Force-Induced Desorption of a Linear Polymer Adsorbed on a Boundary of the Sierpinski Gasket Fractal

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Abstract. During the last decade new experimental methods have emerged allowing micromanipulation of single molecules. Using these methods one can monitor the mechanism of some force-driven phase transitions at the level of a single molecule. Lattice models represent useful tool for theoretical understanding of such transitions. Here we study the force-induced desorption of a linear polymer adsorbed on a boundary of the Sierpinski gasket fractal. The polymer is modeled by a self-avoiding walk, with an attraction for every step of the walk on the boundary, and repulsion for every step in the first layer next to the boundary. The walk is subject to a stretching force which hinders the adsorption. The hierarchical nature of the lattice we consider enables an exact treatment which yields the phase diagram and the critical behavior. We show that for this model there is no low-temperature re-entrance, and we find that the force-induced desorption transition is of first order.

When a polymer chain interacts with an impenetrable surface its conformational properties are strongly modified relative to its bulk properties [1]. This is due to a subtle competition between the gain of internal energy near an attractive surface and a corresponding loss of entropy due to constraints imposed by the impenetrable surface. If the surface is strongly attractive, the polymer chain sticks to the surface, whereas for weak attraction it prefers to stay away from the surface. Thus, when the temperature is increased, there is a transition from adsorbed to desorbed state, marked by a transition temperature T_a. If additionally a force f is applied to the polymer, this transition is altered, which can be investigated experimentally by using micromanipulation techniques [2]. When force pulls the polymer away from the surface, one expects a critical value $f_c(T)$, such that for $f < f_c(T)$ the polymer will be adsorbed, while for $f > f_c(T)$ it will be desorbed. The curve $f_c(T)$, therefore, can be regarded as a boundary that separates the desorbed phase from the adsorbed phase in the (T, f) plane.

In order to investigate the corresponding phase diagram analytically we model the polymer by a self-avoiding walk (SAW) on Sierpinski gasket (SG) fractal. Pure adsorption of SAW on SG was analyzed in [3], where one boundary of the SG lattice represented an attractive surface, whereas to each N-step walk, having M steps along the wall, and R steps in the layer adjacent to the wall, the weight $x^N w^M t^R$ was associated. Here Boltzmann factor $w = \exp(-\varepsilon_w/k_BT) > 1$ was introduced to take into account attractive interaction between the surface and the polymer chain segments lying in the surface. The second Boltzmann factor $t = \exp(-\varepsilon_t/k_BT) < 1$ takes into account repulsive interaction

between the surface and the chain segments in the first neighborhood of the wall. It is necessary to introduce it since for $t \geq 1$ the chain is always adsorbed. Now, to model the influence of force f on polymer behavior in these conditions, we add the third Boltzmann factor $y = \exp(f/k_BT)$, so that the weight of SAW is $x^N w^M t^R y^L$, where L is length of SAW's projection on the direction of f, measured in elementary triangle edges (N, M and R have the same meaning as in the pure adsorption case). For instance, weight of the SAW depicted in Fig. 1 is equal to $x^{18}w^2t^3y^8$.

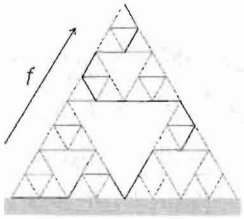

FIGURE 1. An example of self-avoiding walk traversing the structure obtained after the third step of the recursive construction of the Sierpinski gasket fractal. Horizontal boundary of the lattice represents the attractive wall, whereas the force f is directed along the second boundary.

We investigate the phase diagram within the framework of exact real-space renormalization group (RG) method. For the complete RG description we introduce 12 RG parameters, each of them having the form

$$B^{(k)}(x) = \sum_{N,M,R,L} \mathscr{B}^{(k)}(N,M,R,L) x^N w^M t^R y^L ,$$

where $\mathscr{B}^{(k)}(N,M,R,L)$ is the number of N-step SAWs traversing the structure obtained at the kth step of the SG construction in a particular way (see Fig. 2). It can be shown

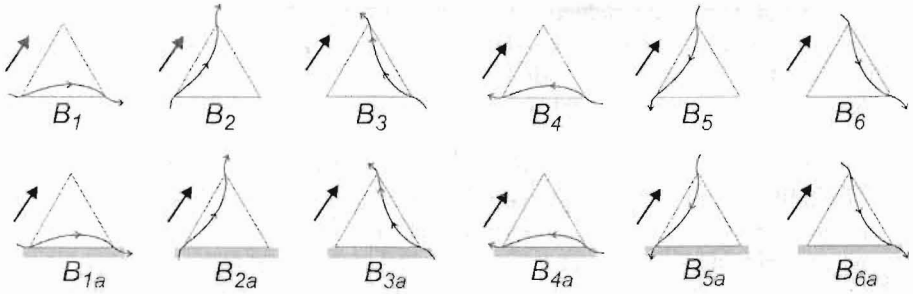

FIGURE 2. The particular ways in which SAWs traverse the SG structure (represented by the triangle), for each RG parameter. Thick gray lines represent the attractive wall, whereas heavy arrows correspond to the direction of the force **f** acting on the polymer chain.

TABLE 1. Possible nontrivial RG fixed points, obtained for different values of the Boltzmann parameter w, and the critical value of the fugacity x. Value of B_{2a}^* depends on the values of t and y.

w, x	B_1	B_2	B_3	B_4	B_5	B_6	B_{1a}	B_{2a}	B_{3a}	B_{4a}	B_{5a}	B_{6a}
$w < w^*(t,y), x = x_c(y)$	0	1	0	0	0	0	0	B_{2a}^*	0	0	0	0
$w = w^*(t,y), x = x_c(y)$	0	1	0	0	0	0	1	B_{2a}^*	0	0	0	0
$w > w^*(t,y), x = x_c(y,t,w)$	0	0	0	0	0	0	1	0	0	0	0	0

that RG parameters satisfy the following recursion relations:

$$
\begin{aligned}
B_1' &= B_1^2 + B_1 B_2 B_6\,, \quad B_2' = B_2^2 + B_1 B_2 B_3\,, \quad B_3' = B_3^2 + B_4 B_3 B_2\,,\\
B_4' &= B_4^2 + B_3 B_4 B_5\,, \quad B_5' = B_5^2 + B_4 B_5 B_6\,, \quad B_6' = B_6^2 + B_5 B_6 B_1\,,\\
B_{1a}' &= B_{1a}^2 + B_{2a} B_{6a} B_1\,, \quad B_{2a}' = B_{2a} B_2 + B_{1a} B_{2a} B_3\,, \quad B_{3a}' = B_{3a} B_3 + B_{4a} B_{3a} B_2\,,\\
B_{4a}' &= B_{4a}^2 + B_{3a} B_4 B_{5a}\,, \quad B_{5a}' = B_5 B_{5a} + B_6 B_{5a} B_{4a}\,, \quad B_{6a}' = B_6 B_{6a} + B_5 B_{6a} B_{1a}\,,
\end{aligned}
$$

where "prime" denotes RG parameters at the $(k+1)$th stage of the SG construction, whereas the parameters on the right-hand side of these equations correspond to the kth stage. Starting with the initial conditions: $B_1^{(0)} = x\sqrt{y}$, $B_2^{(0)} = xy$, $B_3^{(0)} = x\sqrt{y}$, $B_4^{(0)} = x/\sqrt{y}$, $B_5^{(0)} = x/y$, $B_6^{(0)} = x/\sqrt{y}$, $B_{1a}^{(0)} = xw\sqrt{y}$, $B_{2a}^{(0)} = xty$, $B_{3a}^{(0)} = xt\sqrt{y}$, $B_{4a}^{(0)} = xw/\sqrt{y}$, $B_{5a}^{(0)} = xt/y$, $B_{6a}^{(0)} = xt/\sqrt{y}$, corresponding to the unit triangle, one can explore the flow-diagram, and subsequently establish the phase diagram.

Numerical analysis of the flow-diagram shows that for each combination of t and y values there is a particular value of $w = w^*(t,y)$, such that for $w < w^*(t,y)$ polymer chain is desorbed, and for $w > w^*(t,y)$ it is adsorbed, so that the value $w = w^*(t,y)$ marks the desorption transition. The corresponding RG fixed points are summarized in Table 1. In Fig. 3 we show the dependence of the critical fugacity x_c on the value of w, for $t = 0.6$, $y = 3$. It can be seen that the first derivative of $x_c(y,t,w)$ is discontinuous, indicating that the corresponding phase transition is of the first order. The similar plots are obtained for other values of t and y, except for $y = 1$, for which the line $x_c(y = 1, t, w)$ is smooth. Of course, value $y = 1$ corresponds to the "pure-adsorption" case [3], and, indeed, presence of the force changes the nature of the phase transition under study.

From the definition of Boltzmann factors w and y follows that temperature and force can be expressed as: $T = |\varepsilon_w|/(k_B \ln w)$, and $f = |\varepsilon_w| \ln y / \ln w$. Thus, knowing $w^*(t,y)$, one can calculate corresponding T and $f_c(T)$, and by varying y, with t fixed, the phase diagram in the (T,f) plane can be obtained. Critical line $f_c(T)$, plotted for several values of t and $|\varepsilon_w| = 1$, is shown in Fig 4. One can see that the critical force $f_c(T)$ decreases when T increases, *i.e.* there is no re-entrance. The same result was obtained for regular 2d lattice: exactly for directed random walks in [4], for SAWs, using Monte Carlo simulation in [5], and also for SAWs in [6], using an exact enumeration technique. Re-entrant phase diagram (with a pronounced maximum at low temperatures) was found for 3d lattices in these papers, as well as for DNA unzipping models [7]. Therefore, it would be interesting to investigate force-induced desorption of SAW on 3d Sierpinski gasket lattice, which is a more realistic, as well as more complicated case, but still amenable to exact RG treatment. The work on this problem is in progress.

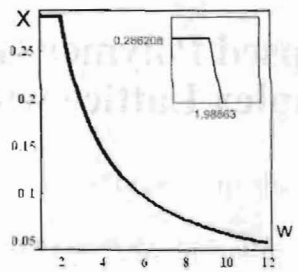

FIGURE 3. Critical value of the fugacity x as function of w, for $t = 0.6$, and $y = 3$. From the zoomed inset it is seen that the first derivative of $x_c(y,t,w)$ is discontinuous.

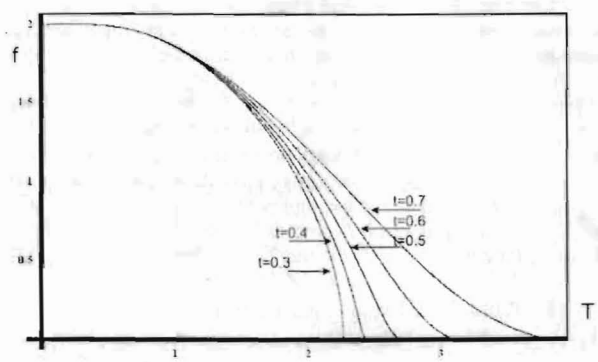

FIGURE 4. Force-temperature phase diagram for several values of the Boltzmann parameter t.

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