Self-interacting polymer chains terminally anchored to adsorbing surfaces of three-dimensional fractal lattices

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HIGHLIGHTS

- Self-interacting polymers in poor solvent near an adsorbing surface are studied.
- Polymers and the poor solvent are situated on three-dimensional fractal lattices.
- Exact results for entropic critical exponents are obtained for various polymer phases.

ARTICLE INFO

ABSTRACT

We have studied the adsorption problem of self-attracting linear polymers, modeled by self-avoiding walks (SAWs), situated on three-dimensional fractal structures, exemplified by 3d Sierpinski gasket (SG) family of fractals as containers of a poor solvent. Members of SG family are enumerated by an integer b ($b \geq 2$), and it is assumed that one side of each SG fractal is an impenetrable adsorbing surface. We calculate the critical exponents γ_1, γ_{11}, and γ_s, which are related to the numbers of all possible SAWs with one, both, and no ends anchored to the adsorbing boundary, respectively. By applying the exact renormalization group (RG) method (for the first three members of the SG fractal family, $b = 2, 3$, and 4), we have obtained specific values of these exponents, for θ-chain and globular polymer phase. We discuss their mutual relations and relations with corresponding values pertinent to extended polymer chain phase.

1. Introduction

The statistical properties of linear polymers in various types of solvents near an impenetrable short-range attractive boundary have been extensively studied in the last few decades. 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 the bonds between consecutive monomers along the polymer, while the solvent surrounding has been represented by a lattice. Here we assume that polymer is immersed in poor solvent so that two adjacent nonconsecutive monomers, along the polymer chain, interact via a short-range interaction causing the so-called θ transition from extended chain polymer phase, that exists at high temperatures, to a globule (collapsed) phase polymer, that appears at low temperatures. Also, we assume that, in each of these phases, polymer chain interacts with an adsorbing surface bounding the polymer container interior, so that for strong enough monomer–surface interaction, it undergoes transition from the bulk (desorbed) phase to the adsorbed chain phase.

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Since the polymer adsorption has been comprehended as a surface critical phenomenon, it has been possible to describe various polymer quantities in terms of power laws characterized by concomitant critical exponents. In the early investigations of the polymer adsorption problem, polymer chains were immersed in homogeneous spaces with planar adsorbing boundaries (for a review see [1]). These studies have been extended to polymers in porous (inhomogeneous) media, which were modeled by fractal lattices embedded in two-dimensional (2d) [2–4] and three-dimensional (3d) [5,6] space. In these studies mainly two critical exponents have been studied: the end-to-end distance critical exponent ν and the crossover exponent ϕ, which governs the number of contacts between the polymer and the surface. However, a complete picture of the adsorption problem requires knowledge of surface critical exponents that describe numbers of polymer configurations grouped according to different ways of terminally anchoring to the adsorbing boundary. In terms of the SAW model, these exponents are defined by the following power laws for numbers of possible different configurations averaged over the number of sites on the impenetrable surface

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

where $N \gg 1$ is the number of SAW steps. Here C_1, C_{11} and C_s are numbers of all possible SAWs with one, both, and no ends anchored to the boundary, respectively, $\mu = \mu(T)$ is temperature dependent connectivity constant, and γ_1, γ_{11} and γ_s are concomitant surface critical exponents that can take different values in various polymer phases. So far, surface critical exponents have been studied mostly for polymer immersed in a good solvent (where the only intra-chain interaction is due to the excluded volume effect) near the boundary surfaces of two- and three-dimensional Euclidean spaces. These studies were performed using various techniques including exact enumeration [7,8], mapping between the considered polymer problem and percolation with a boundary surface [9], conformal invariance theory [10–13], Coulomb gas method [14], field theoretical approach [15,16], and Monte Carlo simulations [17–20]. In porous (non-Euclidean) media, the surface critical exponents were also studied only for SAW without self-interactions on fractal lattices embedded in 2d [21,22], 3d [23] and higher-dimensional [24] space. In this paper we extend such a study [23] by including the intra-chain interactions within the polymer situated in tree-dimensional porous media, modeled by fractals that belong to the three-dimensional 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 an exact renormalization group (RG) method for the SAW model that include both the monomer–monomer and monomer–surface interactions, we have calculated critical exponents γ_1, γ_{11}, and γ_s, for $b = 2$, 3 and 4 fractal lattices.

This paper is organized as follows. In Section 2 we describe the 3d SG fractals for general scaling parameter b, and introduce the self-interacting SAW model in the case when a boundary of 3d SG fractal is adsorbing surface. Then, we present the framework of the general RG method for studying the polymer adsorption problem on these fractals, taking into account the presence of the intra-chain interactions. 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.

2. Framework of the renormalization group approach

In this section we are going to expound on the RG approach for calculating critical exponents γ_1, γ_{11}, and γ_s for the adsorption problem of SAWs immersed in a poor solvent, whose containers are modeled by fractals belonging to the 3d SG family of fractals. Here we give a brief summary of 3d SG fractals basic properties. We start with recalling the fact that each member of this 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 attracting (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 both the effect of monomer–monomer interaction and the effect of attractive (adsorbing) surface, one should introduce three Boltzmann factors: $v = e^{-\varepsilon_v / k_B T}$, $w = e^{-\varepsilon_w / k_B T}$, and $t = e^{-\varepsilon_t / k_B T}$, where ε_v is the energy corresponding to interaction between two nonconsecutive neighboring monomers, ε_w is the energy of a monomer lying in the adsorbing surface, and ε_t is the energy of a monomer in the layer adjacent to the surface (see Fig. 1). If we assign the weight x to a single step of the SAW walker, then the weight of a walk having N steps, with P nearest neighbor contacts, M steps on the surface, and K steps in the layer adjacent to the surface, is $x^N v^P w^M t^K$. Depending on the polymer ends position (with respect to the adsorbing surface) one can introduce the following three generating functions

$$G_1(x, T) = \sum_{N=1}^{\infty} x^N \sum_{P,M,K} \mathcal{G}_1(N, P, M, K) v^P w^M t^K = \sum_{N=1}^{\infty} C_1(N, T) x^N, \tag{2}$$

$$G_{11}(x, T) = \sum_{N=1}^{\infty} x^N \sum_{P,M,K} \mathcal{G}_{11}(N, P, M, K) v^P w^M t^K = \sum_{N=1}^{\infty} C_{11}(N, T) x^N, \tag{3}$$