Proceedings of International Scientific Conference "Surfactants and Dispersed Systems in Theory and Practice", Ed: K.A. Wilk, PALMAPress, Wrocław, 2007

SAW chain, static MC method

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MODELLING OF SINGLE POLYMER CHAIN IN THE SOLUTION. MODIFICATION OF THE SAW METHOD

Some modifications of non-unbiased SAW chains have been studied as models of the polymer molecule in solution. The universal scaling exponents have been applied as characteristic parameters determining the thermodynamic properties of the solution. The models studied have been found to permit simulation the polymer chain behaviour in a wide range of the solvent quality.

1. INTRODUCTION

The self avoiding walk (SAW) on a cubic lattice has been widely used as a model of unperturbed polymer chain immersed in a good solvent. The basic (100) SAW version consists in generation of succeeding chain segments in such a way that the positions of the neighbouring segments differ by a distance a in the direction of one of the co-ordinate axes (a – the network constant equal to the distance between neighbouring nodes in the lattice). The essential assumption of the SAW method is that the random walking chain cannot intersect itself. The assumption allows incorporation of the excluded volume effects to the model of a polymer solution.

Unfortunately, it is not easy to generate a SAW conformation of a large number of segments N because the probability of choice of a filled node during the chain construction increases with N [1]. All generations in which two monomers try to occupy the same node should be rejected. The difficulty in generation of long SAW chains is called the 'attrition problem'. In order to avoid this problem, the chain generating algorithm may be modified in such a way that it chooses the succeeding segments only from the empty lattice nodes. However, the conformation obtained is 'biased' towards a more compact one. The results of the method can be improved by the Rosenbluth-Rosenbluth weighting factors [2] or 'enrichment methods' [3] but the convergence of results obtained for long chains is still poor or the methods are not suitable for studies of the polymer chain in confined environment.

The general aim of the work is to test some variants of the SAW method based i) on the modification of rules of the choice of segment positions in the lattice and ii) on the introduction of a new procedure which blocks some nodes neighbouring the segments already accepted.

2. MODEL

The system considered consists of the unperturbed single linear polymer chain modelled on the three dimensional cubic lattice of the lattice constant a. The periodic

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boundaries of the simulation box were adopted. The box contained 601^3 nodes. The polymer chain was represented by the following models: random walk (RW), self avoiding walk (SAW) and several SAW modifications further referred as self-repelling self avoiding walks (SRSAWs). Two different types of modifications were implemented. The first one consists in the method of generation of position of each succeeding segment. Instead of the classical (100) SAW algorithm, in which each segment links the two nearest lattice nodes, in the method of generation of position of each succeeding segment. Instead of the classical (100) SAW algorithm, in which each segment links the two nearest lattice nodes, a new position was calculated as a sum of coordinates of the penultimate segment $\boldsymbol{X}=(x_1,x_2,x_3)$ and the permutation of the set of shift coordinates $p(\pm a,\pm a,\pm 2a)$ (see Fig. 1.). The other modification was made in order to enhance the excluded volume effect. It involved blocking of some additional network nodes (neighbouring the chain) for the subsequent generation steps. Three different modifications presented in Table I were considered.

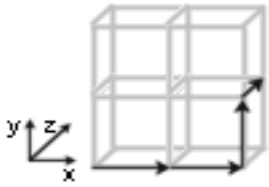

Fig. 1. Schematic representation of a (112) movement.

Table I. The set of SAW models studied

Method	Succeeding segment coordinates	Segment length b	Coordinates of blocked nodes	Maximum(SAW +blocked)/average number of blocked nodes
(100) SAW	$\boldsymbol{X}+p(0,0,\pm a)$	1	–	(1+0)/1
(112) SAW	$\boldsymbol{X}+p(\pm a,\pm a,\pm 2a)$	$\sqrt{6}$	–	(1+0)/1
(112) SRSAW1	$\boldsymbol{X}+p(\pm a,\pm a,\pm 2a)$	$\sqrt{6}$	$Y=p(\pm a,\pm a,\pm 2a)$	(1+23)/16
(112) SRSAW2	$\boldsymbol{X}+p(\pm a,\pm a,\pm 2a)$	$\sqrt{6}$	Y $Y\pm a; Y\pm 2a$	(1+119)/71
(112) SRSAW3	$\boldsymbol{X}+p(\pm a,\pm a,\pm 2a)$	$\sqrt{6}$	$Y; Y+p(\pm a,\pm a,\pm a)$ $Y+p(0,\pm a,\pm a)$ $Y+p(0,0,\pm a)$	(1+273)/115

The conformation of the polymer coil was characterized by means of the universal exponent ν of power laws describing the linear dimensions of the coil. Two linear dimension characteristics were applied: the mean squared end-to-end distance (R_h) and mean radius of gyration (R_G):

$$R_h = b_{Rh} N^{\nu_{Rh}} \tag{1}$$

$$R_G = \frac{b_{RG} N^{\nu_{RG}}}{\sqrt{6}} \tag{2}$$

where b is the polymer segment length and N is the segment number in the chain. The universal scaling exponent ν takes a value of 1/3 for the globular structure of the polymer chain, 1/2 for the ideal (RW) or Θ chain, 3/5 (Flory approximation [4]) or 0,588 (found by the renormalization group theory [5]) for the SAW chain and 1 for the stiff rod.

The exponent ν can be also calculated on the basis of the hypothesis that the segment density distribution around the coil mass center can be expressed by the extended radial Gauss distribution [6]:

$$\rho = \frac{(r/b)^{1/\nu_\rho}}{B\sqrt{\pi N}b^2}\exp\left(-\frac{9}{N}\left(\frac{r}{b}\right)^{1/\nu_\rho}\right) \tag{3}$$

where r is the distance between a particular segment and the coil mass center and B – the normalization constant.

3. RESULTS

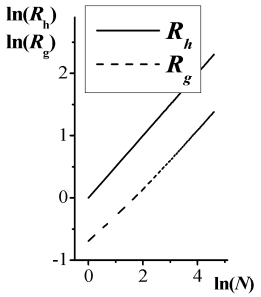

Fig. 2. The R_h and R_g vs. N dependencies obtained for (100) chain (N_{max}=101).

The algorithm developed for simulation of the SRSAW chain was previously tested as a generator of conformations of the RW chain (the chain immersed in the ideal solution). The test results are collected in Fig. 2 and Table II. As seen, both $\ln(R_h)=f(\ln(N))$ and $\ln(R_G)=f(\ln(N))$ relationships are straight-linear functions. The obtained scaling exponents and segment lengths take values close to the theoretically expected ν=1/2 and b=1 and $\sqrt{6}\approx 2.45$ for (100) RW chain and (112) RW chain, respectively. No short chain artifacts were observed since the obtained results are practically independent of the chain length.

The results of the simulation of conformations of different types of SAW coils are gathered in Fig. 3 and Table III. As seen the non-unbiased basic (112) SAW method gives the straight-linear $\ln(R_G)=f(\ln(N))$ dependencies with ν exponents approximately of 0.5. Since the method adopts the excluded volume rule, the model results can be related to the macromolecule in the Θ solution.

Table II. The set of ν exponents and segment lengths b obtained for the RW model.

Method	N	ν_{Rh}	ν_{RG}	b_{Rh}	b_{RG}
(100) RW	1001	0,50	0,51	1,00	1,21
(112) RW	1001	0,50	0,49	2,45	2,50
(100) RW	101	0,50	0,47	1,00	1,12
(112) RW	101	0,50	0,47	2,45	2,73

Table III. The set of ν exponents and segment lengths b for different chain lengths

Method	N=1001					N=101				
	ν_{Rh}	ν_{RG}	b_{Rh}	b_{RG}	ν_ρ	ν_{Rh}	ν_{RG}	b_{Rh}	b_{RG}	ν_ρ
(112) SAW	0,51	0,50	2,56	2,60	0,58	0,51	0,48	2,51	2,76	0,60
(112) SRSAW1	0,53	0,53	3,02	2,94	0,56	0,57	0,55	2,60	2,74	0,56
(112) SRSAW2	0,56	0,56	3,35	3,09	0,57	0,57	0,55	2,60	2,74	0,56
(112) SRSAW3	0,55	0,55	4,53	4,15	0,55	0,62	0,62	3,47	3,26	0,55

The log-log relationships obtained for models with additional blocking are characterized by higher slopes than those obtained for the basic SAW method. However, as seen in Fig. 3 there are two regimes of the dependencies observed for short and long chains. The scaling exponents for short chains (N<20) are close to 0.6, thus the models applied to this range of N can be related to macromolecules in the athermal solution. The exponents for longer chains depend on the blocking method and vary from 0.5 to 0.6, *i.e.* from Θ to the athermal solution.

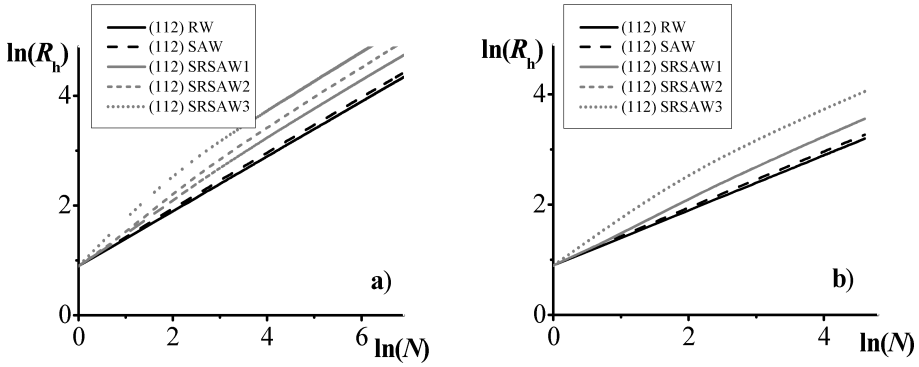

Fig. 3. The dependencies of R_h on N for the model (112) SRSAW at a) N_{max}=1001 b) N_{max}=101.

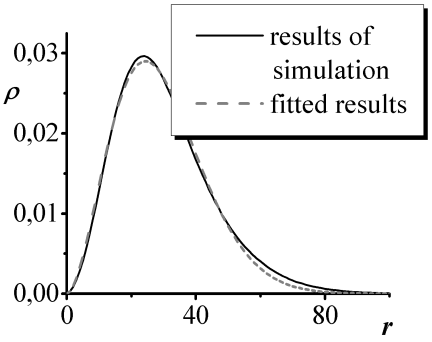

Fig. 4. The segment density distribution around the coil mass centre obtained by the simulation and by fitting of parameters of Eq. 3 to the simulation results.

As follows from Fig. 4, the segment density distribution around the coil mass centre can be sufficiently well described by the modified Gauss distribution (Eq. 3). However, a comparison of the data collected in Tables III shows that ν_ρ obtained from the distribution (Eq. 3) and ν_{Rh} and ν_{RG} found from Eqs (1) and (2) depend on the solution properties in a different manner: when ν_{Rh} and ν_{RG} increase, ν_ρ exponent decreases.

Summarizing the above one can conclude that the developed methods of generation of polymer coil conformation based on some modifications of SAW algorithm permit simulation of the polymer chains in a wide range of the solution properties – from Θ to athermal (ν = 0.5 – 0.6). The methods can be also applied for modelling of the influence of the solvation effect on the polymer chain properties in solution.

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MODELOWANIE ŁAŃCUCHA POLIMERU W ROZTWORZE. MODYFIKACJA METODY SAW

Zbadano niektóre modyfikacje nieskorygowanych łańcuchów SAW jako modeli cząsteczek polimeru w roztworze. Zastosowano uniwersalne wykładniki skalowania jako charakterystyczne parametry określające właściwości termodynamiczne roztworu. Stwierdzono, że badane modele pozwalają na symulację zachowania się łańcuchów polimerowych w roztworach o szerokim zakresie właściwości.