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FORCE-INDUCED DESORPTION OF SEMI-FLEXIBLE POLYMERS IN NON-HOMOGENEOUS MEDIA

Sunčica Elezović-Hadžić[1], *Ivan Živić*[2], *Dušanka Lekić*[3]
[1] University of Belgrade, Faculty of Physics, Studentski trg 12,
Belgrade, Serbia
[2] University of Kragujevac, Faculty of Science, Radoja Domanovića 12,
Kragujevac, Serbia
[3] University of Banja Luka, Faculty of Science, Mladena Stojanovića 2,
Banja Luka, Republic of Srpska

Abstract: Force-induced desorption of semi-flexible linear polymers in good solvents and non-homogeneous media is studied. We apply the model of self-avoiding walk with bending rigidity on 3-simplex fractal lattice. One boundary of the lattice represents an adsorbing wall, while an external force (perpendicular to the wall) pulls the polymer from the wall. Due to the hierarchical structure of the lattice under study, the phase diagram of polymer critical behavior can be exactly studied by real-space renormalization group method. Temperature dependence of the critical force, at which desorption occurs, is obtained and discussed for various values of the bending rigidity. Influence of the force and the polymer rigidity on the nature of desorption phase transition is also analyzed. All obtained results are compared with the related previous ones.

Keywords: polymers, fractals, adsorption, phase transitions.

1. INTRODUCTION

There is a continuous interest in the study of polymer adsorption at surfaces [1], since findings from these studies can improve various technological processes, as well as our understanding of biological systems functioning. This interest has been renewed with the recent development in experimental micromanipulation techniques, which made it possible to pull individual adsorbed polymer off a surface [2]. In the limit of high dilution in a good solvent, one can assume that one polymer chain interacts only with an adsorbing wall. If external force is not present and attractive interaction between polymer and wall is strong enough (or temperature is low enough), the polymer stays close to the wall forming an adsorbed phase. For weaker attraction (or higher temperatures), polymer stays desorbed and behaves almost as if there was no wall. The transition between these two polymer phases, so called pure desorption transition, has been studied theoretically and computationally using various models. When one end of a polymer is attached to an adsorbing wall, and the other end is pulled away by the application of an external force, the polymer is straightened along the force direction, so that properties of both desorbed and adsorbed phase can be changed, and nature of the adsorption transition itself is altered [3]. In addition, the fact that real polymers display some degree of stiffness can also affect the adsorption, which is taken into account in models of semi-flexible polymers [4].

Adsorption of semi-flexible polymers subject to a force was usually studied within the models situated in homogeneous environment, whereas in real situations adsorption occurs in the presence of different kinds of heterogeneities. Deterministic fractal lattices proved to be useful in various studies of polymer behavior in non-homogeneous media, since self-similarity of such lattices often enables an exact treatment [5]. Therefore, in this paper we model linear polymer in a good solvent by semi-flexible self-avoiding walk (SFSAW) on 3-simplex fractal lattice. Here, the stiffness of the polymer is incorporated in the SAW model by introducing an energy penalty $\varepsilon > 0$, for each bend in the walk. Adsorbing wall is represented by one of the edges of the lattice, and it is assumed that every monomer at the wall has energy $\varepsilon_w < 0$, whereas monomer lying in the layer adjacent to the wall has energy $\varepsilon_t > 0$ [6]. Polymer is pulled away from the wall by a force *f*, which is perpendicular to the wall. By applying an exact real-space renormalization group (RG) method, we first analyze the pure adsorption

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[*] Corresponding author: suki@ff.bg.ac.rs

(f=0), and then extend that analysis in the case when the force is applied. We calculate the dependence of critical value f_c on the temperature T, *i.e.* find the boundary in the phase plane (T,f) which separates SFSAW adsorbed ($f<f_c$ (T)) from the desorbed phase ($f>f_c$ (T)), and analyze the influence of the rigidity and the force strength on the nature of the desorption transition.

2. PURE ADSORPTION OF SEMI-FLEXIBLE SAW ON 3-SIMPLEX FRACTAL LATTICE

3-simplex fractal lattice is a well-known fractal lattice [7], which can be constructed starting with a complete graph of three points and replacing each of these points by a new complete graph of three points. This is the first stage of construction of the lattice (so called first order generator), and subsequent stages are constructed self-similarly, by repeating this procedure ad infinitum. Structure obtained in the r^{th} step of construction is called r^{th} order generator. In order to investigate pure adsorption of SFSAW on this lattice, we adopt the real-space renormalization group (RG) method, applied in [6] on pure adsorption (f=0) of fully flexible SAWs. In that approach, one introduces the so called restricted generating functions, which are defined as statistical weights of all possible symmetrically non-equivalent SFSAW conformations that traverse an r^{th} order generator. Statistical weight of a SFSAW, consisting of L monomers (sites), with K bends, M monomers at the adsorbing wall (represented by one of the edges of the lattice) and N monomers in the layer adjacent to the wall is equal to $x^L s^K w^M t^N$ (see Figure 1 for an example), where $s = e^{-\frac{\varepsilon}{k_B T}}$, $w = e^{-\frac{\varepsilon_w}{k_B T}}$, and $t = e^{-\frac{\varepsilon_t}{k_B T}}$ are Boltzmann factors (weights) associated with each bend, monomer at the wall, and monomer at the layer adjacent to the wall, respectively, whereas x (fugacity) is the weight associated with each site of the walk. There are six possible types of such restricted generating functions, $B_1^{(r)}, B_2^{(r)}, B_3^{(r)}, B_{1w}^{(r)}, B_{2t}^{(r)}, B_{3t}^{(r)}$, which correspond to six types of SFSAW conformations at the r^{th} order generator (see Figure 2). In the context of RG method, these functions represent RG parameters, and they fulfill the following RG equations

$$B_1^{(r+1)} = B_1^2 + B_2^2 B_3, \tag{1}$$

$$B_2^{(r+1)} = B_1 B_2 (1 + B_3), \tag{2}$$

$$B_3^{(r+1)} = B_2^2 + B_1^2 B_3, \tag{3}$$

$$B_{1w}^{(r+1)} = B_{1w}^2 + B_{2t}^2 B_3 \tag{4}$$

$$B_{2t}^{(r+1)} = B_1 B_{2t} + B_{1w} B_{3t} B_2, \tag{5}$$

$$B_{3t}^{(r+1)} = B_{2t} B_2 + B_{1w} B_{3t} B_1, \tag{6}$$

where functions on the right-hand side correspond to r^{th} order generators.

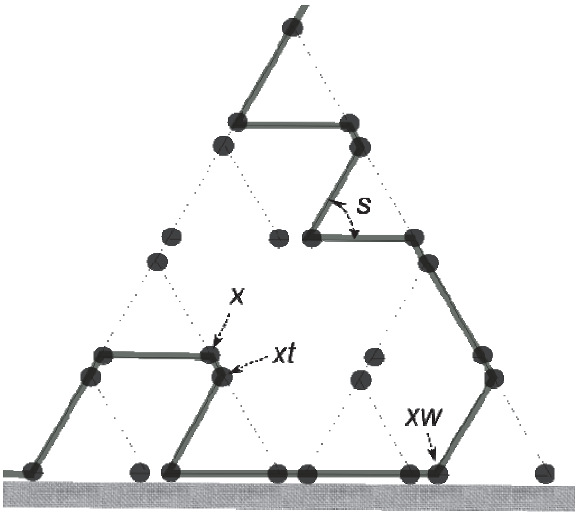

Figure 1. An example of semi-flexible self-avoiding walk (of B_{2t} type) traversing the second order generator of the 3-simplex fractal lattice. Horizontal boundary of the lattice represents the attractive wall. Each of L=19 vertices visited by the walk (thick line) represents a monomer, number of bends within the walk is K=12, number of monomers at the wall is M=6, and the number of monomers at the layer adjacent to the wall is N=3, so that statistical weight of this SFSAW is $x^{19}s^{12}w^6t^3$

Starting with the initial conditions

$$B_1^{(0)} = x^2 + x^3 s^3, \tag{7}$$

$$B_2^{(0)} = x^2 s + x^3 s^2, \tag{8}$$

$$B_3^{(0)} = x^2 s^2 + x^3 s, \tag{9}$$

$$B_{1w}^{(0)} = x^2 w^2 + x^3 w^2 t\, s^3, \tag{10}$$

$$B_{2t}^{(0)} = x^2 w\, t\, s + x^3 w^2 t\, s^2, \tag{11}$$

$$B_{3t}^{(0)} = x^2 w\, t\, s^2 + x^3 w^2 t\, s, \tag{12}$$

one can numerically analyze behavior of the RG parameters, for various values of x, s, w and t, thus finding the following.

For each $0 < s \leq 1$ and $0 < t < 1$ there is a critical value $w = w_c(s,t)$ such that

- For $w < w_c(s,t)$ and $x = x_c^{bulk}(s)$ the fixed point
  $$(B_1, B_2, B_3, B_{1w}, B_{2t}, B_{3t})^* = (B^*, B^*, B^*, 0,0,0), \tag{13}$$
  where $B^* = (\sqrt{5} - 1)/2$, is reached for $r \gg 1$. This corresponds to desorbed (bulk) phase of the SFSAW, which was analyzed in [8].
- For $w > w_c(s,t)$ and $x = x_c(s,t,w) < x_c^{bulk}(s)$ the fixed point
  $$(B_1, B_2, B_3, B_{1w}, B_{2t}, B_{3t})^* = (0,0,0,1,0,0) \tag{14}$$
  is obtained, which corresponds to the adsorbed phase.
- Exactly for $w = w_c(s,t)$ and $x = x_c^{bulk}(s)$ the symmetrical fixed point

$$(B_1, B_2, B_3, B_{1w}, B_{2t}, B_{3t})^* = (B^*, B^*, B^*, B^*, B^*, B^*), \tag{15}$$

is reached, at which the pure adsorption phase transition occurs.

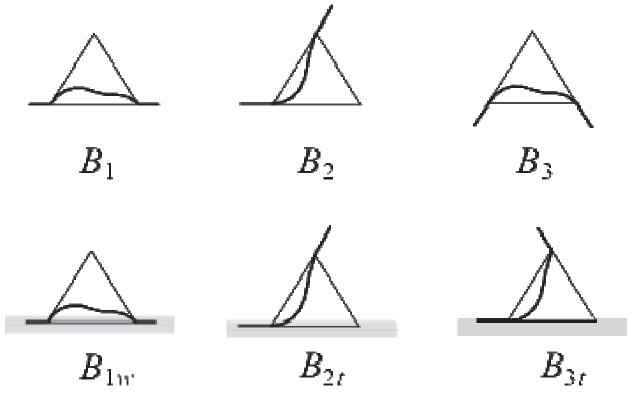

Figure 2. Different types of semi-flexible SAW conformations (wavy lines) that are possible on generators of any order (triangles), which are situated in the bulk (first row) or at the adsorbing wall (second row)

Dependence of the critical fugacity $x_c(s,t,w)$ on *w*, for *t*=0.5, and *s*=0.5 and 1, as well as $w_c(s,t)$ on *s* for *t*=0.1, 0.5 and 0.9 are presented in Figure 3.

Physical meaning of the obtained fixed points can be confirmed by calculating the average number of monomers at the adsorbing wall and comparing it with the average length of the SFSAW. Since the function $\Omega^{(r)} = B_{1w}^{(r)} + B_{2t}^{(r)}$ can be taken as the grand canonical partition function for all possible SFSAWs, starting at the lower-left corner of r^{th} order generator (lying on the adsorbing wall) and leaving it through one of its remaining two corners [6], the average number of monomers at the adsorbing wall $\langle M^{(r)} \rangle$ and the average overall number of monomers $\langle L^{(r)} \rangle$ are equal to

$$\langle M^{(r)} \rangle = \frac{w}{B_{1w}^{(r)} + B_{2t}^{(r)}} \left(\frac{\partial B_{1w}^{(r)}}{\partial w} + \frac{\partial B_{2t}^{(r)}}{\partial w} \right), \tag*{16)}$$

$$\langle L^{(r)} \rangle = \frac{x}{B_{1w}^{(r)} + B_{2t}^{(r)}} \left(\frac{\partial B_{1w}^{(r)}}{\partial x} + \frac{\partial B_{2t}^{(r)}}{\partial x} \right). \tag{17}$$

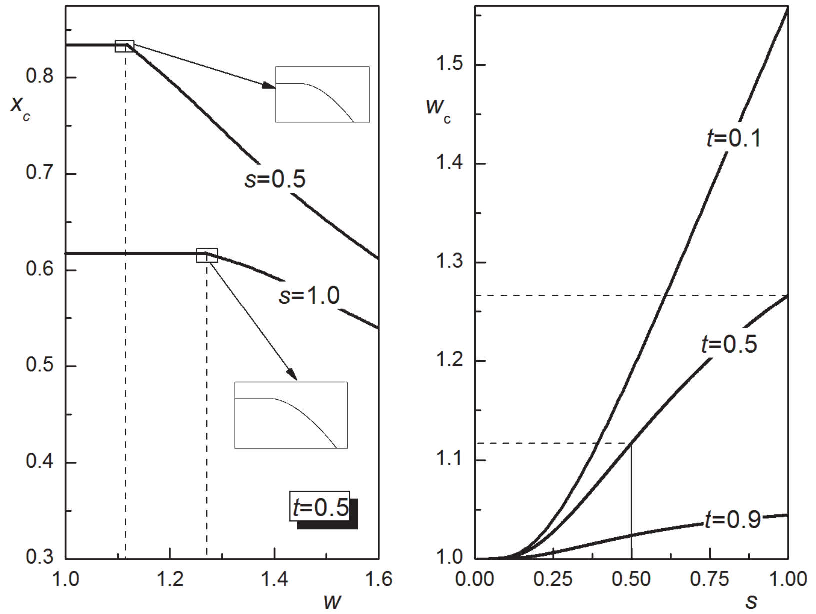

Figure 3. Pure adsorption case. Left: Critical fugacity x_c as a function of the attractive surface interaction factor w, for repulsive surface interaction factor t=0.5, and stiffness parameter values s=0.5 and 1.0. Insets, representing magnified vicinity of the corresponding values of w_c (denoted by dashed vertical lines) show that curves $x_c(w)$ are smooth at $w=w_c$, indicating that the unbinding transition is continuous in both cases. Right: Critical value w_c as a function of s, for t=0.1, 0.5 and 0.9. Area above the line $w_c(s,t)$, for each fixed t, corresponds to the adsorbed phase

From the RG equations (1)-(6), one can straightforwardly obtain recursion relations for the partial derivatives of the restricted partition functions, and then, starting with the corresponding initial values, simultaneously iterate all these recursion relations at each fixed point (13)-(15), for various values of *w*, *t* and *s*, and finally calculate $\langle M^{(r)} \rangle$ and $\langle L^{(r)} \rangle$, for $r \gg 1$. In such a way, we have obtained the following results.

- For $w < w_c(s,t)$ and $x = x_c^{bulk}(s)$ the average number of adsorbed monomers $\langle M^{(r)} \rangle$ quickly approaches some constant value, whereas $\langle L^{(r)} \rangle \to \infty$, so that $\langle M^{(r)} \rangle / \langle L^{(r)} \rangle \to 0$, as expected for the desorbed phase.
- Exactly at $w = w_c(s,t)$ and $x = x_c^{\text{bulk}}(s)$, both $\langle M^{(r)} \rangle$ and $\langle L^{(r)} \rangle$ become indefinitely large for $r \gg 1$, in such a way that again $\langle M^{(r)} \rangle / \langle L^{(r)} \rangle \to 0$.
- For $w > w_c(s,t)$ and $x = x_c(s,t,w)$ again both $\langle M^{(r)} \rangle$ and $\langle L^{(r)} \rangle \to \infty$, but the relative number of

adsorbed monomers $\langle M^{(r)}\rangle/\langle L^{(r)}\rangle$ tends to some value which depends on (w-w_c), and approaches 0 when $w \to w_c$.

This is illustrated in Figure 4 (left-hand side). Since quantity $\langle M^{(r)}\rangle/\langle L^{(r)}\rangle$ represents an order parameter for the adsorption, it follows that transition occurring at w=w_c is a continuous phase transition. On the other hand, $\frac{\langle M^{(r)}\rangle}{\langle L^{(r)}\rangle} \to \frac{w}{x_c}\left|\frac{\mathrm{d}x_c}{\mathrm{d}w}\right|$ [6], which means that $x_c(w)$ should be smooth at w=w_c. That certainly is the case, as can be checked by numerical examination (see left-hand side in Figure 3). In Figure 4 (right-hand side), quantity $\ln\langle M^{(r)}\rangle/\ln\langle L^{(r)}\rangle$ is presented as function of 1/r, for $w = w_c(s,t)$, t=0.2, 0.5 and s=0.1, 0.2, 1.0. It seems that $\ln\langle M^{(r)}\rangle/\ln\langle L^{(r)}\rangle$ approaches ϕ=0.5915 for all values of t and s, when $r \to \infty$, supporting the expectation that the scaling relation

$$\langle M\rangle \sim \langle L\rangle^{\phi} \ , \tag{18}$$

is obeyed for all studied values of s and t, with the value of the crossover exponent ϕ quite close to the value obtained via RG analysis for flexible SAWs on 2d Sierpinski gasket [6]. Similar analysis can be performed for the SFSAW case, as follows.

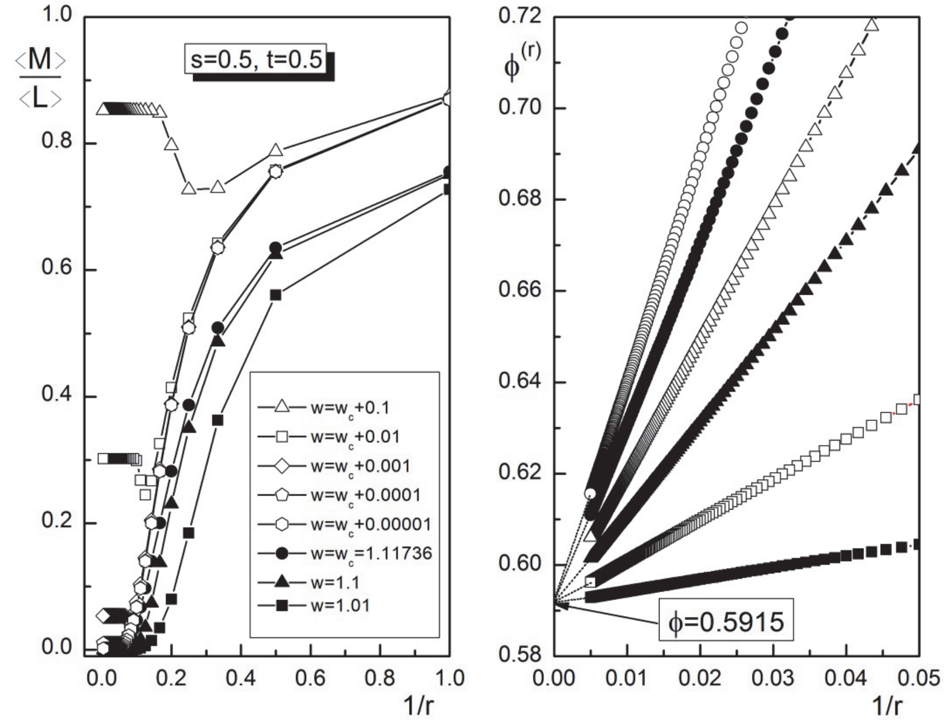

Figure 4. Pure adsorption case. Left: Relative number of adsorbed monomers, for SFSAW traversing r^{th} order generator, as a function of 1/r in the vicinity of the unbinding transition, for s=0.5, t=0.5. Right: $\phi^{(r)} = \ln\langle M^{(r)}\rangle \,/\, \ln\langle L^{(r)}\rangle$ as a function of 1/r, for interaction factors w=w$_c$(s,t), t=0.2 (empty symbols), 0.5 (full symbols) and s=0.1 (circles), 0.2 (triangles), and 1.0 (squares). For all t and s values, $\phi^{(r)} \to \phi$=0.5915, when r→∞

From the RG equations (1)-(6) one can obtain recursion relations for the derivatives of RG parameters in the matrix forms

$$\frac{\partial \boldsymbol{X}_a^{(r+1)}}{\partial w} = \mathbf{R}_a \frac{\partial \boldsymbol{X}_a^{(r)}}{\partial w}, \tag{19}$$

$$\frac{\partial \boldsymbol{X}_b^{(r+1)}}{\partial x} = \mathbf{R}_b \frac{\partial \boldsymbol{X}_b^{(r)}}{\partial x}, \tag{20}$$

$$\frac{\partial \boldsymbol{X}^{(r+1)}}{\partial x} = \mathbf{R} \frac{\partial \boldsymbol{X}^{(r)}}{\partial x}, \tag{21}$$

where $\boldsymbol{X}_a^{(r)}$, $\boldsymbol{X}_b^{(r)}$ and $\boldsymbol{X}^{(r)}$ are columns comprised of the RG parameters in the following way

$$\boldsymbol{X}_a^{(r)} = \left(B_{1w}^{(r)}, B_{2t}^{(r)}, B_{3t}^{(r)}\right)^T, \tag{22}$$

$$\boldsymbol{X}_b^{(r)} = \left(B_1^{(r)}, B_2^{(r)}, B_3^{(r)}\right)^T, \tag{23}$$

$$\boldsymbol{X}^{(r)} = \left(B_1^{(r)}, B_2^{(r)}, B_3^{(r)}, B_{1w}^{(r)}, B_{2t}^{(r)}, B_{3t}^{(r)}\right)^T, \tag{24}$$

and matrices $\mathbf{R}_a$, $\mathbf{R}_b$ and $\mathbf{R}$ are defined as

$$(\mathbf{R}_a)_{ij} = \frac{\partial\left(\boldsymbol{X}_a^{(r+1)}\right)_i}{\partial\left(\boldsymbol{X}_a^{(r)}\right)_j}, \tag{25}$$

$$(\mathbf{R}_b)_{ij} = \frac{\partial\left(\boldsymbol{X}_b^{(r+1)}\right)_i}{\partial\left(\boldsymbol{X}_b^{(r)}\right)_j}, \tag{26}$$

$$(\mathbf{R})_{ij} = \frac{\partial\left(\boldsymbol{X}^{(r+1)}\right)_i}{\partial\left(\boldsymbol{X}^{(r)}\right)_j}. \tag{27}$$

Due to the fact that bulk RG parameters $B_1^{(r+1)}, B_2^{(r+1)}, B_3^{(r+1)}$ do not depend on surface RG parameters $B_{1w}^{(r)}, B_{2t}^{(r)}, B_{3t}^{(r)}$, as can be seen in RG equations (1)-(3), matrix **R** has the block form

$$\mathbf{R} = \begin{pmatrix} \mathbf{R}_b & \mathbf{0} \\ \mathbf{R}_m & \mathbf{R}_a \end{pmatrix}, \quad (\mathbf{R}_m)_{ij} = \frac{\partial\left(X_a^{(r+1)}\right)_i}{\partial\left(X_b^{(r)}\right)_j} . \qquad (28)$$

Since at the symmetrical fixed point (15) matrix $\mathbf{R}_a$ has one eigenvalue $\lambda_S = (\sqrt{5} + \sqrt{37 - 16\sqrt{5}})/2 = 1.6709$ larger than 1, $\mathbf{R}_b$ also has one eigenvalue $\lambda_\nu = (7 - \sqrt{5})/2 = 2.38197$ larger than 1 and $\lambda_S < \lambda_\nu$, from (16) and (17) it follows that at the desorption transition relations

$$\langle M^{(r)} \rangle \sim \lambda_S^r, \qquad (29)$$

$$\langle L^{(r)} \rangle \sim \lambda_\nu^r, \qquad (30)$$

are satisfied and the scaling relation (18) indeed holds, with the crossover exponent

$$\phi = \frac{\ln \lambda_S}{\ln \lambda_\nu} = 0.5915, \qquad (31)$$

exactly the same as for the fully flexible SAW model [6]. Here we note that the eigenvalue λ_ν determines the end-to-end distance critical exponent ν of the SFSAW, for $w \leq w_c$, through the relation

$$\nu = \frac{\ln 2}{\ln \lambda_\nu} = 0.7986, \qquad (32)$$

which indeed corresponds to the SFSAW in the bulk of the 3-simplex fractal lattice [8].

3. FORCE-INDUCED DESORPTION

In this section we assume that SFSAW is attached to the adsorbing wall via one of its ends, while its other end is pulled from the wall by the force *f*, which is perpendicular to the wall. In such a case, one needs 14 restricted generating functions (RG parameters): $B_i^{(r)}, B_{i+}^{(r)}, B_{i-}^{(r)}$, *i*=1,2,3; $B_{1w}^{(r)}$; $B_{jt+}^{(r)}, B_{jt-}^{(r)}$, *j*=2,3, which correspond to the oriented SFSAW conformations, sketched in Figure 5. RG equations in this case have the form

$$B_1^{(r+1)} = B_1^2 + B_{2+}B_{2-}B_3, \qquad (33)$$

$$B_2^{(r+1)} = B_1 B_2 + B_{2+}B_3B_{1-}, \qquad (34)$$

$$B_3^{(r+1)} = B_2^2 + B_3B_{1+}B_{1-}, \qquad (35)$$

$$B_{1\pm}^{(r+1)} = B_{1\pm}^2 + B_{3\pm}B_{2\pm}B_2, \qquad (36)$$

$$B_{2\pm}^{(r+1)} = B_{2\pm}B_{1\pm} + B_1B_{3\pm}B_{2\pm}, \qquad (37)$$

$$B_{3\pm}^{(r+1)} = B_{2\pm}^2 + B_1B_{3\pm}B_{1\pm}, \qquad (38)$$

$$B_{1w}^{(r+1)} = B_{1w}^2 + B_{2t+}B_{2t-}B_3, \qquad (39)$$

$$B_{2t\pm}^{(r+1)} = B_{2t\pm}B_{1\pm} + B_{1w}B_{3t\pm}B_{2\pm}, \qquad (40)$$

$$B_{3t\pm}^{(r+1)} = B_{2t\pm}B_{2\pm} + B_{1w}B_{3t\pm}B_{1\pm}. \qquad (41)$$

One should note here that the end-to-end vectors of the conformations that correspond to the functions $B_i^{(r)}$ and $B_{1w}^{(r)}$ are perpendicular to the direction of the force, therefore these functions do not depend on *f* and actually are the same as in the pure adsorption case, so that initial conditions for these functions are given in (7)-(12). Also, the following relations are satisfied

$$B_{i\pm}^{(r)} = y^{\pm 2^r} B_i^{(r)}, \ i = 1,2,3, \qquad (42)$$

$$B_{jt\pm}^{(r)} = y^{\pm 2^r} B_{jt}^{(r)}, \ j = 2,3, \qquad (43)$$

where functions $B_i^{(r)}, B_{jt}^{(r)}$ were defined in the previous section for the pure adsorption case, and $y = e^{\frac{\sqrt{3} f}{2 k_B T}}$.

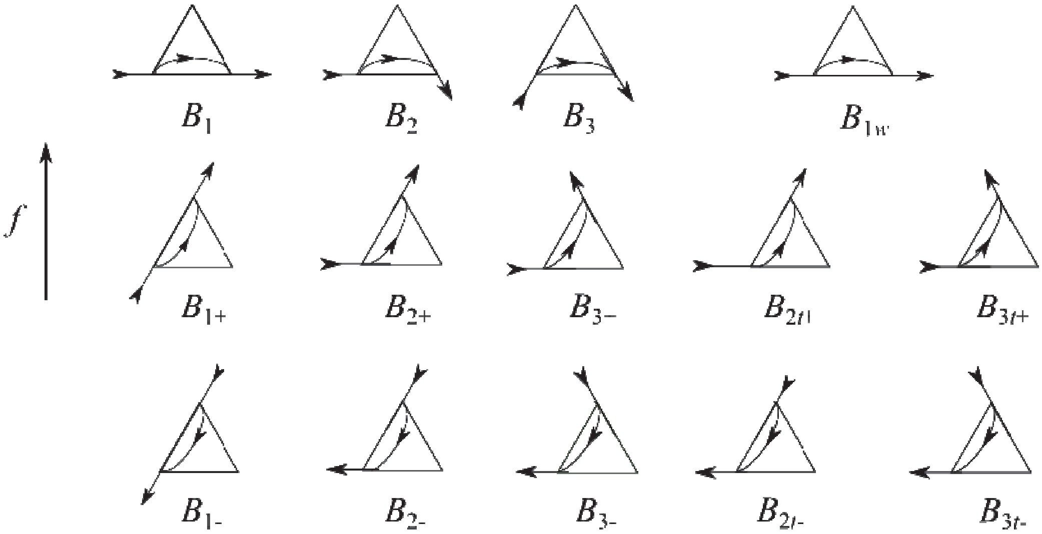

Figure 5. Schematic representation of all possible, symmetrically non-equivalent conformations of SFSAWs subjected to the pulling force f, perpendicular to the adsorbing wall. Oriented lines represent polymer parts traversing the r^{th} order generator (triangle), whereas the wall is indicated by the thick gray line

Therefore, using these relations, together with (7)-(12), one can obtain initial conditions for all 14 RG parameters and subsequently iterate RG equations (33)-(41) for various values of *x, s, w, t* and *y*. In such a way we have found that for all studied $0 < t < 1$ and $0 < s \leq 1$, there is a critical value $w_c(s,y,t)$, such that for $w < w_c(s,y,t)$ SFSAW is desorbed and elongated, for $w > w_c(s,y,t)$ it is completely adsorbed, whereas for $w = w_c(s,y,t)$ desorption transition occurs. In all three cases fixed point of the RG equations is of the form

$$\left(B_i, B_{1+}, B_{2+}, B_{3+}, B_{i-}, B_{1w}, B_{2t+}, B_{3t+}, B_{jt-}\right)^* = (0, B_{1+}^*, B_{2+}^*, (B_{2+}^*)^2, 0, B_{1w}^*, B_{2t+}^*, B_{3t+}^*, 0), \tag{44}$$

where

$$(B_{1+}, B_{2+}, B_{1w}, B_{2t+}, B_{3t+})^* = \begin{cases} (1, B_{2+}^*, 0, B_{2t+}^*, B_{3t+}^*), & \text{for } \ w < w_c, \\ (1, B_{2+}^*, 1, \infty, \infty), & \text{for } \ w = w_c, \\ (0,0,1,0,0), & \text{for } \ w > w_c. \end{cases} \tag{45}$$

Values of B_{jt+}^* depend on *s, y, w* and *t*, and for fixed *s, y* and *t* they tend to ∞ when $w \to w_c(s,y,t)$. The fixed points are reached for critical values x_c of fugacity

$$x_c = \begin{cases} x_c^{\text{bulk}}(s,y), & \text{for } \ w \leq w_c, \\ x_c(s,t,w) < x_c^{\text{bulk}}(s,y), & \text{for } \ w > w_c, \end{cases} \tag{46}$$

which are presented as a function of *w*, for *t*=0.5, *s*=0.5, and several values of *y* in Figure 6. Slope of the curve $x_c(w)$, as $w \to w_c + 0$ is finite for *y>1,* indicating that the phase transition is of the first order, which means that force changes the nature of the desorption transition (compare with Figure 3). This was found for all studied values of $0 < s \leq 1$, $0 < t < 1$ and $y > 1$.

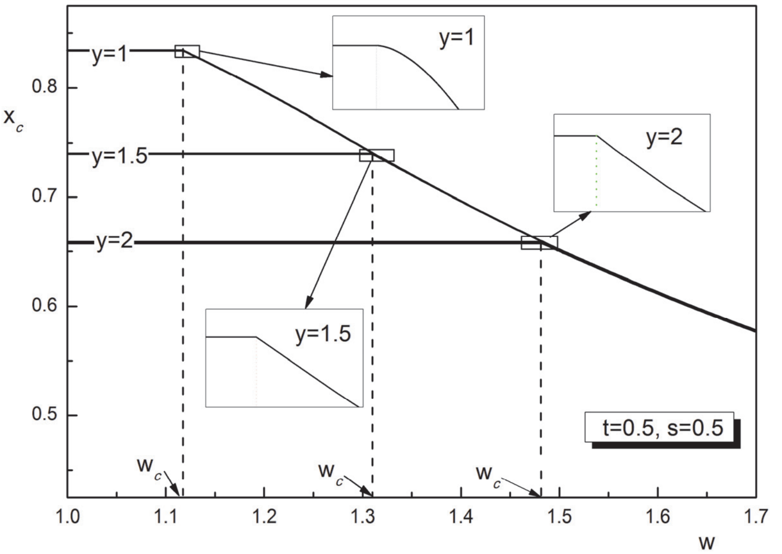

Figure 6. Critical fugacity x_c as a function of the attractive surface interaction factor w, for rigidity factor s=0.5, repulsive surface interaction factor t=0.5, and force factor values y=1.0, 1.5 and 2. Only for the zero-force case, y=1, the curve $x_c(w)$ is smooth in the vicinity of the desorption transition, as can be clearly seen in the corresponding inset (and also in Figure 3). When SFSAW is pulled by the force (y>1),critical fugacity x_c is constant for $1 \leq w \leq w_c$ (but smaller then in the case y=1), and for w>w_c it is equal to the corresponding value for y=1. Therefore, for y>1 lines $x_c(w)$ are not smooth at the desorption transition, indicating that force-induced desorption transition is of the first order, in contrast to the zero-force case

Similar to the pure adsorption case, the average length of SFSAW, as well as the average number of adsorbed monomers can be calculated within the grand canonical formalism, by taking $\Omega^{(r)} = B_{1w}^{(r)} + B_{2t+}^{(r)}$ as grand canonical partition function in this case. In Figure 7 we have plotted $\langle M^{(r)}\rangle / \langle L^{(r)}\rangle$ and $\phi^{(r)} = \ln\langle M^{(r)}\rangle / \ln\langle L^{(r)}\rangle$ as functions of $1/r$, for some values of *s, y, t* and *w*. As one can notice, in the bulk phase, $w < w_c$, the order parameter $\langle M^{(r)}\rangle / \langle L^{(r)}\rangle$ tends to 0, for large *r,* whereas in the adsorbed phase, $w > w_c$, it tends to some finite value, which depends on *w*, and approaches 1, as *w* increases (left-hand side in Figure 7). It can be clearly seen that when $w \to w_c + 0$ the order parameter $\langle M^{(r)}\rangle / \langle L^{(r)}\rangle$ does not tend to 0, thus confirming the conclusion that in non-zero force case desorption transition is first order phase transition. The right-hand side panel in Figure 7 shows that $\phi^{(r)} \to 1$, so that the scaling relation $\langle M\rangle \sim \langle L\rangle^{\phi}$ is satisfied, with the value of the crossover exponent $\phi = 1$. This result can also be obtained by analyzing matrix recursion relations for derivatives of RG parameters with respect to *x* and *w*, at the fixed point which corresponds to the desorption transition. Such analysis leads to the conclusion that both $\langle M^{(r)}\rangle$ and $\langle L^{(r)}\rangle$ behave as 2^r, so that indeed $\langle M\rangle \sim \langle L\rangle$.

Knowing the critical value $w_c(s,y,t)$, one can find the critical force f_c through the relation $\frac{f_c}{|\varepsilon_w|} = \frac{2}{\sqrt{3}} \ln y / \ln w_c(s,y,t)$ and consequently its dependence on the temperature T (since $T/(|\varepsilon_w|/k_B) = 1/\ln w_c(s,y,t)$). Some of the obtained results are presented in Figures 8 and 9. The main conclusions that follow from these results are:

- Critical force f_c monotonically decreases with temperature T.
- At $T \to 0$, critical force f_c approaches the value which does not depend on s and t. Numerically obtained limiting value for $\frac{f_c}{|\varepsilon_w|}$, when $T \to 0$, is close to $\frac{4}{\sqrt{3}} = 2.3094$. This particular value follows from the observation that for large y (low T) one obtains the fixed point value $B_{1+}^{*} = 1$ almost already for the initial value $B_{1+}^{(0)}$, and, similarly, for $w = w_c$, one has $B_{1w}^{(0)} \approx B_{1w}^{*} = 1$. Taking into account how $B_{1+}^{(0)}$ and $B_{1w}^{(0)}$ depend on y and w, the limiting value $4/\sqrt{3}$ is directly obtained.
- For $T > 0$, as s decreases, critical force increases (which can be seen in Figure 8), *i.e.* larger force is needed to detach less flexible SFSAW from the wall.
- For fixed rigidity factor s (Figure 9), larger force is required to detach SFSAW for larger values of t (*i.e.* weaker repulsive part of the interaction between the polymer and the wall).

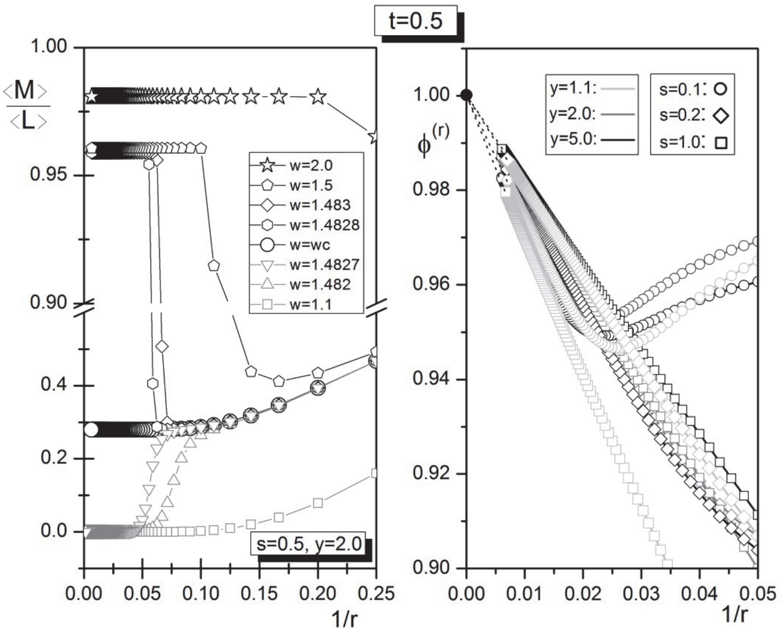

Figure 7. Left: Relative number of adsorbed monomers on r^{th}generator, as function of 1/r, for rigidity factor s=0.5, force factor y=2.0 and various values of attractive surface interaction factor w. Critical value of w is w_c=1.48272… Right: $\phi^{(r)} = \ln\langle M^{(r)}\rangle / \ln\langle L^{(r)}\rangle$ *as function of 1/r for y=2.0,5.0 and s=0.1,0.2,1.0* $(w = w_c)$. *For all presented y and s combinations* $\phi^{(r)} \to 1$ *(full circle) when r→ ∞.On both panels lines serve only as guides to the eye. For all data, iteration number r was enlarged up to the value at which RG parameters leave the vicinity of the corresponding fixed point*

5. DISCUSSION AND CONCLUSION

In this paper, we have studied the force-induced desorption of a linear polymer in a good solvent in non-homogeneous media, modeled by a semi-flexible self-avoiding walk (SFSAW) on 3-simplex fractal lattice. SFSAW interacts with the adsorbing wall, represented by one of the lattice edges, and it is pulled away from the wall by an external force f, perpendicular to the wall. By applying an exact real-space renormalization group approach, which can also be interpreted as a grand canonical ensemble formalism, we have first analyzed the pure adsorption of SFSAWs (f=0). Comparing to the previously studied adsorption of fully flexible SAWs [6], we have found that inclusion of the rigidity alters the phase diagram (temperature at which desorption occurs), but does not change the value of the crossover exponent ϕ. Then, we have performed detailed numerical analysis of the non-zero force case, for various values of the interaction parameters, and found that the external force changes the nature of the desorption transition, which is continuous for $f = 0$, and first order for $f > 0$. Similar conclusion was obtained in previous studies of directed walk models on homogeneous lattices [9,10].

The desorption transition from adsorbed to desorbed phase occurs at some critical value of the force $f_c(T)$, which is presented in Figures 8 and 9, for some values of the rigidity factor s and the surface interaction factor t, corresponding to the repulsive part of the interaction between the polymer and the adsorbing wall. In general, $f_c(T)$ does not differ significantly from the corresponding curves obtained for flexible SAWs, either on 2d homogeneous lattices [11,12,13] or on fractal lattices embedded in 2d spaces [14], *i.e.* the critical force monotonically decreases with temperature, which is in accord with the intuitively plausible expectation that external force should lower the temperature at which SAW unbinds from the adsorbing surface. To conclude, we may say that approach we have applied here enabled us, systematically numerically, but in an exact manner, to investigate the influence of the rigidity on the phase boundary $f_c(T)$, which, to the best of our knowledge, has not been done previously for the SAW model on any lattice. It would be interesting to extend this study to the case of lattices embedded in three-dimensional space, which corresponds to more realistic physical situations.

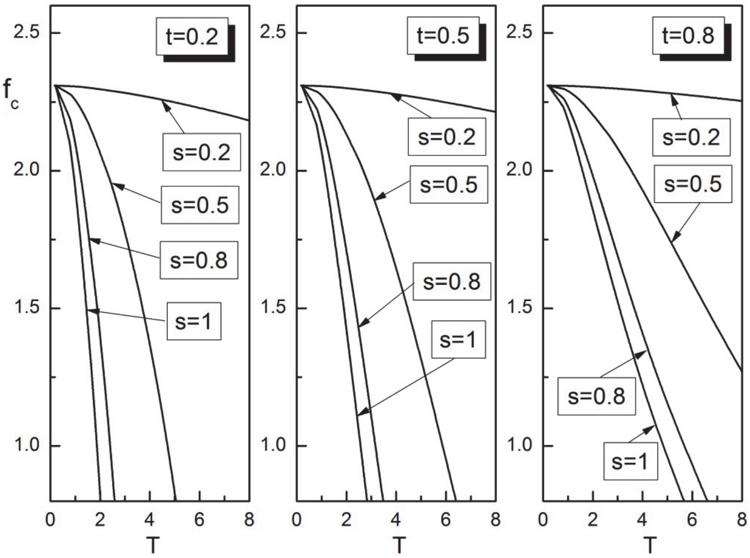

Figure 8. Critical force f_c (measured in units of $|\varepsilon_w|$) as a function of the temperature T (measured in units of $|\varepsilon_w|/k_B$), for various values of t and s

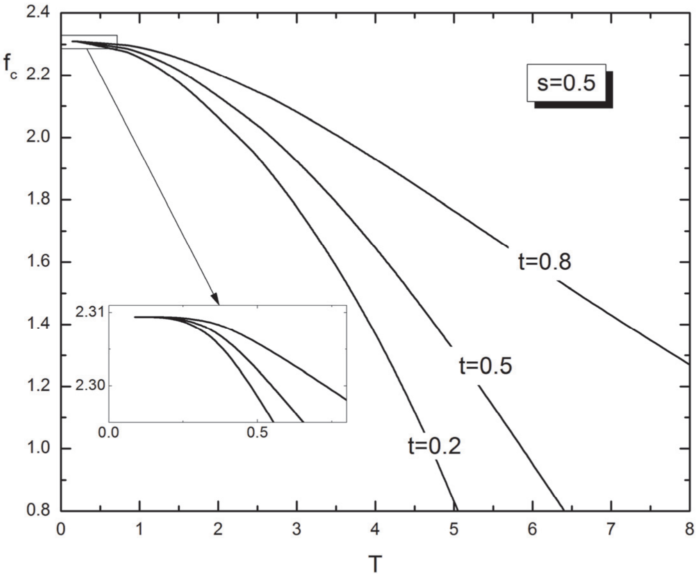

Figure 9. Critical force f_c (measured in units of $|\varepsilon_w|$) as a function of the temperature T (measured in units of $|\varepsilon_w|/k_B$), for rigidity factor s=0.5, and t=0.2, 0.5 and 0.8. In the inset graph it can be seen that difference between the values of f_c for various t disappears at low temperatures

6. ACKNOWLEDGMENT

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ДЕСОРПЦИЈА СЕМИ-ФЛЕКСИБИЛНИХ ПОЛИМЕРА ИНДУКОВАНА СИЛОМ У НЕХОМОГЕНОЈ СРЕДИНИ

Сажетак: Проучавана је десорпција семи-флексибилних линеарних полимера индукована силом, у добрим растварачима и нехомогеној средини. Примењен је модел случајних непресецајућих шетњи, које се опиру промени правца, на 3-симплекс фракталној решетки. Једна граница решетке представља адсорбујући зид, а спољашња сила (ортогонална на зид) вуче полимер од зида. Хијерархијска структура посматране решетке омогућава егзактно проучавање фазног дијаграма критичног понашања полимера методом ренормализационе групе у реалном простору. Добијена је и дискутована зависност критичне силе, при којој долази до десорпције, од температуре, а за разне вредности параметра крутости. Утицај силе и крутости полимера на природу десорпционог фазног прелаза је такође анализиран. Сви добијени резултати поређени су са одговарајућим резултатима ранијих проучавања овог проблема.

Кључне речи: полимери, фрактали, адсорпција, фазни прелази.

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