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Entropy and Free Energy of a Polymer Chain from Dynamic Monte Carlo Simulations on the Lattice. An Extension of the Statistical Counting Method.

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Abstract. The main assumptions of the statistical counting (SC) method [D. Zhao et al., J. Chem. Phys. 104, 1672 (1996)] for the calculation of the conformational entropy of a chain modeled on the lattice are presented. The method is discussed in terms of its applicability to different physical systems and the integrity of results. Also, an extension of the SC method for the analysis of the statistics of some Verdier-Stockmayer algorithms in the Metropolis Monte Carlo simulation is proposed. The results of the application of this new method, named here as the micomodification probabilities (MMP) method, for the study of the effect of different solvent conditions, different types of geometrical constraints and deforming external forces on the free energy of a polymer chain, are presented. The use of the MMP method for the investigation of a charged polymer in the presence of other charged objects (ions, nanoparticles) is also reported.

Keywords: conformational entropy, Verdier-Stockmayer algorithms, SAW chain.
PACS: 36.20.-r

The knowledge of the free energy of a polymer is essential for understanding of many complex processes in which macromolecules take part. However, it is often not possible to analytically compute the free energy of a process and, particularly, its component – the conformational entropy. This problem can be overcome by using simulation methods which provide the ability to study complex systems in great detail. One of the most universal and effective approaches to the problem is the Monte Carlo (MC) method. Numerous computer simulation techniques that allow evaluation of thermodynamic quantities of macromolecular systems, and which are based on the MC sampling, have been developed. A relatively simple and efficient method for calculating the thermodynamic properties of polymer solutions, known as the statistical counting (SC) method, has been described by Zhao et al. [**1**] This method, however, is only appropriate for polymer chains simulated with static MC simulation. In this contribution, we presented an extension of the SC method for computing the entropy and free energy of a chain simulated with Metropolis MC and non-equlibrium MC techniques.

INTRODUCTION: ASSUMPTIONS OF THE SC METHOD

The SC method developed by Zhao et al. [1] for the calculation of conformational entropy of linear self-avoiding walk (SAW) chains employs the Rosenbluths' weighting factors [2] and is based on the computation of the probability of successful – that is not violating the SAW limitation – generation of a new segment. This generation probability, P(G), can be related to the effective coordination number ω_{eff} by the equation:

$$\omega_{\mathrm{eff}} = (\omega - 1)P_{\mathrm{E}}(\mathrm{G})_0 \tag{1}$$

where ω is the coordination number of the lattice (for the algorithm for generation of chain segments along the edges of the regular cubic lattice, which we abbreviate as (001) algorithm, ω is equal to 6), whereas subscripts 0 and E indicate that the simulation concerns a free, unconstrained chain (index 0) and that it respects the excluded volume restriction (index E). The ω_{eff} is the average number of free lattice nodes $\omega_{\mathrm{i,n}}$ available for segment i, calculated over all segments in the chain and all chains in the MC sample n; $\omega_{\mathrm{i,n}}$ refers to numbers Ω of possible conformations of the chain built of i or i+1 segments.

$$\omega_{\mathrm{i,j}} = \frac{\Omega_{\mathrm{i+1,j}}}{\Omega_{\mathrm{i,j}}} \tag{2}$$

where j is the number of the sample.

If $\omega_{\mathrm{i,j}}$ values are obtained in the simulation, the total number of conformations of the chain built of N segments can be calculated from the recursive formula:

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$$\Omega_{\mathrm{N,j}} = \prod_{i=1}^{N-1} \omega_{\mathrm{i,j}} \tag{3}$$

For a large set of chains generated by the MC sampling method, the average value of $\omega_{\mathrm{i,j}}$ can be found from the formula

$$\overline{\omega}_{\mathrm{i}} = \lim_{n\to\infty} \frac{\sum_{j=1}^{n} W_{\mathrm{i,j}}\ \omega_{\mathrm{i,j}}}{\sum_{j=1}^{n} W_{\mathrm{i,j}}} \tag{4}$$

based on the Rosenbluths' weighting factors W defined as

$$W_{\mathrm{m+1,j}} = \left(\frac{\omega_{\mathrm{m}}}{\omega - 1}\right) W_{\mathrm{m,j}} \tag{5}$$

where m is the number of a segment ranging from 0 to i and j is the number of sample.

Finally, the conformational entropy of the chain of N segments reads:

$$\frac{S_{\mathrm{N}}}{k_{\mathrm{B}}} = \sum_{i=1}^{N-1} \ln\left(\overline{\omega}_{\mathrm{i}}\right) \approx (N-1)\ln(\omega_{\mathrm{eff}}) \tag{6}$$

SOME APPLICATIONS OF THE SC METHOD AND ITS LIMITATIONS

Zhao et al. [1], in order to verify the applicability of the SC method for prediction of the conformational entropy of a linear polymer chain, have compared the results of this method, obtained for both free and confined SAW chains, with the corresponding results following from the direct counting method (for chains up to N=20 segments) and the renormalization group theory approximation for chains of $N\to\infty$. A good agreement between entropies estimated by these different approaches confirmed the validity of the SC method.

We employed the SC method in several applications. And thus, for instance, we used it for the investigation of the influence of different geometrical constraints on the conformational entropy of linear chains [3–5]. Both free chains and the chains whose starting segment was fixed at an arbitrarily chosen position were studied. Also, the algorithms of different values of the coordination number (i.e., of different ways of choosing the position of a segment in the lattice, like, for instance, a simple step or chess knight algorithms ((112) and ((012)) with values of ω equal to 24) were used for the generation of SAW chains

Results of these simulations provided valuable information about the number of phenomena involving polymer chains. For example, the relations obtained between the conformational entropies of chains terminally attached to surfaces of flat, concave and convex objects and the chain length (expressed by N) allowed i) estimation of negative pressure exerted on the surface by a polymer chain tethered to it [4], ii) formulation of the equation of state of a chain located in the cavity[4], iii) determination of the full free energy landscape of a chain translocation through a narrow channel between two chambers of different geometries [4] and iv) predictions about the structure of complexes composed of long linear macromolecules and nanoparticles [5]. Simulations of a chain tethered to Brownian, fractional Brownian and uncorrelated Gaussian surfaces allowed formulation of a simple analytical model describing the chain behavior near the rough fractal-like surfaces [6].

However, despite of the successful use of the SC method for computation of thermodynamic quantities of several polymer chain models, the method suffers some drawbacks that limit its application. Although the parameter values obtained from MC simulation are correct because of the employment of the Rosenbluths' weighting factors, the generated chain conformations remain biased from the true population, which makes them unsuitable for detailed and realistic analysis of the polymer coil structure. A serious drawback of the method is its restriction to chains with at least one free (not fixed) end. Moreover, since the method was invented for SAWs, it is limited to chains in athermal environment, where all intra- or intermolecular interactions are neglected. Nonetheless, it is noteworthy here that some results of our investigation on the SC method applicability indicate that it can be used for non-athermal linear chains as well. There are, however, situations in which the SC method fails dramatically, yielding completely wrong results, as it is – for instance – in the case of chains deformed by external forces. Namely, if such chains are stretched, their conformational entropy decreases, as intuitively obvious. However, because the chain

stretching is accompanied by an increase in the value of ω_{eff}, the SC method predicts erroneously an entropy increase.

THE MICROMODIFICATION PROBABILITIES (MMP) METHOD

In order to extend the applicability of the SC method we replaced the analysis of the probability $P_{\text{E}}(\text{G})$ of generation of a segment satisfying the SAW requirement (see Eq.1) by that of the probabilities of some chain micromodifications (and, hence, the abbreviation MMP is used for the modified method) applied in the Metropolis MC simulation. For the simulations performed employing the MMP method, we assumed some standard chain modifications including the local and bilocal Verdier-Stockmayer algorithms of the segment movements (reptation – R, end move – E, kink jump – K and crankshaft – C) as well as the nonlocal cut-and-paste algorithm (to ensure the simulation ergodicity [7, 8]). In the course of simulations, the probabilities P_{E} that a given move does not violate the excluded volume restriction, were calculated. The probability of the micromodification R, $P_{\text{E}}(\text{R})$, is equivalent to that used in the SC method, that is to $P_{\text{E}}(\text{G})$, and hence, it is appropriate only for chains in athermal conditions with at least one end free. Therefore, instead of the micromodification of R-type we chose two other moves for sampling the chain conformation, i.e. those of C- and K-type. We also demonstrated that the probabilities of performing these moves, denoted correspondingly as $P_{\text{E}}(\text{C})$ and $P_{\text{E}}(\text{K})$, can be related to the effective coordination number by the following equations:

$$\omega_{\text{eff}} = (\omega - 1) - 4(1 - P_{\text{E}}(\text{K}))^2 \tag{7}$$

or

$$\omega_{\text{eff}} = (\omega - 1) - 5(1 - P_{\text{E}}(\text{C}))^3 \tag{8}$$

The deformation of a random coil structure (e.g. in an external force field) brings a negative contribution to the conformational entropy of a chain. At the same time this deformation also involves a decrease in the probability of performing K or C moves without violation of the chain continuity. We have found [9] that the probability $P_{\text{S}}(\text{K})$ that a randomly chosen segment can perform the K move which satisfies this skeletal constraint, can be related to the parameter L by the following expression:

$$\frac{L}{bN} = \left(1 - \frac{P_{\text{S}}(\text{K})}{P_{\text{S}}(\text{K})_0}\right)\left|1 - \frac{P_{\text{S}}(\text{K})}{P_{\text{S}}(\text{K})_0}\right|^{\lambda - 1} \tag{9}$$

where $\lambda = 1/5\nu$ (ν being the Flory exponent), b is the segment length and index 0 relates to the free chain. The L parameter is the average value of the projection of the distance L_{H} between chain ends in the deformed coil onto the axis parallel to the direction of deformation. L can be related to L_{H} by the equation:

$$L = \frac{L_{\text{H}} - \left\langle R_{\text{H}}^2 \right\rangle^{\nu}}{1 - (N+1)^{\nu - 1}} \tag{10}$$

where $\langle R_{\text{H}}^2 \rangle$ corresponds to the root-mean-squared end-to-end distance of an unperturbed chain.

Taking into account the above relations we derived the equation allowing the calculation of the conformational entropy of a chain on the basis of ω_{eff} and L parameters accessible from simulations. This equation reads:

$$\frac{S}{k_{\text{B}}} = \ln(\Omega) = \ln\left(\frac{\Gamma(N)}{\Gamma\left(\dfrac{N - 1 - L/b}{\omega_{\text{eff}}} + 1\right)^{\omega_{\text{eff}} - 1} \Gamma\left(\dfrac{N - 1 + (\omega_{\text{eff}} - 1)L/b}{\omega_{\text{eff}}} + 1\right)}\right) \tag{11}$$

where Γ denotes the Euler gamma function.

The method of calculation of the conformational entropy of a polymer chain, based on Eq. 11, is fast and addresses a wider spectrum of applications than the SC method. Namely, the MMP method can be employed for lattice models of polymer chains in different solvent conditions, both in the absence and the presence of different spatial constraints and deforming external forces.

EXEMPLARY APPLICATIONS OF THE MMP METHOD

The influence of the extent of deformation of a random polymer coil on the conformational entropy of a chain in the athermal solution was studied using the MMP method [9]. The results obtained were compared with the corresponding results available in literature and evaluated with the expanded ensemble MC method [10]. The comparison shows a very good agreement, thus confirming the reliability of our method.

After incorporation of the inter- and intramolecular interactions into the model of a polymer solution, we used the MMP method for the calculation of free energy of chains in the theta solution as well as in poor solvent conditions, in which the polymer coil collapses to the globular structure [9]. Moreover, the conformational entropy of the SAW chain with its ends attached to the opposite parallel plates was studied as a function of the distance between the plates [9].

Incorporation of the electrostatic charges to the model gives a possibility to simulate the behavior of more realistic systems. The MMP method was employed in the studies on the behavior of a complex composed of a telechelic charged and flexible polymer chain irreversibly attached with its ends to surfaces of two nanoparticles, which bore the electric charge as well [11] The simulations were performed in the presence of explicit ions in the dispersion medium. The effect of both stretching and compression of the complex on its free energy was examined. We found, on the basis of the results obtained, that the behavior of the complex under stretching conditions is governed by the conformational entropy of the bridging chain, whereas for the complex in equilibrium and under compression, both entropic and energetic effects are significant. The entropy contribution can be strongly affected by the monomer adsorption, while the energy contribution is mainly due to electrostatic interactions in the system. The non-ionic interactions were found to have only minor influence on the properties of the complex examined.

Very recently, we employed the MMP method for some dynamic studies of the process of translocation of polyelectrolytes through narrow nanopores driven by the electrostatic field. The effect of the placement of a single ion at the entrance and/or exit of the nanopore on the translocation process was also studied. Simulations were performed by means of non-equilibrium MC method with umbrella sampling [12] (instead of Metropolis sampling). The temporary conformational entropies of simulated chain, calculated by means of the MMP method, were applied as the umbrella non-equilibrium weights. The MMP method was also used to obtain the full landscape of the translocation of polyelectrolyte through a nanopore.

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