

SEMI-FLEXIBLE COMPACT POLYMERS IN A DISORDERED ENVIRONMENT

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Abstract: Hamiltonian cycles with bending rigidity are studied on the first three members of the fractal family obtained by generalization of the modified rectangular (MR) fractal lattice. This model is proposed to describe conformational and thermodynamic properties of a single semi-flexible ring polymer confined in a poor and disordered (e.g. crowded) solvent. Due to the competition between temperature and polymer stiffness, there is a possibility for the phase transition between molten globule and crystal phase of a polymer to occur. The partition function of the model in the thermodynamic limit is obtained and analyzed as a function of polymer stiffness parameter s (Boltzmann weight), which for semi-flexible polymers can take on values over the interval $(0,1)$. Other quantities, such as persistence length, specific heat and entropy, are obtained numerically and presented graphically as functions of stiffness parameter s .

Keywords: semi-flexible polymer, disordered media, compact phase, persistence length, specific heat.

1. INTRODUCTION

Synthetic polymers such as polyethylene can be quite flexible. Flexibility of polyethylene is primarily caused by almost free rotation about single covalent bond. Strictly speaking, there are three values of torsion angle that are energetically favorable, allowing for trans, gauche +, and gauche- rotational states [1]. The former two can easily be excited by thermal energy, so that linear polymer in solvent looks like a coiled thread of cotton. Typical conformations of a flexible polymer in good solvent conditions are that of random coil type.

One measure of polymer flexibility is the persistence length l_p , which can be defined as a length along the backbone of a polymer over which the polymer segments become orientationally uncorrelated. More intuitively, it is a length of polymer segments that appear straight. For flexible polymers $l_p \ll L$, where L is the contour length of polymer.

Biopolymers usually have complex chemical structure which make them rigid over the range of length scales much smaller than the contour length. Such polymers (e.g. DNA, actin) belong to the class

of semi-flexible polymers for which the persistence length is comparable with the contour length, i.e. $l_p \sim L$. Conformational and thermodynamic properties of semi-flexible polymers are less known compared to their flexible counterparts. For flexible polymers, it is well known that: (i) in good solvent conditions they adopt swollen, coil like conformations, (ii) they undergo collapse transition at θ temperature, (iii) below the θ temperature in poor solvent conditions, they are in compact, liquid like state with globular conformations. Rigidity of polymer affects the behavior in all three regimes. In compact phase, with which we are primarily concerned, semi-flexible polymer takes elongated, toroidal conformations [2,3]. It is confirmed that semi-flexible polymers in compact phase can exist in either of two phases: disordered – liquid-like phase or ordered – crystal phase. But the order of phase transition and the characterization of phases are questions that are far from being settled [4-8].

In this paper, we apply model of weighted (biased) Hamiltonian walks on fractal lattices to describe compact conformations of a semi-flexible polymer adsorbed on a non-homogeneous substrate.

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A model is applicable to biopolymers that are usually confined in small and crowded space such as eukaryotic cell or even adsorbed on surfaces (DNA wrapped around the histone [9,10]).

2. MODEL AND LATTICES

Semi-flexible polymers are quite rigid, they resist to bending. It costs energy to bend a portion of a polymer. To incorporate this property in our model, we introduce an energy penalty for each bend in the conformation represented by Hamiltonian walk (HW). Hamiltonian walks are self-avoiding random walks that visit every lattice site, a property that mimics compactness of conformations. Conformations have different energy, depending on the number of bends in the walks. If $\varepsilon > 0$ is the energy of each bend, then the conformation w with K_w bends will have the energy equal to $E_w = \varepsilon K_w$. Partition function of the model is $Z = \sum_w e^{-\frac{E_w}{k_B T}}$, where the sum runs over all possible conformations (HWs). Inserting energy of conformations into the partition function leads to $Z = \sum_w s^{K_w}$, where $s = e^{-\frac{\varepsilon}{k_B T}}$ is the Boltzmann factor or weight associated with each bend. We call s the stiffness parameter, and we see that it is determined by the energy ε

of each bend and temperature T . There are two opposite limits: (i) rigid rod limit for which $\varepsilon = \infty$ or $T = 0$ so that $s = 0$, and (ii) fully flexible polymer for which $\varepsilon = 0$ or $T = \infty$ so that $s = 1$. For semi-flexible polymers $0 < s < 1$, which can be achieved by keeping one of the parameters fixed while varying another. It should be noted that stiffness (rigidity) of polymer decreases with such defined stiffness parameter s .

Our model is restricted to lattices [11], which in this case are taken to be modified rectangular (MR) fractal lattice and other two lattices which can be obtained by simple generalization of MR lattice. All three considered lattices are parameterized with an integer p which take values $p = 2, 3$ and 4 . Case $p = 2$ correspond to MR lattice. Construction of fractal lattices is iterative, starting from the common initiator which is a unit square. Then p unit squares are connected in the rectangle to obtain first order generator. In the next step, p rectangles are connected into a square, and so on. Fractal lattice in each of the cases is obtained repeating the process ad infinitum. First four steps of construction for fractals with $p = 2$ and $p = 3$ are depicted in Figure 1. Structure obtained in the l^{th} step of construction is called l^{th} order generator.

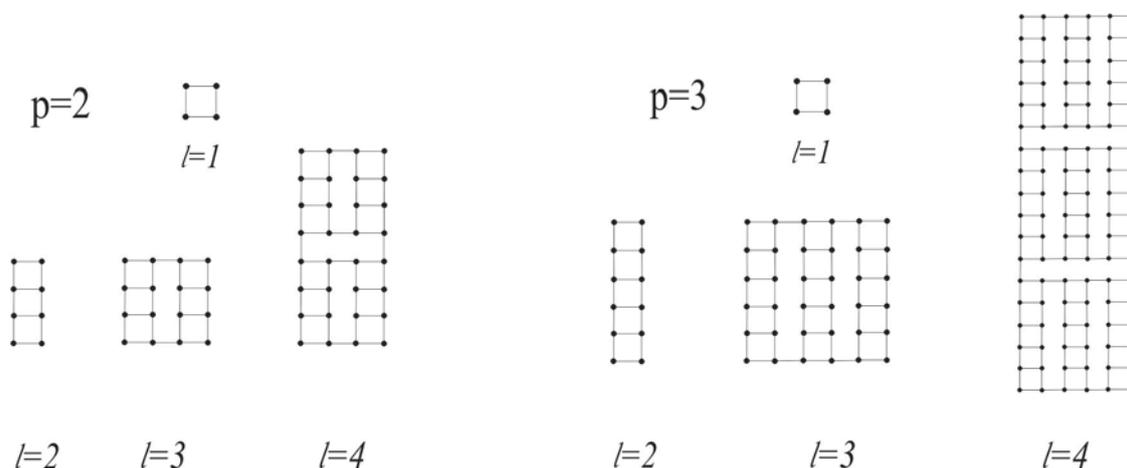


Figure 1. First four steps of the iterative construction of MR fractal lattice with $p = 2$ and lattice with $p = 3$

3. ASYMPTOTIC FORM OF PARTITION FUNCTION

Partition function of our model is $Z = \sum_w s^{K_w}$, where s^{K_w} can be seen as overall weight of particular Hamiltonian walk, and the partition function is then the total weight of all walks. One closed HW on the fifth stage of construction of MR lattice is shown in Figure 2. There are 44 turns in this walk,

so that its contribution to the partition function on that generator would be s^{44} . It would be a formidable task to find all closed walks and their weights on generators of higher order in that way. So we utilize self-similarity of fractal lattices and adopt a coarse-graining method according to which we schematically represent generator of arbitrary order and walks on them. This enables us to determine the weights recursively. For example, fifth order genera-

tor of MR lattice in Figure 2. is shown on right hand side in coarse-graining scheme, where all substructures except fourth order generator are left out. Now, due to self-similarity, this picture actually represents two consecutive generators for arbitrary l . Complete cycle from the left side becomes two ‘step’ walk in coarse-graining scheme on the right side, and all Hamiltonian cycles on l^{th} order generator of MR lattice would be represented by the same coarse-graining cycle. ‘Step’ denoted by B_1 represent all Hamiltonian walks that enter and leave $(l - 1)^{th}$

order generator through the vertices that belong to different generators of order $(l - 2)$, and whose entering and exiting direction makes an angle of 180° . Assuming that $B_1^{(l-1)}$ denotes overall weight of all walks represented by step B_1 on $(l - 1)^{th}$ order generator, partition function on l^{th} order generator of MR lattice can be written as $Z^{(l)} = (B_1^{(l)})^2$. Weight $B_1^{(l)}$ should be determined recursively, which involves different types of steps or configurations on generators .

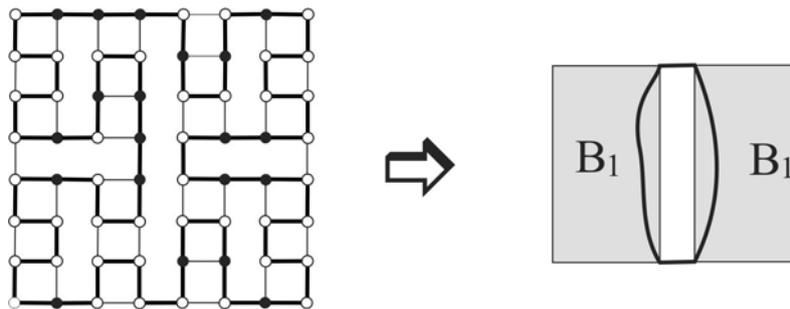


Figure 2. An example of closed compact conformation (thick line) on 5th order generator of MR fractal. All lattice points are visited (compactness) only once (self-avoidance). Vertices are colored white if the walk makes right angle turn on them. The same walk is represented in coarse-graining scheme on the right

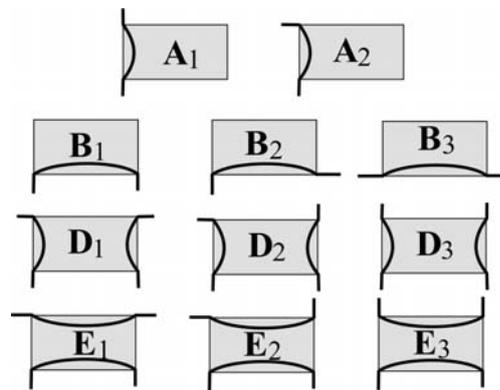


Figure 3. Different types of configurations that are possible on generators of any order for fractals with $p = 3$ and $p = 4$

Due to the lattice geometry and connectivity, applying symmetry considerations, we find that there are 9 symmetrically non-equivalent configurations that are possible on MR fractal ($p = 2$) and 11 configurations possible on fractals with $p = 3$ and $p = 4$. All eleven are represented schematically in Figure 3. Configurations denoted by D_3 and E_3 cannot exist on $p = 2$ fractal. Weights of configurations that appear on fractal with $p = 2$ satisfy following recurrence equations

$$A_1^{(l+1)} = B_1^{(l)} D_1^{(l)}, \quad A_2^{(l+1)} = B_1^{(l)} D_2^{(l)}, \quad (1)$$

$$B_1^{(l+1)} = (A_2^{(l)})^2, \quad B_2^{(l+1)} = A_1^{(l)} A_2^{(l)}, \quad B_3^{(l+1)} = (A_1^{(l)})^2, \quad (2)$$

$$D_1^{(l+1)} = (B_2^{(l)})^2 + 2D_2^{(l)} E_2^{(l)}, \quad D_2^{(l+1)} = B_2^{(l)} B_3^{(l)} + D_1^{(l)} E_2^{(l)} + D_2^{(l)} E_1^{(l)}, \quad (3)$$

$$E_1^{(l+1)} = (D_2^{(l)})^2, \quad E_2^{(l+1)} = D_1^{(l)} D_2^{(l)}, \quad (4)$$

while on fractal with $p = 3$ they are given by

$$A_1^{(l+1)} = B_1^{(l)} D_1^{(l)} D_3^{(l)}, \quad A_2^{(l+1)} = B_1^{(l)} D_2^{(l)} D_3^{(l)}, \quad (5)$$

$$B_1^{(l+1)} = A_1^{(l)} \left(A_2^{(l)} \right)^2, B_2^{(l+1)} = \left(A_1^{(l)} \right)^2 A_2^{(l)}, \quad B_3^{(l+1)} = \left(A_1^{(l)} \right)^3, \quad (6)$$

$$D_1^{(l+1)} = 2B_1^{(l)} B_2^{(l)} D_2^{(l)} + 2D_2^{(l)} D_3^{(l)} E_2^{(l)} + \left(D_2^{(l)} \right)^2 E_3^{(l)}, \quad (7)$$

$$D_2^{(l+1)} = B_1^{(l)} B_2^{(l)} D_1^{(l)} + B_1^{(l)} B_3^{(l)} D_2^{(l)} + D_1^{(l)} D_2^{(l)} E_3^{(l)} + D_1^{(l)} D_3^{(l)} E_2^{(l)} + D_2^{(l)} D_3^{(l)} E_1^{(l)}, \quad (8)$$

$$D_3^{(l+1)} = 2B_1^{(l)} B_3^{(l)} D_1^{(l)} + \left(D_1^{(l)} \right)^2 E_3^{(l)} + 2D_1^{(l)} D_3^{(l)} E_1^{(l)}, \quad (9)$$

$$E_1^{(l+1)} = \left(D_2^{(l)} \right)^2 D_3^{(l)}, E_2^{(l+1)} = D_1^{(l)} D_2^{(l)} D_3^{(l)}, E_3^{(l+1)} = \left(D_1^{(l)} \right)^2 D_3^{(l)}. \quad (10)$$

On $p = 4$ recurrence equations are similar to the case $p = 3$ but more cumbersome, so that they are omitted here. On all three fractals recurrence equations satisfy the same initial conditions:

$$A_1^{(1)} = s^4, A_2^{(1)} = s^3, B_1^{(1)} = s^2, B_2^{(1)} = s^3, \\ B_3^{(1)} = s^4, D_1^{(1)} = s^2, D_2^{(1)} = s, D_3^{(1)} = 1, \\ E_1^{(1)} = s^2, E_2^{(1)} = s^3, E_3^{(1)} = s^4.$$

Partition functions of the model can be written as:

$$Z^{(l+1)} = \left(B_1^{(l)} \right)^2 \quad (11)$$

$$Z^{(l+1)} = \left(B_1^{(l)} \right)^2 D_3^{(l)} \quad (12)$$

$$Z^{(l+1)} = \left(B_1^{(l)} \right)^2 \left(D_3^{(l)} \right)^2 \quad (13)$$

for fractals with $p = 2, 3$ and 4 respectively. In order to obtain asymptotic form of the partition function, it is more convenient to introduce new rescaled variables whose values for arbitrary l are defined as: $a_i^{(l)} = A_i^{(l)} / E_1^{(l)}$ for $i = 1, 2$; $b_i^{(l)} = B_i^{(l)} / E_1^{(l)}$ for $i = 1, 2, 3$; $d_i^{(l)} = D_i^{(l)} / E_1^{(l)}$ for $i = 1, 2, 3$ and $e_i^{(l)} = E_i^{(l)} / E_1^{(l)}$ for $i = 2, 3$. Recurrence equations for new variables on fractal with $p = 2$, that follow from equations (1)-(4) are:

$$a_1^{(l+1)} = \frac{b_1^{(l)} d_1^{(l)}}{\left(d_2^{(l)} \right)^2}, a_2^{(l+1)} = \frac{b_1^{(l)}}{d_2^{(l)}}, \quad (14)$$

$$b_1^{(l+1)} = \left(\frac{a_2^{(l)}}{d_2^{(l)}} \right)^2, b_2^{(l+1)} = \frac{a_1^{(l)} a_2^{(l)}}{\left(d_2^{(l)} \right)^2}, b_3^{(l+1)} = \left(\frac{a_1^{(l)}}{d_2^{(l)}} \right)^2, \quad (15)$$

$$d_1^{(l+1)} = \frac{\left(b_2^{(l)} \right)^2 + 2a_2^{(l)} e_2^{(l)}}{\left(d_2^{(l)} \right)^2}, d_2^{(l+1)} = \frac{b_2^{(l)} b_3^{(l)} + a_2^{(l)} + d_1^{(l)} e_2^{(l)}}{\left(d_2^{(l)} \right)^2}, \quad (16)$$

$$e_2^{(l+1)} = \frac{a_1^{(l)}}{d_2^{(l)}}. \quad (17)$$

For fractals with $p = 3$ and $p = 4$ recurrence equations for the variables a_1, a_2 and e_2 are the same as for $p = 2$, while recurrence equation for the variable e_3 is $e_3^{(l+1)} = \left(e_2^{(l+1)} \right)^2$. Recurrence equations for variables b_i and d_i are different from those given by equations (15) and (16) and more complicated. In new variables, all three partition functions can be written as

$$Z^{(l+1)} = \left(b_1^{(l)} \right)^2 \left(d_3^{(l)} \right)^{p-2} \left(E_1^{(l)} \right)^p, \quad (18)$$

and for all three p considered, recurrence equation for the variable E_1 can be written as

$$E_1^{(l+1)} = \left(d_2^{(l)} \right)^2 \left(d_3^{(l)} \right)^{p-2} \left(E_1^{(l)} \right)^p. \quad (19)$$

Analyzing the system of non-linear difference equations (14)-(17) and equation given by (19) for $p = 2$, and similarly for other two fractals, we establish the following asymptotic form (as $l \rightarrow \infty$) of equation (18):

$$Z_l \sim \begin{cases} C_e \omega^{N_l} \mu_e^{(N_l)^\sigma}, & \text{for even } l \\ C_o \omega^{N_l} \mu_o^{(N_l)^\sigma}, & \text{for odd } l \end{cases}$$

where C_e and C_o are some constants (scaling amplitudes) and $N_l = 4 \cdot (p)^{l-1}$ is the number of lattice sites. Scaling exponent σ is $\sigma = \frac{1}{2}$ on all three fractals. Asymptotic form (20) is the same as those obtained in [12] in the case of fully flexible polymers, but now ω, μ_e and μ_o are functions of stiffness parameter s . Dependence of ω, μ_e and μ_o on s for all three fractals is graphically presented in Figure 4. Connectivity constant ω determines leading exponential factor in partition function, an generally is defined as $\ln \omega = \lim_{N \rightarrow \infty} \frac{\ln Z}{N}$. From equation (18) it follows that $\ln \omega = \lim_{N_l \rightarrow \infty} \frac{\ln E_{1l}}{N_l}$, which can be obtained by numerical iteration from equation (19). This quantity is crucial since free energy in the thermodynamic limit is proportional to it.

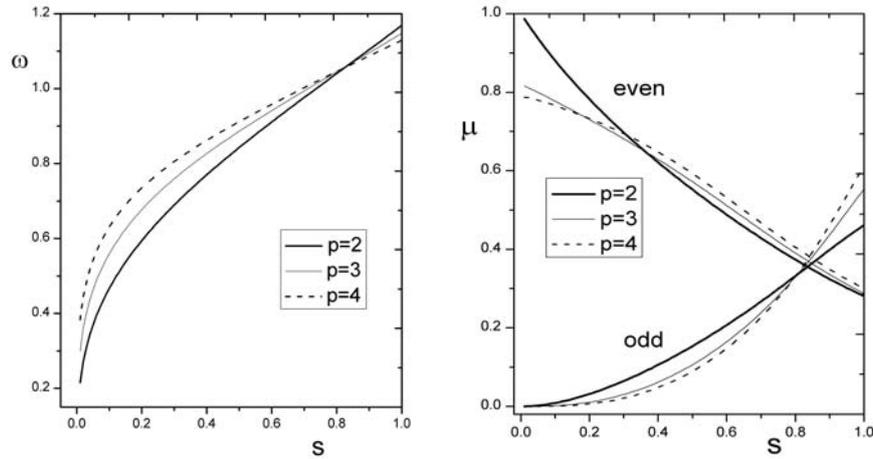


Figure 4. Scaling parameters as functions of stiffness parameter s on three considered fractals: $\omega(s)$ is shown on the left and $\mu_e(s)$ and $\mu_o(s)$ are shown on the right

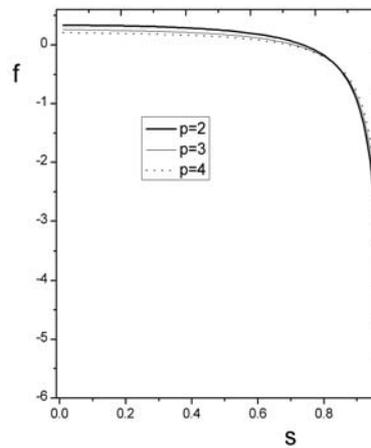


Figure 5. Free energy of semi-flexible HWs as function of stiffness parameter s on three considered lattices

4. THERMODYNAMICS

To obtain thermodynamic quantities, we start from the free energy $F = -k_B T \ln Z$ which in the thermodynamic (TD) limit is $f = \lim_{N \rightarrow \infty} \frac{F}{N}$. From equation (20) we obtain $f = -k_B T \ln \omega = \varepsilon \frac{\ln \omega}{\ln s}$. Free energy of our model in the TD limit on all three fractals is shown in Figure 5. It is clear from the figure that free energy is continuous and differentiable function of s on all three lattices.

Mean number of bends is given by definition as $\langle K \rangle = \frac{1}{Z} \sum_w K s^K$, and can be expressed as $\langle K \rangle = \frac{\partial \ln Z}{\partial \ln s}$. Internal energy is proportional to the mean number of bends: $U = \langle E \rangle = \varepsilon \langle K \rangle = \varepsilon \frac{\partial \ln Z}{\partial \ln s}$, which in the TD limit is given by $u = \varepsilon s \frac{\partial}{\partial s} (\ln \omega)$. Persistence length in our model can be defined as the mean number of steps in one direction, i.e. $l_p =$

$\lim_{N \rightarrow \infty} \frac{N}{\langle K \rangle}$, where N is the total number of steps in the cycle equal to the number of lattice sites. Persistence length can be expressed as $l_p = \frac{\varepsilon}{u}$. Dependence of internal energy and persistence length on s are presented in Figure 6. We see that internal energy is increasing function of stiffness parameter s (decreasing function of stiffness) on all three fractals. At low temperatures or large bending energy, that is for small s , conformations with smaller number of bends dominate, but for larger value of s conformations with larger number of bends become more probable, and mean energy is higher. For the same reason the persistence length is monotonically decreasing function of s .

For low stiffness parameter, mean number of bends is small so that there are long straight segments of polymer.

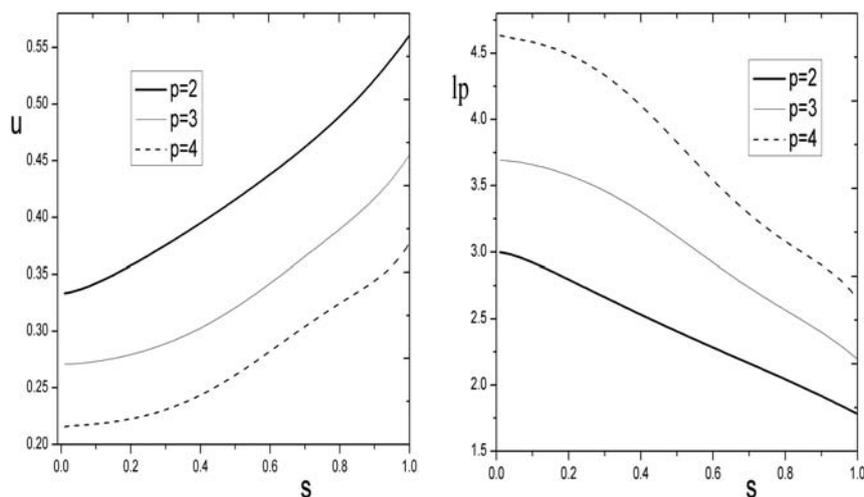


Figure 6. Internal energy of our model in the TD limit as function of stiffness parameter s , on lattices with $p = 2, 3$, and 4 (left). Persistence length as function of stiffness parameter (right)

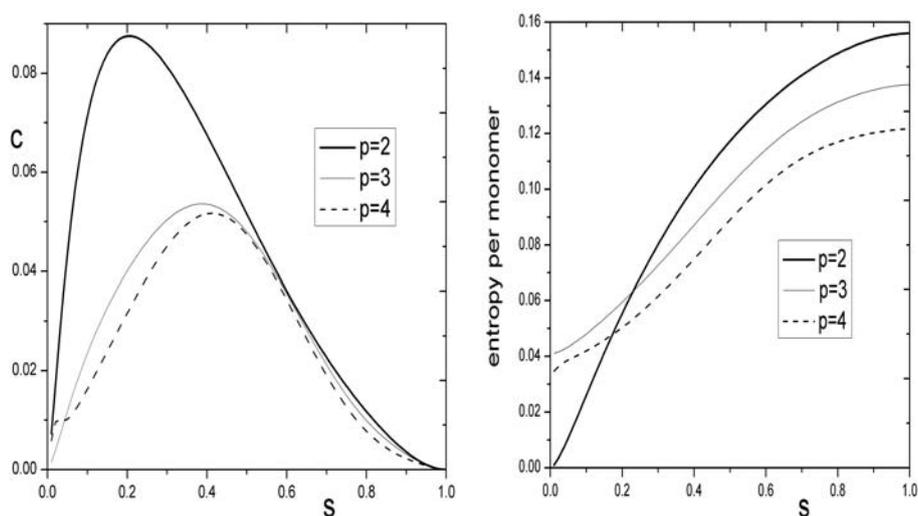


Figure 7. Specific heat (left) and entropy (right) in the TD limit as functions of stiffness parameter s on lattices with $p = 2, 3$, and 4

Finally, specific heat and entropy of our model are presented in Figure 6. There is peak in specific heat in TD limit on all three fractal lattices, and on lattice with $p = 4$ one small peak for $s = 0$. 0264 additionally appeared. Entropy per monomer increases with stiffness, but while in the case $p = 2$ entropy is zero for zero stiffness, for $p = 3$ and $p = 4$ there is residual entropy for zero stiffness. This means that ground state is almost non degenerate for $p = 2$, whereas for $p = 3$ and $p = 4$ it is highly degenerate, with exponentially large number of conformations.

5. DISCUSSION AND CONCLUSIONS

In this paper, we have proposed and analyzed a model of semi-flexible polymers in disordered media, represented by fractal lattices. These lattices

are embedded in $d = 2$ space, and can be viewed as square lattice from which some bonds are deleted. We established asymptotic form of partition function, given by equation (20), and further determined various thermodynamic quantities such as free and internal energy in the thermodynamic limit, persistence length, specific heat, and entropy. Values of these quantities for different values of stiffness parameter s are obtained by numerical iteration for each of the considered fractals, and their graphical presentation is given in Figure 5., Figure 6., and Figure 7. We can observe how physical properties of the model are changed by the gradual change of the underlying lattices. From Figure 6. it is obvious that internal energy of the model is largest for $p = 2$ and decreases with p . Consequently, persistence length increases with p . This is understandable if we have a look on geometry of lattices. For each value of p , there is an asymmetry in the number of bonds in the

horizontal and vertical direction. For lattices shown in Figure 1. there are more vertical than horizontal bonds, and these discrepancy is more pronounced for larger p . On lattices with larger p , conformations generally have smaller number of bends, since they are forced in vertical direction by the lattice. But, although many vertical bonds are missing from our lattices in comparison with square lattice, there is still a large number of horizontal steps in conformations that prevent ordered state such exists on square lattice. Since entropy and specific heat are continuous, smooth functions of s , there is no finite order phase transition in our model. Compact phase is disordered one. Similar results are found on other fractal lattices [13].

6. ACKNOWLEDGMENT

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ПОЛУФЛЕКСИБИЛНИ КОМПАКТНИ ПОЛИМЕРИ У НЕУРЕЂЕНОЈ СРЕДИНИ

Сажетак: Затворене Хамилтонове шетње са отпором ка закретању разматране су на прва три члана фракталне фамилије добијене генерализацијом модифициране правоугаоне (МП) фракталне решетке. Овај модел је предложен у циљу описивања конформационих и термодинамичких особина полуфлексбилног прстенастог полимера заточеног у лошем и неуређеном (нпр. претрпаном) растварачу. Надметање између термалних ефеката и ефеката крутости полимера може довести до фазног прелаза између отопљене глобуле и кристалне фазе полимера. У раду је одређена статистичка сума модела у термодинамичком лимесу, и анализирана је у функцији параметра крутости s (Болцманова тежина), чије вриједности за полуфлексбилне полимере попримају вриједности у интервалу (0,1). Остале величине, као што су дужина перзистенције, специфична топлота и ентропија добијене су нумерички и представљене графички као функције параметра s .

Кључне ријечи: полуфлексбилни полимер, неуређена средина, компактна фаза, дужина перзистенције, специфична топлота.

