КОНСТАНТА ПОВЕЗАНОСТИ БЕСКОНТАКТНИХ, САМО-НЕПРЕСЈЕЦАЈУЋИХ СЛУЧАЈНИХ ШЕТЊИ НА ФРАКТАЛНОЈ РЕШЕТЦИ

THE CONNECTIVITY CONSTANT OF NEIGHBOR-AVOIDING WALKS ON A FRACTAL LATTICE

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Сажетак: Разматрана је једна врста случајних шетњи-NAWs (од енглеског Neighbor-Avoiding Walks) на фракталној, 3-симплекс решетци. NAWs су само-непресјецајуће шетње које не посјећују чворове решетке који су најближи сусједи претходно посјећеног чвора (контакти). Користе се као једноставни модели полимерних конформација у изузетно добром растварачу (за који се обично каже да је супер-савршени растварач). Добијен је егзактан израз за константу повезаности на 3-симплекс решетци, која у термодинамичком лимесу одређује ентропију полимера моделованог са NAWs. Тај израз је такође нумерички потврђен. Искључење најближих сусједа довело је до смањења константе повезаности и стога ентропије, у поређењу са обичним само-непресјецајућим шетњама.

Abstract: We consider Neighbor-avoiding walks (NAWs) on the fractal, 3-simplex lattice. NAWs are self-avoiding random walks that never visit any site of the lattice that is a nearest neighbor of the previously visited site (contact). They are simple models of polymer conformations in an extraordinary good solvent (usually referred to as super-perfect solvent). A closed form expression for the connectivity constant of NAWs on the 3-simplex lattice, which determines the entropy of a polymer in the thermodynamic limit, is obtained and confirmed numerically. The exclusion of the nearest neighbors has led to a reduced value of the connectivity constant and thus the entropy, in comparison with ordinary self-avoiding walks, as expected.

Кључне ријечи: случајне шетње, полимерне конформације, константа повезаности

Keywords: neighbor-avoiding walks, polymer conformations, connectivity constant

1. INTRODUCTION

A linear polymer, with the simplest architecture among all polymers, consists of many repeating units (monomers) arranged in a straight line that forms the polymer backbone. Monomers usually have small side groups. The main features of the linear polymer, such as the chain-like structure and the excluded volume of the monomers, are well described by Self-avoiding walks (SAWs). SAWs are random walks that never visit the same lattice site more than once. Each SAW represents one possible conformation of the polymer dissolved in a good solvent when monomers effectively repel each other. Visited lattice sites (or sometimes steps of the walk) represent monomers, whereas sites not visited by the walk represent molecules of a solvent. In a very dilute solution one can study properties of just one isolated chain. Experimental techniques, such as light scattering and hydrodynamic viscosity measurements, give information about the universal critical exponent ν that determines the gyration radius as a measure of the 'size' of the space

occupied by the polymer [1]. It is assumed that the gyration radius R_g of a polymer scales with the number of monomers N according to the power law $R_g \sim const N^{\nu}$. Exact enumerations of SAWs and Monte Carlo simulations in three dimensional space give $\nu \approx 0.588$ [2] , which is in a good agreement with the value extracted from experiments $\nu_{exp} \approx 0.58 - 0.60$ [3] as well as Flory's mean –field value $\nu_F = \frac{3}{5} = 0.6$ [4].

If the solvent is extraordinary good ("super-perfect"), monomers strongly prefer to be surrounded by the solvent molecules, i.e. they effectively strongly repel each other. In that case Self-avoiding walk is not allowed to visit any lattice site that is a nearest-neighbor of the sites visited previously [5-8]. Non-consecutively visited nearest-neighbor sites are called contacts, so that SAWs that represent a polymer in an exquisitely good solvent are not only self-avoiding but also nearest-neighbor (contact) avoiding. This subset of SAWs is known as Neighbor-avoiding walks (NAWs) [5-8] . NAWs are also used to represent polymer in an ordinary good solvent if the polymer has bulky side groups so that excluded volume is enhanced [5,6].

Exact enumeration of NAWs is similar to those of SAWs, with an additional restriction that the walks are forbidden to visit contacts. It is assumed that the number of N-step NAWs Z_N, grows with the number of steps (or visited sites) N, as

$$Z_N \sim const\ \omega^N N^{a-1}, \tag{1}$$

where ω is the connectivity constant, whereas a is the critical exponent. The assumed expression for Z_N can be confirmed by studying the generating function

$$G(x) = \sum_{N=0}^{\infty} Z_N x^N, \tag{2}$$

where x is the weight of each step in the walk. From (1) and (2) it can be shown that $G(x)$ has the leading singularity of the form $(1 - x\omega)^{-a}$, as $x \to x_c = 1/\omega$ from below. Thus, ω can be determined from the convergence radius x_c of the generating function, while the exponent a emanates from the asymptotic singularity form.

The entropy of the polymer is given by $S = k_B \ln Z_N$, and from (1) it follows that the entropy per monomer in the thermodynamic limit $\sigma = \lim_{N\to\infty} \frac{S}{N}$ is $\sigma = k_B \ln \omega$. We see that the connectivity constant is a measure of the polymer entropy. This quantity is lattice dependent, i.e. nonuniversal, which implies that it varies with the polymer-solvent system.

In the present paper, we determine ω on the 3-simplex, deterministic fractal lattice. In contrast to regular lattices which possess translational invariance and represent homogeneous solvents, fractal lattices do not have this symmetry and are often used to simulate some inhomogeneous environments. On fractal lattices it is possible to enumerate walks recursively, and here, by utilizing this method, we obtain a closed form expression for ω in a similar manner as ω_{SAW} for ordinary Self-avoiding walks is found on the same lattice [9].

In Section 2 we present the recursive enumeration method and obtained result, while the summary and conclusions are given in Section 3.

2. RECCURSIVE ENUMERATION OF NAWs ON THE 3-SIMPLEX

The 3-simplex lattice is constructed in iterative steps. The procedure starts with a unit triangle, also called the first order generator $G^{(1)}$. In the first step, three copies of $G^{(1)}$ are arranged into a triangular structure (the second order generator $G^{(2)}$) in such a way that the vertices of the composing triangles are

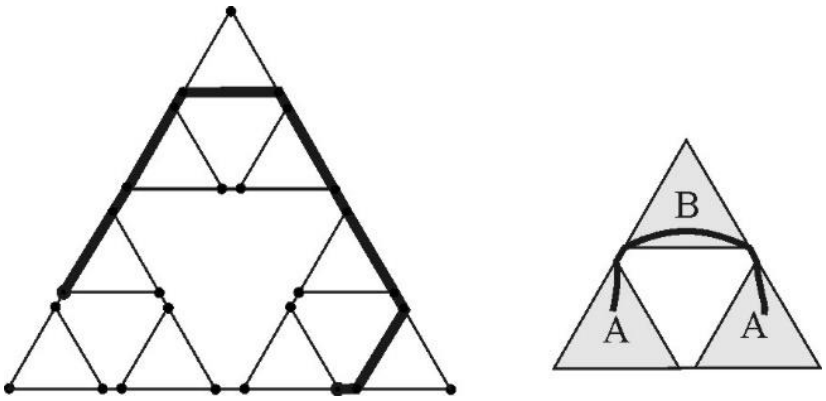

Figure 1. A neighbor-avoiding walk that consists of $N=12$ steps (on the left). It contributes to the coefficient of the term with x^{12} in the generating function (7). The right hand-side of the figure represents the same walk in the coarse-grained scheme.

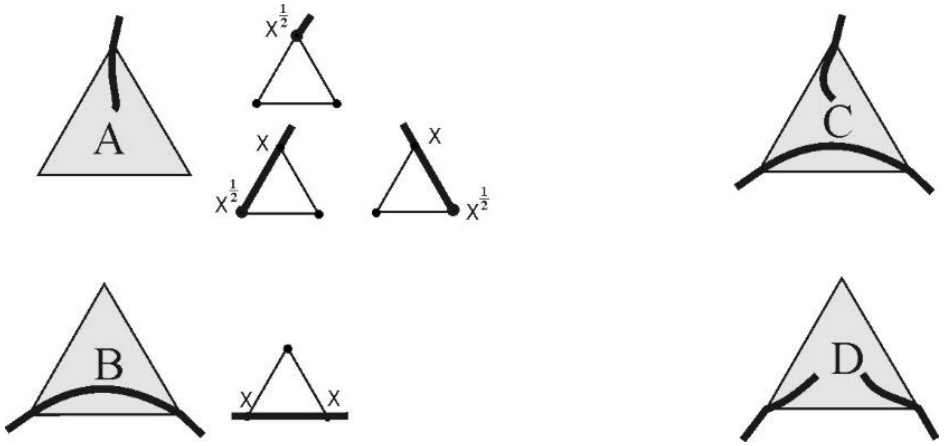

Figure 2. Four possible types of walks, denoted as A, B, C and D, are schematically shown on a generator of an arbitrary order r. Also, the initial conditions for the walks A and B are shown, while for walks C and D they are zero.

infinitesimally spaced. After $r-1$ repeated steps one gets the $r\text{-}th$ order generator $G^{(r)}$. The third order generator, which consists of three $G^{(2)}$ (and nine $G^{(1)}$), is shown in Figure1. The fractal lattice is obtained in the limit when $r \to \infty$. Each $G^{(r)}$ consists of three $G^{(r-1)}$ and has twice larger side than each $G^{(r-1)}$, so that the fractal dimension of the 3-simplex lattice is $d_f = \frac{\ln 3}{\ln 2}$.

In Figure 1 one NAW on $G^{(3)}$ is presented in the left-hand side, while the coarse-grained, schematic representation of that walk is shown on the right hand side of the figure. In the coarse-grained scheme, the internal structure of the generators $G^{(2)}$ is not shown, whereas the parts of the walk through each $G^{(2)}$ are represented as 'steps' denoted as A, A and B. There A represents the part of the walk that starts (ends) in any lattice point of $G^{(2)}$ and leaves it through one corner vertex, while B represents part of the walk that traverses $G^{(2)}$ through the two corner vertices. Two more configurations are possible, and all four are presented schematically in Figure 2. Each step of the walk in Figure 1 is weighted with the Boltzmann factor x, which in recursive enumeration is accomplished by assigning a factor $\sqrt{x}$ to each site that is a starting or ending point of the walk, and a factor x to each site through which the walk passes by. Initial weighted walks (walks on the unit triangle) are shown in Figure 2 for configurations A and B, while configurations of the type C and D are not possible on the unit triangle. Denoting the total weight (restricted generating function) of the configuration with the same label as the corresponding configuration, the recurrence equations are

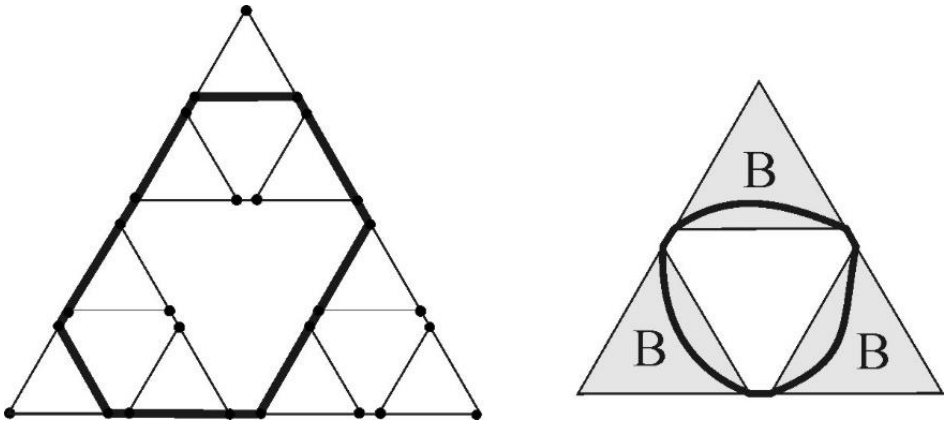

Figure 3. Left:Neighbor-avoiding polygon that consists of N=16 steps, contributing to the term with x^{16} in the generating function (8). Right:Coarse-grained, schematic representation of the same polygon.

$$A' = A + 2AB + 2AB^2 + 2B^2C, \tag{3}$$

$$B' = B^2 + B^3, \tag{4}$$

$$C' = AB^2 + 3B^2C, \tag{5}$$

$$D' = A^2 + 2A^2B + 4ABC + 6BC^2 + 2BD + 3B^2D. \tag{6}$$

These equations express weights of the walks A,B, C and D on $G^{(r+1)}$ (on the left hand side) through their weights on $G^{(r)}$ (on the right hand side). Starting values, the weights of the walks on the unit triangle depicted in Figure 2, are $A^{(1)} = \sqrt{x} + 2x^{\frac{3}{2}}$, $B^{(1)} = x^2$, $C^{(1)} = 0$ and $D^{(1)} = 0$. Recurrence equations (3)-(6) for NAWs are the same as the recurrence equations for SAWs [9], but the initial conditions differ. NAWs do not alow for the configurations where all three sites of the unit triangle are visited. They can visit at most two (if visited consecutively) out of three sites of each unit triangle, as can be seen in Figure 1 and Figure 2.

One can notice that Equation (4) decouple from other equations, and actually the weights of the walks B are the only weights that are necessary for the construction of the generating function for Neighbor-avoiding polygons (NAPs). One such polygon and its coarse grained version are shown in Figure 3. The generating function for NAWs can be written as

$$G_W(x) = x + \sum_{r=1}^{\infty} \frac{1}{3^{r+1}} [3A_r(x)^2 + 3B_r(x)A_r(x)^2 + 3B_r(x)^2D_r(x)], \tag{7}$$

while the generating function for polygons is simpler, it consists only of B configurations

$$G_P(x) = \sum_{r=1}^{\infty} \frac{1}{3^{r+1}} (B_r(x))^3. \tag{8}$$

By the iteration of the generating functions (7) and (8), together with Equations (3-6) and their initial conditions, one can numerically find the radius of convergence of the generating functions. In that way, we find that for each $x < 0.78615\ldots$ both generating functions converge, while for $x > 0.78615\ldots$ they both diverge. We then conclude that $x_c = 0.78615\ldots$ so that $= \frac{1}{x_c} = 1.2720\ldots$, the same for Neighbor-avoiding walks and Neighbor-avoiding polygons.

However, since Equation (2) is independent of other equations and its fixed points can be found exactly, one can find closed form solution for the connectivity constant. Fixed point equation is

$$B^* = (B^*)^2 + (B^*)^3, \tag{9}$$

and has nonnegative trivial solutions 0 and ∞, and one nontrivial solution $B^* = \frac{\sqrt{5}-1}{2}$. For each $B < B^*$, variable B iterates to zero, while for each $B > B^*$ it diverges. For $B = B^*$ it does not change with the iterations. Since the generating function for polygons depends only on B, it follows immediately from Equation (8) that G_P stays finite for $B < B^*$ and diverges for $B > B^*$. As the variable B depends on x and iteration starts from $B^{(1)} = x^2$, we see that $(x_c)^2 = \frac{\sqrt{5}-1}{2}$ and $x_c = \left(\frac{\sqrt{5}-1}{2}\right)^{\frac{1}{2}}$. Then

$$\omega = \left(\frac{2}{\sqrt{5}-1}\right)^{\frac{1}{2}} = 1.272019649 \ldots. \quad (10)$$

From the recurrence equations (3)-(6) and the expression (7) it follows that the same ω holds for open walks too. Namely, Equations (3) and (5) decouple from (6), and they are linear over variables A and C with the coefficients that depend on B. This implies that they have the same ω as the variable B, and linearity leads to different exponent a in the power law correction factor (expression (1)) for open walks in comparison with the polygons.

Connectivity constant can also be found from the Interacting self-avoiding walk model (ISAW, [10] and [11] for $s = 1$) in the limit of infinitly repulsive contact energy when the interaction parameter tends to zero. Here, from the ISAW model also, we have obtained numerically the value of ω in accordance with the closed-form expression.

3. SUMMARY AND CONCLUSIONS

We have considered Neighbor-avoiding walks and polygons as simple lattice models of linear and ring polymer conformations in an exceptionally good solvent. Walks are constrained on the 3-simplex fractal lattice where an exact recursive method for the generating functions of all walks and polygons of different lengths has been applied. The closed form expression (10) for the connectivity constant ω of Neighbor-avoiding walks on this lattice, is found. The connectivity constant characterizes the leading order exponential growth of the number of walks with the number of steps. This nonuniversal quantity determines the free energy and entropy of a polymer modeled by NAWs. It is found that the connectivity constant is the same for walks and polygons, which is also the case for ordinary Self-avoiding walks and polygons. But, the connectivity constant of Neighbor-avoiding walks and polygons ($\omega = \left(\frac{2}{\sqrt{5}-1}\right)^{\frac{1}{2}} = 1.2720 \ldots$) is smaller than the connectivity constant of ordinary Self-avoiding walks and polygons ($\omega_{SAW} = \frac{2}{\sqrt{5}-1} = 1.6180 \ldots$ [9]) as could be expected, since Neighbor avoiding walks are the subset of Self-avoiding walks. This means that the entropy is smaller, as a consequence of the reduced number of microstates. Furthermore, as the recurrence equations for NAWs are the same as those for ordinary SAWs, the critical exponent a of NAWs in the expression (1) is the same as the corresponding exponent of SAWs ($a = \gamma = 1.3752 \ldots$) found in [9]. Also, the corresponding exponent for NAPs is the same as for SAPs ($a = \alpha - 2 = -1.2658 \ldots$ [1][9]). Finally, the critical exponent ν ($\nu = 0.7986 \ldots$) is the same for both types of walks. This implies that NAWs (NAPs) belong to the same universality class as SAWs (SAPs). The same conclusion has already been confirmed on regular lattices. Although NAWs are well studied problem on regular lattices, we are not aware of any such study on fractal ones, and we think that the future work should be conducted in order to see how lattice parameters: the coordination number (the number of the nearest neighbor sites) and the minimal contact length [11,12] (the minimal number of steps necessary to reach the nearest neighbor site), affect the connectivity constant of NAWs.

[1] A negative value of the exponent a indicates that the polygon generating function stays finite at $x = x_c$.

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