower bound for $12 \leq b \leq 100$. The violation of the lower bound can be also observed for the θ–polymer problem

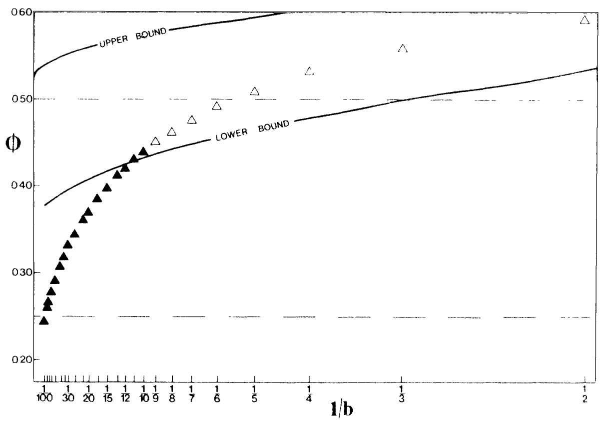

FIG. 3. Data for the adsorption critical exponent ϕ for the SG family of fractals. The exact RG results are represented by open triangles, while the MCRG results are depicted by solid triangles. The solid curves represent the upper and lower bounds (1.2) for ϕ, proposed in Ref. [2]. The dashed horizontal line represents the Euclidean value 0.5 of ϕ, whereas the lower dotted-dashed horizontal line represents the limiting value of the lower bound $\phi = 0.25$ obtained for $b \to \infty$ [3]. The error bars related to the MCRG data are not depicted in the figure since in all cases they lie within the corresponding symbols.

analyzed using the $\varepsilon = 3 - d$ expansion [8], as well as in the case of the same problem in the two-dimensional Euclidean space [9,10]. In the case under study, the possible reason for the violation of the lower bound can be found in the assumption that the number of accessible sites $\rho(z)$, as a function of distance z from the adsorbing wall, decreases according to the power law $\rho \sim z^{-x}$, where $x = 1 + d_s - d_f$ [2]. The assumed power law requires too fast a decrease of the accessible sites. Indeed, if the assumption were valid, then it would imply that the corresponding monomer density, for $b \geq 12$, must be an increasing function of z, which is physically untenable.

Finally, one can notice in Fig. 3 that the MCRG data for ϕ definitely cross the limiting value of 0.25 found for the lower bound [3] when $b \to \infty$, so that $\phi = 0.2444 \pm 0.0009$ for $b = 100$. What happens beyond $b = 100$ is hard to predict, although one could expect that ϕ will reach the Euclidean value $\phi = 0.5$ in the limit $b \to \infty$. Such an expectation for the bulk critical exponent ν has been corroborated by the means of the finite-size scaling arguments [11], but, at the same time, it was argued that the bulk critical exponent γ (associated with the total number of distinct SAW's) should be, in the limit $b \to \infty$, three times ($133/43 \approx 3$) larger than the corresponding Euclidean value $\gamma = 43/32$. Therefore, in addition to an effort to extend our data beyond $b = 100$, it would be interesting to make a finite-size scaling theory of the adsorption of linear chain polymers on fractals that would include a prediction about the behavior of the critical exponent ϕ in the limit $b \to \infty$.

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