

# Polymer adsorption on a fractal substrate: Numerical study

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We study the adsorption of flexible polymer macromolecules on a percolation cluster, formed by a regular two-dimensional disordered lattice at critical concentration  $p_c$  of attractive sites. The percolation cluster is characterized by a fractal dimension  $d_s^{p_c} = 91/49$ . The conformational properties of polymer chains grafted to such a fractal substrate are studied by means of the pruned-enriched Rosenbluth method. We find estimates for the surface crossover exponent governing the scaling of the adsorption energy in the vicinity of transition point,  $\phi_s^{p_c} = 0.425 \pm 0.009$ , and for adsorption transition temperature,  $T_A^{p_c} = 2.64 \pm 0.02$ . As expected, the adsorption is diminished when the fractal dimension of the substrate is smaller than that of a plain Euclidean surface. The universal size and shape characteristics of a typical spatial conformation which attains a polymer chain in the adsorbed state are analyzed as well. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3691102>]

## I. INTRODUCTION

The conformational properties of polymer macromolecules in the vicinity of substrates are the subject of continuous interest in polymer science, playing an important role both in technology (adhesion, stabilization of colloidal dispersions<sup>1</sup>) and biological physics (proteins adsorption on membranes<sup>2,3</sup>). The presence of an energetically neutral surface produces only trivial effects of steric restrictions for polymers. More interesting is the case of an attractive substrate, when below a critical temperature  $T_A$ , a second-order phase transition into an adsorbed state takes place.<sup>4</sup> The peculiarities of adsorption of grafted polymers on attractive surfaces are thoroughly studied by now both analytically<sup>5–9</sup> and numerically.<sup>6,10–15</sup> As an order parameter of the adsorption transition, one considers the fraction of the average number of monomers  $N_s$  adsorbed to the surface and the total length  $N$  of the polymer chain, which tends to zero in the usual bulk regime and becomes macroscopic close to  $T_A$ , obeying the scaling law

$$\frac{\langle N_s \rangle}{N} \sim N^{\phi_s - 1}, \quad N \rightarrow \infty. \quad (1)$$

Here,  $\phi_s$  is the surface crossover exponent, a basic parameter in scaling analysis of the adsorption transition ( $0 < \phi_s < 1$ ). Recent estimates of the crossover exponent  $\phi_s$  along with numerical values for the adsorption temperature  $T_A$  are given in Table I.

The study of polymers near disordered surfaces is of great importance, since most naturally occurring substrates are rough and energetically (or structurally) inhomogeneous. Surface heterogeneity has a crucial effect on polymer adsorption phenomena.<sup>16–24</sup> In fact, already simple physical arguments lead to the conclusion that upon increasing the

surface irregularity the number of polymer-surface contacts is strongly influenced, leading to a shift of the adsorption critical temperature. Energetical inhomogeneity arises due to the presence of various chemical compounds in the substrate, interacting with the monomers of the polymer chain in a different manner. In the language of lattice models, such surfaces can be modeled as a two-dimensional regular lattice with different types of randomly distributed sites, e.g., one type with attractive interactions with the monomers and the other one being neutral (treated as defects or impurities). Similarly as it holds in the bulk case,<sup>25,26</sup> presence of uncorrelated point-like defects of low concentration (well below the percolation threshold  $p_c = 0.592746$  (Ref. 27)) is expected to be irrelevant for the scaling properties of the adsorption transition of polymers. Numerical simulations<sup>21,24</sup> reveal, however, a continuous dependence of the transition temperature  $T_A$  on the concentration  $p$  of attractive sites. In particular, close to  $p_c$ , the estimate  $T_A^{p_c} \simeq 2.3$  was obtained. The related problem of the impact of long-ranged correlations in the distribution of defects on the surface, leading to a non-trivial influence on scaling near the adsorption transition point, was studied recently in Ref. 23.

Since most chemical substrates are proved to be of fractal nature,<sup>28</sup> studying the influence of a non-trivial surface geometry on polymer adsorption is of particular interest. In Ref. 29 it was found that the crossover exponent  $\phi_s$  for a substrate characterized by the fractal dimension  $d_s^f$  has upper and lower bounds given as

$$1 - (3 - d_s^f)\nu \leq \phi_s \leq d_s^f/3, \quad (2)$$

where  $\nu$  is the bulk radius of gyration exponent for a polymer chain in a good solvent ( $\nu = 0.5887 \pm 0.0006$  (Ref. 30)). One can thus conclude that adsorption is enhanced (diminished) when the fractal dimension of the substrate is larger (smaller) than that of a plain Euclidean surface. A number of studies has been dedicated to polymer adsorption on a family of finitely ramified fractals.<sup>31–34</sup> Also of great importance is the study

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by a percolation cluster are more anisotropic than those of a homogeneously attractive surface.

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