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SAW chain, polymer adsorption, conformational entropy

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APPLICATION OF MODIFIED SAW METHOD IN THE STUDY OF CONFORMATION OF THE SINGLE POLYMER CHAIN TERMINALLY ATTACHED TO THE FLAT SURFACE

Some modified SAW models of the polymer chain and the statistical counting method have been applied in order to estimate the conformational entropy of the chain in the bulk and the chain terminally attached to the flat surface. The scaling laws describing the binding entropy vs. chain length obtained from simulations are confronted with the theoretical predictions.

1. INTRODUCTION

The properties of layers formed by tethering polymers to a surface are of great interest because of their technological applications including the stabilization of colloidal suspensions, biocompatibility of artificial implants, detergency and many others [1]. The properties of chains end-grafted on planar surfaces have been extensively studied using different theoretical and experimental methods [2]. However, the details of thermodynamics of the single end-grafted chain, even in the case of simple lattice models, have not been yet fully understood.

The conformational entropy of the free unperturbed SAW chain generated in the 3D cubic lattice can be calculated by means of the renormalization group theory as [3]:

$$S / k_{\mathrm{B}} = \ln(C) + (\gamma - 1)\ln(N) + N \ln(\omega_{\mathrm{eff}}) \tag{1}$$

where N is the number of segments in the chain and C, γ and ω_{eff} are coefficients dependent on the lattice coordination number [4]. The change in the conformational entropy of the chain caused by its terminal attachment to the surface can be expressed by [5]:

$$\Delta S / k_{\mathrm{B}} = \beta \ln(N) \tag{2}$$

Eq 2 was derived from Eq 1 assuming very long polymer chains. For short chains, as far as we know, the reasonable relationship $\Delta S=f(N)$ valid for good solvents does not hold.

The goal of this work is to study the scaling arguments of the $\Delta S=f(N)$ function using some modifications of the self avoiding walk (SAW) on cubic lattice model [6] for modeling different regimes of the solvent properties.

2. MODEL

The system considered consists of the single linear polymer chain modelled on the three dimensional cubic lattice of the lattice constant a. Both the free unperturbed chain and the chain terminally attached to the flat surface were simulated. The latter simulations started at the surface-bound segment placed at a node in the layer nearest to the surface.

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The simulation box contained 601^3 nodes. Only a half of the space was used in the simulation of the attached chain. The polymer chain was represented by three models: the self avoiding walk (SAW) and two SAW modifications further referred as self-repelling self avoiding walks (SRSAWs). The SAW chain was generated using two algorithms differing in the method of the calculation of the positions of succeeding segments: the classical ((100) SAW) and the so-called (112) SAW, where each position of the segment is calculated as a sum of coordinates of the previous segment location and the permutation of the shift coordinate set $p(\pm a,\pm a,\pm 2a)$. In order not to violate the SAW requirements, the nodes just filled with the segments introduced to the lattice are blocked for subsequent generation steps. This limitation introduces the excluded volume effect to the model. Moreover, this effect is enhanced by blocking of some additional nodes neighbouring to those that contain already accepted segments. The blocked nodes were selected by two different algorithms: i) blocking of the nodes whose one coordinate differs by ±1 from the segment's coordinate (the SRSAW1 method which forms "a star" around each segment) and ii) blocking of all nodes neighbouring to the segment (the SRSAW2 method which forms "a box" around each segment). The modification details are presented in Table I.

Table I. The set of SAW models studied

Method	Succeeding segment coordinates	Segment length	Coordinates of blocked nodes	Maximum(SAW+blocked)/ average number of blocked nodes
(100) SAW	$p(0,0,\pm a)$	1	–	(1+0)/1
(112) SAW	$p(\pm a,\pm a,\pm 2a)$	$\sqrt{6}$	–	(1+0)/1
(100) SRSAW1	$p(0,0,\pm a)$	1	$p(0,0,a)$	(1+6)/1
(112) SRSAW2	$p(\pm a,\pm a,\pm 2a)$	$\sqrt{6}$	$p(0,0,a)$ $p(0,a,a)$ $p(a,a,a)$	(1+26)/19

The calculations of the conformational entropy of the polymer chain were performed by means of the statistical counting method (SCM) described by Zhao at al. in [7]. The method is based on the effective coordination number of the lattice defined as

$$\omega_{\mathrm{eff,i}} = \frac{\Omega_{\mathrm{i+1}}}{\Omega_{\mathrm{i}}} \tag{3}$$

where Ω_{i} is the number of conformations of a chain of i segments. In the model, ω_{eff} was calculated at each iteration as the number of free nodes available for generation of the succeeding segment in the chain. According to (3) the total number of chain conformations can be calculated as the product of ω_{eff} values of the whole chain:

$$\Omega_{\mathrm{N}} = \prod_{i=1}^{N-1} \omega_{\mathrm{eff,i}} \tag{4}$$

where N is the segment number in the chain. Thus the average conformational entropy of the chain reads:

$$\frac{S}{k_{\mathrm{B}}} = \sum_{i=1}^{N-1} \ln\left\langle \omega_{\mathrm{eff,i}} \right\rangle \tag{5}$$

The conformational entropy was calculated as the average of results of 10^5 different independently simulated conformations.

The properties of the solution of the modeled macromolecules was related to the scaling exponent characterizing the dependence of the mean squared end-to-end distance, R_h, on the segment number N:

$$R_h = bN^{\nu} \tag{6}$$

where b is the length of the polymer segment.

3. RESULTS

The dependencies of the effective coordination number on the number of segments in the polymer chain obtained for both the unperturbed chain in the bulk and the chain terminally attached to the flat surface are shown in Fig. 1. As seen the initial ω_{eff} value is equal to the maximum coordination number of the lattice ω=24 ((112) SAW) for the free chain and to ω/2 for the anchored chain. The increase in the chain length causes an asymptotic change in ω_{eff} but the values obtained for the highest N studied are significantly different. This observation contradicts the assumptions needed to derive Eq. 2. As a result, Eq. 2 poorly fits the simulation data, as shown in Fig. 2.

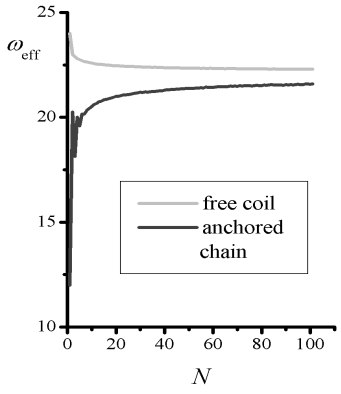

Fig. 1. The ω_{eff} vs. N dependence obtained by SCM for free and anchored chain ((112) SAW).

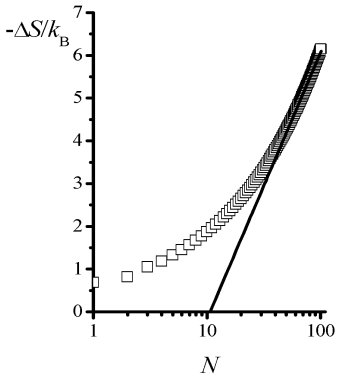

Fig. 2. The dependence of ΔS on the chain length, squares – result of the simulation, line – results of fitting of Eq. 2 ((112) SAW)

The $\ln(\Delta S)=f(\ln(N))$ dependencies obtained for different SAW models are depicted in Fig. 3. As seen, all relationships are rectilinear, except the initial fragments at extremely low N. Hence, the $\Delta S=f(N)$ function can be expressed by the simple power law:

$$\Delta S = kN^{a} \tag{7}$$

where k and a – are constants dependent on the effective coordination number.

The scaling exponents of $\Delta S=f(N)$ and $R_G=f(N)$ relationships obtained by modified SAW methods are collected in Table II. As results from the Table, the methods used allow a simulation of the conformation of macromolecule in different solutions from Θ (ν=0.5) to athermal one (ν=0.6). The blocking procedure affects not only the scaling behaviour of the linear dimensions of the coil but simultaneously influences the exponent in Eq. 7.

As seen from Table II, for the macromolecule immersed in the Θ solution ((112) SAW), the change in the conformational entropy of the chain caused by its terminal attachment to the surface is proportional to the square root of the segment number in the chain.

$$\Delta S = k\sqrt{N} \tag{8}$$

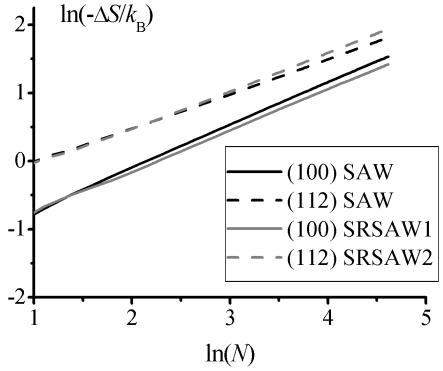

Fig 3. Dependencies of the ΔS on the chain length obtained from different SAW models.

Table II. The scaling exponents of relations (2) and (6).

Method	*v*	*a*
(100) SAW	0.55	0.64
(100) SRSAW1	0.59	0.62
(112) SAW	0.51	0.50
(112) SRSAW1	0.51	0.50
(112) SRSAW2	0.55	0.55

As results from a comparison of the data obtained by SAW and SRSAW methods, the increase in the scaling exponent of Eq. 6, which indicates a shift from the Θ to athermal conditions, is accompanied by a similar increase in the value of the scaling exponent describing the entropy–segment number relationship. However, some further studies for polymer solutions of *v* from 1/3 to 1 (*i.e.* from globular to rod-like polymer conformations) are needed to formulate the universal ΔS=f(N) relationship valid for all types of polymer solutions.

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ZASTOSOWANIE ZMODYFIKOWANEJ METODY SAW W BADANIACH KONFORMACJI ŁAŃCUCHA POLIMERU ZAKOTWICZONEGO KOŃCEM NA PŁASKIEJ POWIERZCHNI

Niektóre zmodyfikowane modele SAW łańcuchów polimerowych w połączeniu z metodą zliczania statystycznego zastosowano do obliczeń entropii konformacyjnej łańcucha swobodnego i przyczepionego jednym końcem do płaskiej powierzchni. Otrzymano prawa skalowania opisujące zależność pomiędzy entropią adsorpcji i długością łańcucha. Prawa te skonfrontowano z przewidywaniami teoretycznymi.