Behavior of a Polyion at the Charged Wall of the Same Sign in Presence of Counterions and of a System of two Equal Uncharged Polymer chains. Study by Monte Carlo Method

A. Yu. Antipina, M. A. Antyukhova, A. A. Yurchenko, P. N. Vorontsov-Velyaminov*

Summary: In this paper Monte Carlo simulations of two polymer systems are presented. The first system is a single polyion near the plane charged wall of the same sign with presence of counterions. The interest in studying this system is stimulated by experiments on binding of negatively charged DNA deposited on the negatively charged substrate.[1] The second system contains two non-charged polymer chains with attractive or repulsive intrachain interaction and attraction between chains in both cases. Treatment of this system is aimed at further simulation of a system of polyions as the next step. In both cases the continuous and discrete models of chains were considered and Monte Carlo simulation method within Wang–Landau algorithm was used. It allowed to obtain the energy-distribution functions that in its turn made it possible to calculate various thermal properties of the systems in a wide temperature range: thermodynamic quantities and structural characteristics (root mean-square radius of gyration, root mean-square distance between the centers of mass of two polymers).

Keywords: lattice models; Monte Carlo simulation; polyelectrolytes; thermodynamics

Introduction

Monte Carlo (MC) method proposed by Metropolis et. al. sixty years ago[2] proved to be a powerful tool in studying a large variety of highly nonideal molecular systems.[3,4] On the other hand, the conventional MC procedure becomes ineffective in a number of important physical situations. In order to study systems with rough landscape of potential energy with great number of local minima, or considering phase transitions and other phenomena taking place at low temperatures, high densities or in presence of complex molecular components it is necessary to modify the standard approach. Such modifications are known now as generalized ensembles MC.[5,6] They include the expanded ensemble MC[7,8] and entropic sampling (ES)[9,10] which proved to be effective in solving the above mentioned problems. Their common drawback was that they required a preliminary procedure to obtain a set of initially unknown parameters (''balancing factors'')[7] which play a key role in the simulation. In 2001 Wang and Landau (WL) proposed an algorithm, in which automatic adjustment of these parameters in entropic sampling is performed.[11]

In our molecular simulation group (at Dep.Mol.Biophys.) the WL algorithm is actively used for sampling of polymer systems.[12–15] In particular we decided to simulate the process of approachment of the DNA to the substrate. The aspect of interest is that the negatively charged DNA is deposited on the negatively charged

Faculty of Physics, St. Petersburg State University, Ul'yanovskaya ul. 1, Petrodvorets, 198504 Russia
E-mail: aaju@yandex.ru

substrate.[1] The first part of our paper is aimed at simulation of this phenomenon. In the preceding paper "Study of the polymer interaction with a surface by entropic sampling"[16] the behavior of an uncharged polymer chain near an uncharged wall was studied.

In the second part a system of two uncharged polymer chains with attractive or repulsive intrachain interaction and variable attraction between chains is considered. In an actual single component polymer system all interactions should be chosen equal. This case is also presented in the paper. Extension of interaction types is made in methodological purpose as a first step for further simulation of polyionic systems which is being performed now.

In this paper the ES–WL method is applied to study both systems within lattice and continuum models. We consider the thermal case, in which interaction between monomers is introduced. For both models the energy distribution functions are calculated that provides further calculation of the internal energy, the mean-square radius of gyration and mean-square distance between the centers of mass of two polymers in a wide temperature range.

The article is organized as follows. First, the methods and algorithms used for obtaining distribution functions and calculation of averages are described. Then follow the descriptions of each of two models with further sections containing the obtained results and their discussion. Finally conclusions of the work are presented.

The Entropic Modeling Method and the Wang–Landau Algorithm

The purpose of the method is to obtain density of energy states Ω. Entropic modeling method[9,10] has the following basis. Performing a random walk in the energy space with transition probabilities proportional to the inverse density of states $1/\Omega(E)$, we compensate the natural distribution of the energy and this way get uniform visiting rates of all energy states. Let us write the configuration integral in the canonical ensemble in the form

$$Z(\beta) = \int \epsilon^{-\beta\Theta(\vartheta)}\delta\vartheta = \int \Omega(\mathrm{E})\epsilon^{-\beta\Theta(\vartheta)}\delta\mathrm{E} = \int \epsilon^{\Sigma(\mathrm{E})-\beta\mathrm{E}}\delta\mathrm{E},$$

where β is the inverse temperature, $\Omega(E) = \int \delta(U(q) - E)dq$ and $S(E) = \ln\Omega(E)$ is the entropy for a given value of E. Wang–Landau algorithm[11] solves the problem of determining Ω. The range of energy of the system $E_{\min} \le E \le E_{\max}$ is divided into a finite number of N_b equal segments ("boxes"). We introduce an array of Ω consisting of N_b elements, which correspond to these segments. In calculations it is convenient to use the entropy $S(E) = \ln\Omega(E)$. Initially, all Ω_k are taken to be equal. At each MC step the conformation of the system is being changed. Let E_1 and E_2 be the initial and the trial energies of the MC-step. Each conformation corresponds to its "box" i-th and j-th. The trial state j is accepted with probability

$$p(E_1 \to E_2) = \min\left(1, \frac{\Omega_i}{\Omega_j}\right) = \min(1, e^{S_i - S_j}).$$

In the case of failure, the system remains in its initial state, and the procedure is repeated for the new MC-step. Each time when visiting the k-th "box" (in the case of transition the state k is equal to the trial state j, in the case of failure $k = i$) k-th element of the array Ω is multiplied by the increment $c > 1$ (the term $\Delta S = \ln c$ is added to S_k): $\Omega_k \to \Omega_k c$, $S_k \to S_k + \Delta S$. In each m-th series of MC-steps c remains constant. In the next series c decreases so that for example $c_{m+1} = \sqrt{c_m}$ ($\Delta S_{m+1} = 0.5\Delta S_m$).[11] We also introduce an array of visits n, initially its elements are zero. At each MC step unity is added to the cell n_k while $S_k \to S_k + \Delta S$. Wang–Landau algorithm provides automatic adjustment and further fine tuning of uniform visiting rates distribution of the n_k boxes, which indicates the correct determination of densities Ω. At the end of calculation density Ω is normalized on unity.

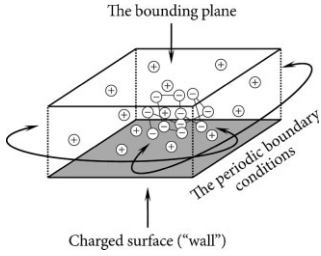
This way, during the computer experiment the shares of $\Omega(E_i)$ are determined,

corresponding to i-th segments of the energy. The canonical average of any quantity f is calculated using the following formula $\langle f\rangle(\beta) = \sum_{i=1}^{N_b} f_i \Omega_i \exp(-\beta E_i) \Big/ \sum_{i=1}^{N_b} \Omega_i \exp(-\beta E_i)$, where f_i is the value of f for the i-th segment of energy.

Behavior of a Polyion at the Charged Wall of the Same Sign: Model

The polyion is a sequence of $N+1$ nodes-monomers each possessing a unit negative charge and connected by the N immaterial segments of unit length. We studied the interaction of a single polyion with infinite charged homogeneous ''wall'', which occupies half-space with infinite flat surface. The charge of the ''wall'' is uniformly distributed over its surface with the density $\sigma = -0.01$. Also the counterions are presented in the system, their charges can range from 1 to 4 (in different experiments) and their number is chosen so as to provide electrical neutrality of the entire system. Coulomb interaction between all elements is introduced.

The system is placed in a cell with the size of $2N \times 2N \times N$ (N is the length of the polyion) with periodic boundary conditions imposed in X and Y directions along the ''wall'' and with a restriction in the Z-direction perpendicular to the ''wall''. In presence of the ''wall'' the system is limited in Z direction with $Z = N$. In the discrete model the lattice for the ions is shifted with respect to the lattice of monomers by half the length of the lattice unit in all three directions.



Position of two monomers or two ions at the same point is considered to be a selfintersection in the system. In the case of the continuum model the monomers and the ions are spheres with unit diameter (segment length). Location of centers of two monomers and (or) of ions at a distance smaller than the diameter of the system is a self-intersecting.

It is generally accepted that the Ewald summation is the most consistent way to treat long-range electrostatic interactions. In [14] it was shown that the minimum image approach gives results practically coinciding with the Ewald summation for short ($N = 10, 30$) flexible polyelectrolyte. At the same time the minimum image convention works much faster. So for self-nonintersecting conformations the energy is calculated as the sum of pair electrostatic interaction between all the elements by using method of minimum image convention.

The natural units for our model are the lattice constant l (segments length) and monomers charge q. So the energy is measured in q^2/l units and the temperature in $q^2/(l \cdot k_B)$.

At each MC-step the polyion chain conformation or one of the position of counterions is modified with equal probability 0.5. There are three ways of chain modification:

1) Shift: the chain is moved as a whole a few steps along the Z axis and the rest of the system remains unchanged.
2) Reptation: the first few units (not more than $N/5$, i.e. the chain ''head'') are cut off, and the ''tail'' is built up so that the chain retains its length.
3) Cutting off the ''tail'': the last few units of the ''tail'' are cut off and the new random ones are built up.

A counterion is displaced by a small distance.

Behavior of a Polyion at the Charged Wall of the Same Sign: Results

The results are presented as the plots for the discrete (Figure 1–3) and continuum

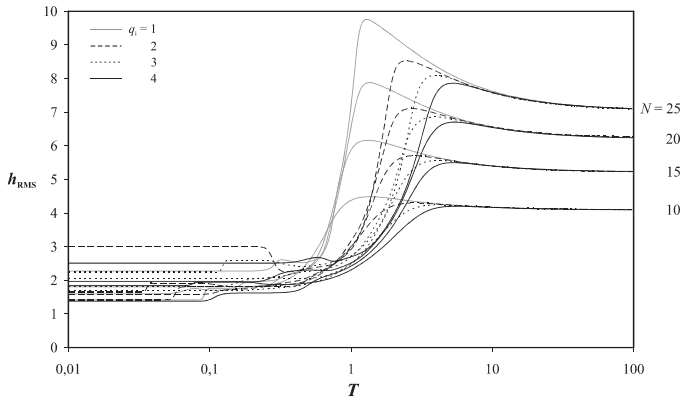


Figure 1.
Lattice model: the dependence of the root mean square end-to-end distance on the temperature for different lengths of polymers N and charges of ions q_i.

(Figure 4–6) models. One can make the following conclusions. Effect of deposition of the polyion on the substrate with the same charge was clearly observed. It is explained by dominance of positive charge counterions, which surround either polyion or ''wall'' producing the so called overcharging effect. Thus by lowering the temperature, the polyion approaches (deposits) to the surface of the wall (Figure 2, 5). The mean distance from the center of mass of polyion to the ''wall'' tends to zero with decreasing temperature. The effect increases with the ion charge increase.

On the whole polyion behaves as a flexible free polyion in the solution (Figure 1, 4).[14] At high temperatures, the mean distance between the ends of the polyion tends to the distance between the ends of the uncharged polymer without self-intersection $h_{RMS} = N^{3/5}$. At temperatures $T = 1 \div 5$ swelling of the coil polyion is observed due to the repulsion of monomers from each other. But at low temperatures due to condensation of counterions compaction of polyion occurs, the so-called transition to a globule.

Behavior of Two Equal Polymer Chains: Model

The polymer is presented as a sequence of $N+1$ nodes-monomers connected by the N

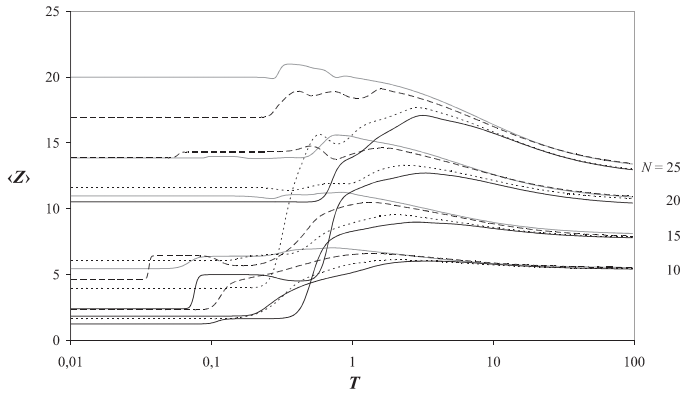


Figure 2.
Lattice model: the dependence of the mean distance from the center of mass of polyion to the ''wall'' on the temperature. (See legend of Figure 1).

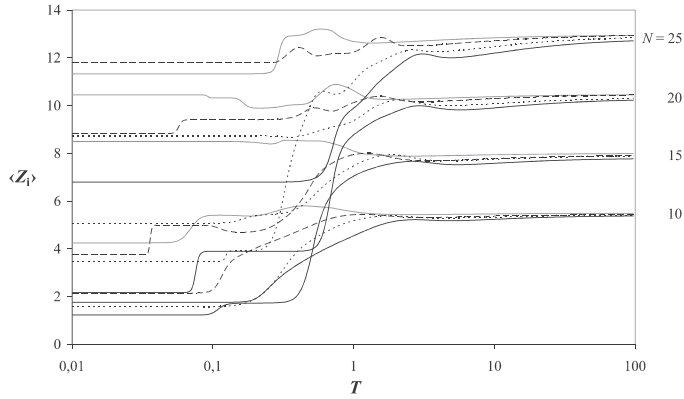


Figure 3.
Lattice model: the dependence of the mean *z*-coordinates of the ions on the temperature. (See legend of Figure 1).

immaterial segments of unit length. The system is placed in a cubic cell with the edge length L being equal to the double length of the polymer chain. The periodic boundary conditions are imposed in all three Cortesian directions. Thus we have specific volume (determined as $L^3/(2N+2)$) from 83,33 to 2403,85.

In the lattice model the non-reversal random walks (NRRW) are used for generating of the chain. In this model the k-th node-monomer can not overlap with the $(k-2)$-th one, such chains are called semi-phantom.[12,13]

At each MC-step one of the two polymer chains is modified. The chain is chosen with probability 0.5. Coordinates of the chosen chain X are modified in one of the four following ways (with probability 0.25):

1) $X_k^{\text{new}} = X_k^{\text{old}}$, $0 \le k \le N - N_c$ and for $N - N_c + 1 \le k \le N$ X_k^{new} are generated randomly by NRRW (the "head" of the chain is preserved, but the "tail" is modified);
2) $X_k^{\text{new}} = X_k^{\text{old}}$, $N_c \le k \le N$ and for $0 \le k \le N_c - 1$ X_k^{new} are generated

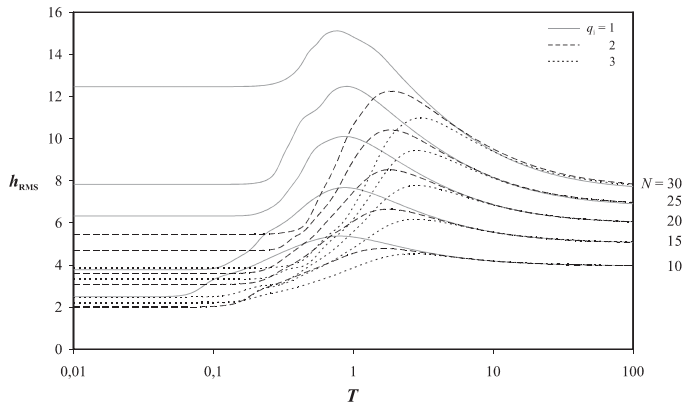


Figure 4.
Continuum model: the dependence of the root mean square end-to-end distance on the temperature for different lengths of polymers N and charges of ions q_i.

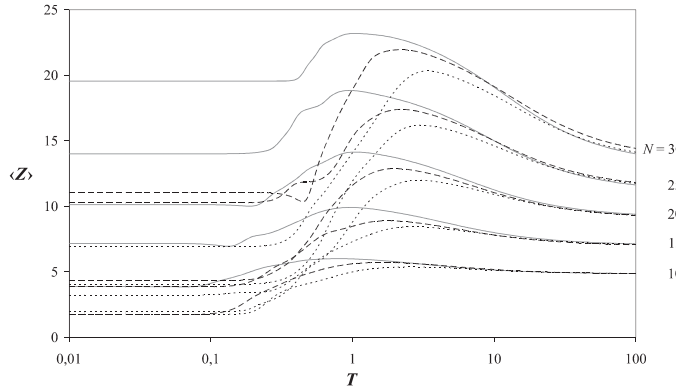


Figure 5.
Continuum model: the dependence of the mean distance from the center of mass of polyion to the "wall" on the temperature. (See legend of Figure 4).

randomly by NRRW (the "tail" of the chain is preserved, but the "head" is modified);

3) $X_k^{\text{new}} = X_{k+N_c}^{\text{old}}$, $0 \le k \le N - N_c$ and for $N - N_c + 1 \le k \le N$ X_k^{new} are generated randomly by NRRW (the "head" of the chain is removed and the "tail" is newly grown);
4) $X_k^{\text{new}} = X_{k-N_c}^{\text{old}}$, $N_c \le k \le N$ and for $0 \le k \le N_c - 1$ X_k^{new} are generated randomly by NRRW (the "tail" of the chain is removed and the "head" is newly grown).

Here X_k^{new} is a three-dimensional vector of coordinates of the k-th monomer for the newly built chain conformation. N_c is randomly chosen from 1 to $N/5$ at each MC-step. In the process of computer modeling for each conformation of the constructed system it is determined whether the conformation is self-intersecting one or not. In the discrete model the location of two monomers at the same point is considered to be a self-intersection of the system. In the continuum model nodes are spheres with a diameter d, and the approach of any pair of monomers (except those linked in the chain) at a distance less than their diameter, is considered as a self-intersection in the system.

For non-self-intersecting conformations the energy is calculated as a sum of pair potentials of interaction between monomers (excluding linked ones). In the case of the lattice model each contact (the location of the monomers at a unit distance) corresponds to the energy ε_{ij}, where i, j are the indices of polymer chains (1 or 2). In the continuum model the interaction between monomers is described by Lennard–Jones potential $U(r) = -4\varepsilon_{ij}((d/r)^{12} - (d/r)^6)$ (for $\varepsilon_{ij} < 0$) and its repulsive part $U(r) = 4\varepsilon_{ij}(d/r)^{12}$ (for $\varepsilon_{ij} > 0$), where r is the distance between the centers of monomers, d is the diameter of monomers.

We investigate only attractive interchain interaction ($\varepsilon_{12} < 0$). Parameters ε_{11} and ε_{22} are equal ($\varepsilon_{11} = \varepsilon_{22} = \varepsilon$). We investigate situations when interchain interactions are essentially less ($\varepsilon_{12} = 0.2\varepsilon$), coincide ($\varepsilon_{12} = \pm\varepsilon$) and greatly higher ($\varepsilon_{12} = 5\varepsilon$) than intrachain interaction.

So the energy is measured in ε-units and the temperature in $|\varepsilon|/k_B$.

The variation range for E was determined in preliminary runs (computer experiments). This range of the energy $E_{\min} \le E \le E_{\max}$ was divided into N_b «boxes».

As long as the share of non-self-intersecting chains is very small (especially for long polymers), and the share of self-intersecting chains is large, sorting by the number of intersections was carried out: four "boxes" were introduced instead of a single one. The first box corresponds to

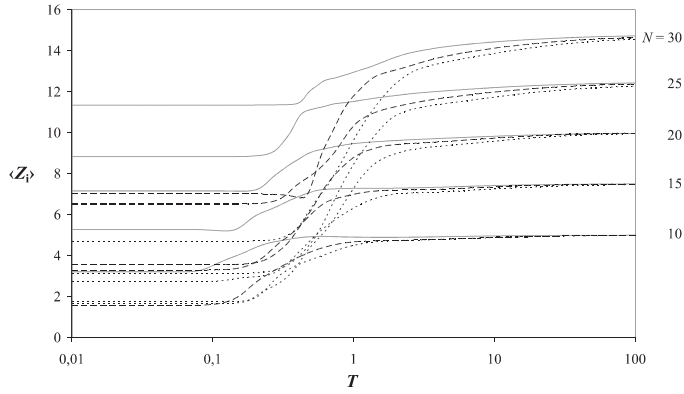


Figure 6.
Continuum model: the dependence of the mean *z*-coordinates of the ions on the temperature. (See legend of Figure 4).

chains with 1–4 self-intersections, the second, the third and the forth ones were for 5–10, 11–18 and for chains with more than 19 self-intersections correspondingly. This allowed us to avoid ''freezing'' the system in a single ''box'', corresponding to the much larger volume of conformational space compared to others.

As a result of computer simulation using the Wang–Landau algorithm the distribution function over ''boxes'' (Ω_i) was determined. With the aid of this function the canonical values of the internal energy, the mean-square radius of gyration and the mean-square distance between the centers of mass of two polymers were determined.

Behavior of Two Equal Polymer Chains: Results

As a result of computer simulation we have determined the energy distributions for polymers with length $5 \leq N \leq 25$ and different energies of interaction of the monomers.

Figure 7 shows a normalized visiting histograms for boxes n_k for the lattice model, their flatness indicates the correct tuning of densities Ω. The dependences are presented in the plot with parameters $\varepsilon_{12} = \varepsilon < 0$ (for other investigated systems box visiting are similar). Good uniform visiting is observed at all energy ranges except a small deviation at smallest energy for $N = 25$.

The resulting distributions Ω for both models are shown in Figure 8 and 9. Note that the figures show the energy distributions only for non-self-intersecting chains.

Figure 10 and 11 present the results for the root mean-square radius of gyration (R) and the root mean-square distance between the centers of mass of polymers (D) as a function of temperature for the lattice model. Same dependences for continuum model are presented in Figure 12 and 13. The dependences $R(T)$ demonstrate contraction of the polymer size at low temperatures. At the same time in Figure 11 and 13 one can observe sharp approach of centers of mass of polymers with the decrease of temperature that corresponds to a coil-globule transition.

Two regimes of compactization are observed. If the interaction within each chain is either repulsive ($\varepsilon > 0$) or weakly attractive ($|\varepsilon| < |\varepsilon_{12}|$), at low temperatures due to mutual attraction of their monomers ($\varepsilon_{12} < 0$) there occurs common compactization of the system with tightly interwoven chains. Another regime corresponds to strong attraction inside each polymer ($|\varepsilon| >> |\varepsilon_{12}|$). In this case each chain becomes compact separately and then two separate globules attract each other

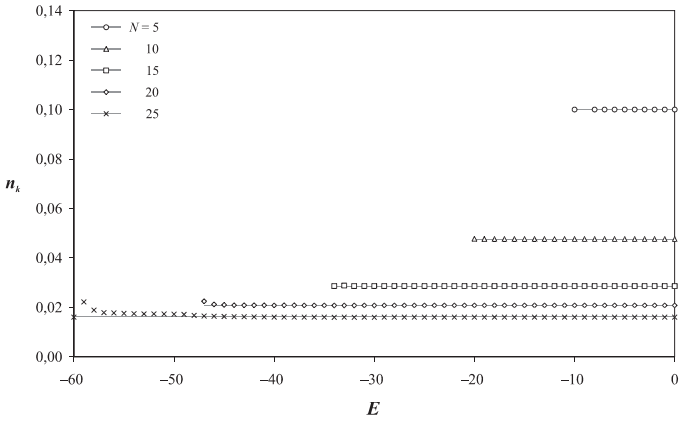


Figure 7.
Normalized visit rates, compared with prescribed levels (horizontal lines) for different lengths of polymers N (lattice model, energy parameters are $\varepsilon_{12} = \varepsilon < 0$).

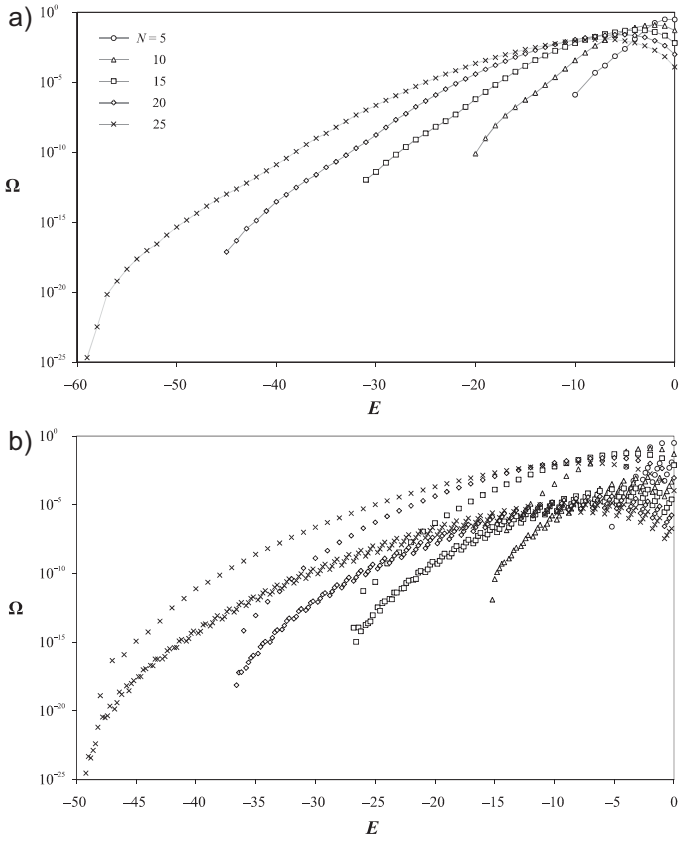


Figure 8.
Lattice model: the energy-distribution function for different lengths of polymers N and energy parameters: $\varepsilon < 0$ and $\varepsilon_{12} = \varepsilon$ (a), $\varepsilon_{12} = 0.2\varepsilon$ (b), $\varepsilon_{12} = 5\varepsilon$ (c); $\varepsilon > 0$ and $\varepsilon_{12} = -\varepsilon$ (d) (The lines were drawn to guide the eye).

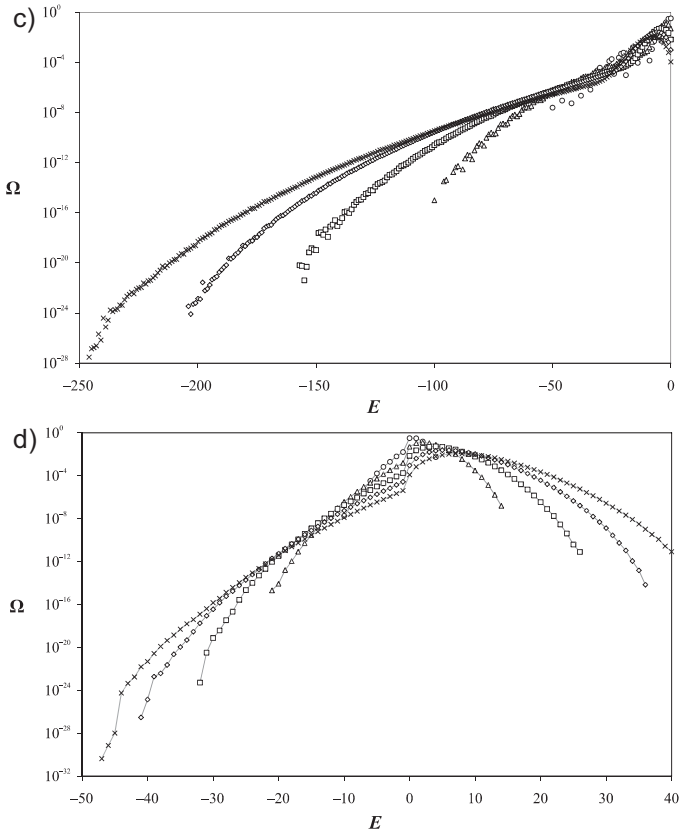


Figure 8.
(Continued).

"sticking" finally together with their surfaces. "Sticking" becomes significant at lower temperatures.

Conclusion

Wang–Landau algorithm used in the present work allows to calculate the energy distribution function in a wide energy range needed to calculate physical quantities in a wide range of temperatures. The advantage of this algorithm is that it finds and properly accounts for the states of the system with very small probabilities (within 20–25 orders).

The investigation of the behavior of a polyion at the charged wall of the same sign gave the result corresponding to the experimental data of other researchers for DNA[1] where the deposition of the polyion on the substrate was observed. At this point we can say that our simulation is reliable and can be extended to the modeling of more complicated systems with more elements.

We investigated the interaction of two semi-phantom polymer chains with different energies of interaction. The length of the chains were taken relatively small, since in the case of longer chains longer computer time is needed to obtain satisfactory results. This system can be comparatively easy modified into a more complicated one, for instance by introducing charges located on node-monomers and adding counter ions to the system, i. e. considering a polyelectrolyte.

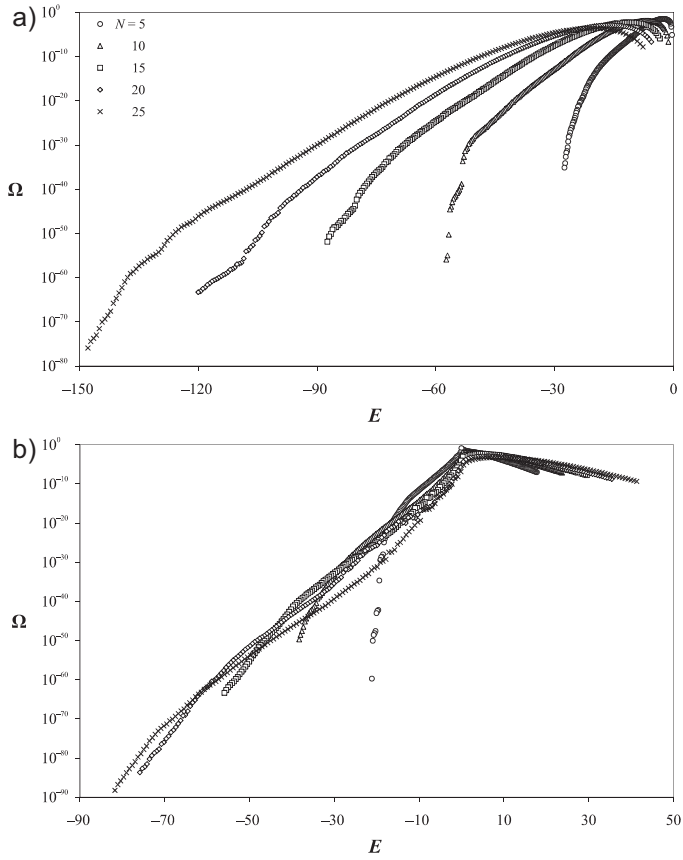


Figure 9.
Continuum model: the energy-distribution function for different lengths of polymers N and energy parameter: a) $\varepsilon < 0$, $\varepsilon_{12} = \varepsilon$; b) $\varepsilon > 0$, $\varepsilon_{12} = -\varepsilon$.

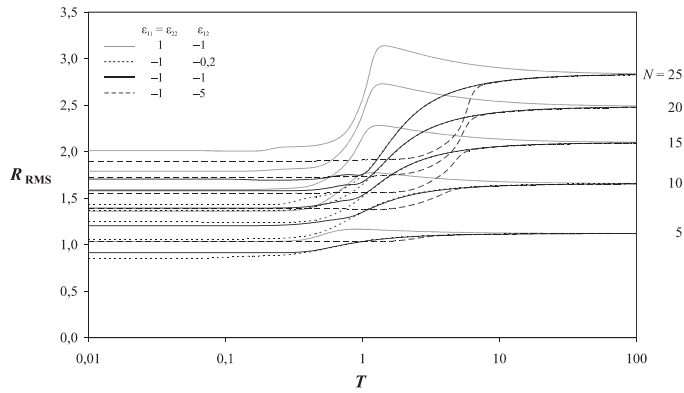


Figure 10.
Lattice model: The dependence of the mean radius of gyration of the polymer on temperature ($|\varepsilon|/k_B$ units).

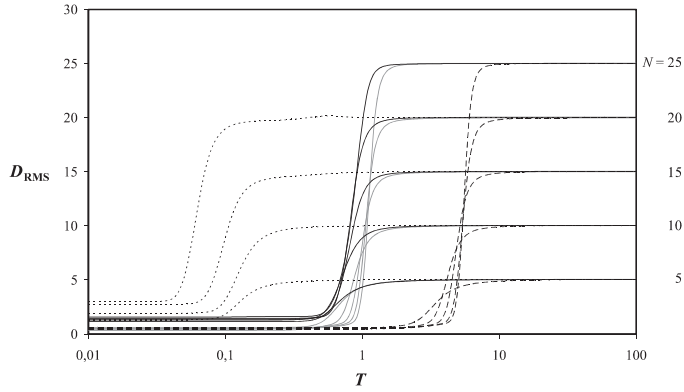


Figure 11.
Lattice model: the dependence of the mean distance between the centers of mass of polymers on temperature ($|\varepsilon|/k_B$ units) for different lengths N and energy parameters ε_{11}, ε_{22}, ε_{12} (see legend of Figure 11).

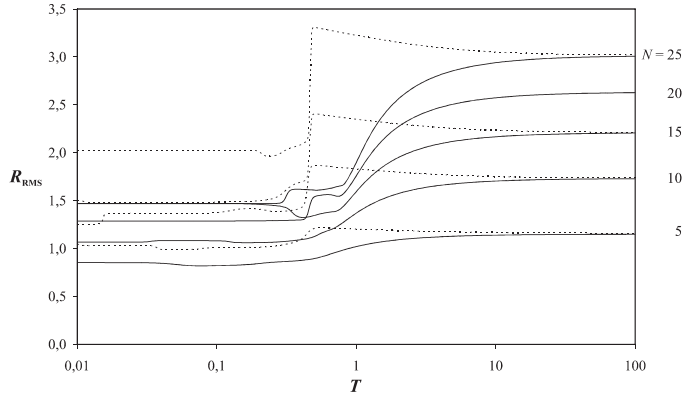


Figure 12.
Continuum model: The dependence of the mean radius of gyration of the polymer on temperature ($|\varepsilon|/k_B$ units) for different lengths N in the cases of attraction (solid line) and repulsive (dashed lines) of the monomers in a single chain. $d = 1$.

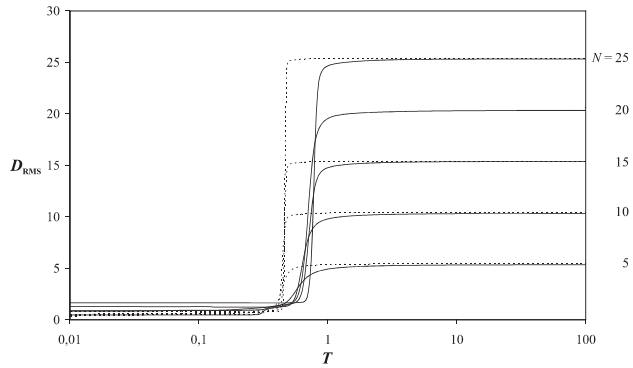


Figure 13.
Continuum model: The dependence of the mean distance between the centers of mass of polymers on the temperature ($|\varepsilon|/k_B$ units) at different lengths N in the cases of attraction (solid line) and repulsive (dashed lines) of the monomers in one chain. $d = 1$.

Acknowledgements: The work was supported by the grant of RFBR 11-02-00084.

[1] A. O. Puchkova, P. Sokolov, Yu. V. Petrov, N. A. Kasyanenko, *Journal of Nanoparticle Research*. **2011**, February *16*, 1.
[2] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, *J. Chem. Phys.* **1953**, *21*, 1087.
[3] K. Binder, ''*Monte Carlo Methods in Statistical Physics*'', Springer, Berlin **1979**.
[4] M. P. Allen, D. J. Tildesley, ''*Computer Simulation of Liquids*'', Clarendon, Oxford **1987**.
[5] Y. Iba, *Int. J. Mod. Phys. C* **2001**, *12*, 623.
[6] A. Mitsutake, Y. Sugita, Y. Okamoto, *Biopolymers* **2001**, *60*, 96.
[7] A. P. Lyubartsev, A. A. Martsinovskii, S. V. Shevkunov, P. N. Vorontsov-Velyaminov, *J. Chem. Phys.* **1992**, *96*, 1776.
[8] E. Marinari, G. Parisi, *Europhys. Lett.* **1992**, *19*, 451.
[9] B. A. Berg, T. Neuhaus, *Phys. Rev. Lett.* **1992**, *68*, 9.
[10] J. Lee, *Phys. Rev. Lett.* **1993**, *71*, 211.
[11] F. Wang, D. P. Landau, *Phys. Rev. Lett.* **2001**, *86*, 2050.
[12] P. N. Vorontsov-Velyaminov, N. A. Volkov, A. A. Yurchenko, *J. Phys. A: Math. Gen.* **2004**, *37*, 1573.
[13] N. A. Volkov, A. A. Yurchenko, A. P. Lyubartsev, P. N. Vorontsov-Velyaminov, *Macromol. Theory Simul.* **2005**, *14*, 491.
[14] N. A. Volkov, P. N. Vorontsov-Velyaminov, A. P. Lyubartsev, *Phys. Rev. E.* **2007**, *75*, 016705.
[15] P. N. Vorontsov-Velyaminov, N. A. Volkov, A. A. Yurchenko, A. P. Lyubartsev, *Polymer Science, Ser A.* **2010**, *52*, 1133.
[16] A. A. Yurchenko, M. A. Antyukhova, P. N. Vorontsov-Velyaminov, *Journal of Structural Chemistry* **2011**, *52*, 1179.

