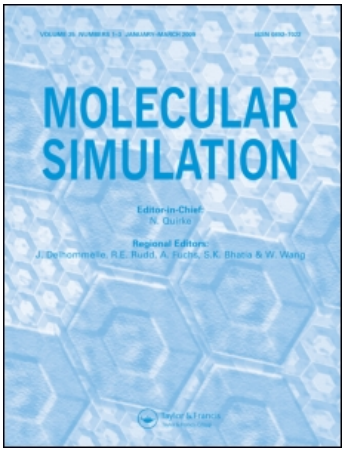

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The Distribution of the Gyration Radius of a Model of Ionomer Studied by Multicanonical Monte Carlo Simulation

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THE DISTRIBUTION OF THE GYRATION RADIUS OF A MODEL OF IONOMER STUDIED BY MULTICANONICAL MONTE CARLO SIMULATION

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We investigated the behavior of a chain with stickers on two dimensional lattice using multicanonical Monte Carlo simulation. In our model, the stickers interact with all the other stickers. We calculated the radius of gyration, the end-to-end distance, and the specific heat to study the temperature dependence of the chain configurations. We obtained the distribution of the radius of gyration and found that the distribution has two peaks at temperature $kT = 0.10u_0 \sim 0.15u_0$, in contrast to other models with interactions only between paired stickers. At this temperature, the polymer makes a transition from the state with separated stickers to the state with combined stickers.

Keywords: Ionomer; sticker; multicanonical Monte Carlo simulation; radius of gyration; end-to-end distance

1 INTRODUCTION

Ionomers are polymers that have ionic monomers on the chain and are neutralized by monovalent or divalent metallic ions. With neutralization, the interactions work between ionic monomers, and the chain behaviors are much different from those without interaction. [1–3]

Some studies [4–7] have shown that the chain behavior depends on the positions of ionic groups on the chain. Such ionic groups are called "stickers". Baljon [7] studied the change from ordinary chain behavior to a collapsed chain behavior as a function of sticker position in the large N monomers limit. They calculated the chain configuration at $T = 0$.

In our previous paper, [8] we investigated the temperature dependence of the chain behavior on a two dimensional lattice by using the model where the interactions worked between pairing stickers. For that model, the radius of gyration and the end-to-end distance changed drastically at some temperature, and the distribution of the radius of gyration had one peak for any temperature.

In this paper, using the model where the interactions between stickers can work between more than two stickers, we investigated the temperature dependence of the chain behavior on a two dimensional lattice. The results of the distribution of the radius of gyration are quite different from those for our previous model. This kind of the distribution of the radius of gyration is observed experimentally in other polymers. [9]

In Section 2, we describe the positions of stickers on the chain and the interactions between stickers for our model. Details of the simulation methods are described in Section 3. The simulation results are given in Section 4, and the paper is concluded in Section 5.

2 MODEL

In our simulations, we have used a simple model of ionomer as shown in Figure 1. The chain has several monomers called stickers, and the stickers are equally spaced to the chain.

We have treated the chain as a self-avoiding random walk (SAW) on a two dimensional square lattice. Two monomers cannot occupy the same lattice site at the same time. The interaction between stickers is assumed to work for both the nearest neighbor sites and the next nearest neighbor sites. We have used the bond fluctuation method [10] to move the chain, and the interaction is

$$u = \begin{cases} -u_0 & (r = 2A) \\ -u_0/2 & (r = \sqrt{5}A) \\ 0 & (\text{otherwise}), \end{cases} \tag{1}$$

where r is the distance between stickers, A is the lattice constant of the square lattice, and u_0 denotes the unit energy ($u_0 > 0$). This interaction works between all stickers.

FIGURE 1 The chain architecture. ● are stickers, and ○ are non-stickers. The stickers are equally spaced on the chain.

3 SIMULATION METHOD

To move the chain, we have used the bond fluctuation method, devised by Carmesin and Kremer [10]. In this method, the bond length l between two adjacent monomers is allowed to be $2 \leq l \leq \sqrt{13}$ on the two dimensional square lattice. This method is ergodic and one could obtain the scaling law in the case of random walk and self-avoiding random walk.

For ionomers, the attraction energy between stickers is very large, of order kT, and many stickers combine with other stickers at the room temperature. We have to simulate at lower temperature than the attraction energy between stickers. But in the Metropolis method, the probability to disconnect the combination of stickers is $e^{-\beta \Delta U}$, where ΔU denotes the attractive energy, $\beta = 1/kT$, k is the Boltzmann constant, and T is the temperature. At low temperature, this probability becomes very small, and the state of the chain does not easily transfer to other states. We have to simulate for a long time to obtain accurate data. To overcome this problem, we use multicanonical Monte-Carlo algorithm. [11, 12]

The basic idea of this method is that the Monte-Carlo simulation is performed in a multicanonical ensemble instead of the canonical ensemble. We use the weight factor $e^{\alpha(U)-\beta(U)U}$, where U denotes the total energy of the chain, instead of $e^{-\beta U}$. In the multicanonical ensemble, the energy distribution is approximately flat. It is easier to overcome the barriers between local minima, and we could sample the various configurations of the chains. In addition to that, we can calculate the physical values at all temperatures in only one simulation.

In order to make the energy distribution approximately flat, $\alpha(U)$ and $\beta(U)$ are determined as follows:

$$\begin{aligned} \beta(U_k) &= 9.0/u_0 + \frac{1}{U_{k+1} - U_k} \log \frac{P(U_{k+1})}{P(U_k)} \\ \alpha(U_{k+1}) &= \alpha(U_k) - (\beta(U_{k+1}) - \beta(U_k))U_{k+1} \end{aligned} \tag{2}$$

where $P(U)$ denotes the canonical distribution, the subscripts k denote the energy levels. First, we perform a simulation with the Metropolis sampling method at $\beta = 9.0/u_0$ to obtain the canonical distribution. At $\beta = 9.0/u_0$, we can sample all energy states. Next, we substitute $P(U)$ for Equation (2). By choosing the initial value $\alpha(U_1)$, we can make the energy distribution approximately flat.

4 RESULTS

We performed multicanonical simulations for a linear polymer with 36 monomers, including 4 stickers. In those simulations, we calculated the radius of gyration and its distribution, the end-to-end distance, and the specific heat. The radius of gyration R_g is defined by

$$R_g^2 = \frac{1}{N}\left\langle \sum_{i=1}^{N} (r_i - r_0)^2 \right\rangle, \tag{3}$$

where $\langle\rangle$ is the statistical average, N denotes the number of monomers, r_i is the position vector of the i-th monomer, and r_0 is the position vector of the center of gravity of a chain. The end-to-end distance R is defined by

$$R = \langle |r_1 - r_N| \rangle. \tag{4}$$

We also calculated the specific heat both from the energy fluctuation and the numerical derivative of the energy.

$$C = \frac{\langle U^2 \rangle - \langle U \rangle^2}{NkT^2} \tag{5}$$

$$C = \frac{1}{N}\frac{dU}{dT} \tag{6}$$

where U denotes the total energy of the chain.

Here we define 1 Monte-Carlo Step (MCS) as N trials of bond fluctuation method, where N denotes the total number of monomers in a chain. We carried out 3×10^8 MCS in one simulation, and measured the physical quantities over every 10 MCS. To estimate error bars, we performed five different runs with different initial configurations and random number seeds.

In Figure 2 we show the temperature dependence of the radius of gyration. This result shows that at high temperature the chain elongates and at low temperature the chain collapses. This transformation of the chain occurs between $kT = 0.1u_0$ and $0.2u_0$. In Figure 3 we show the temperature

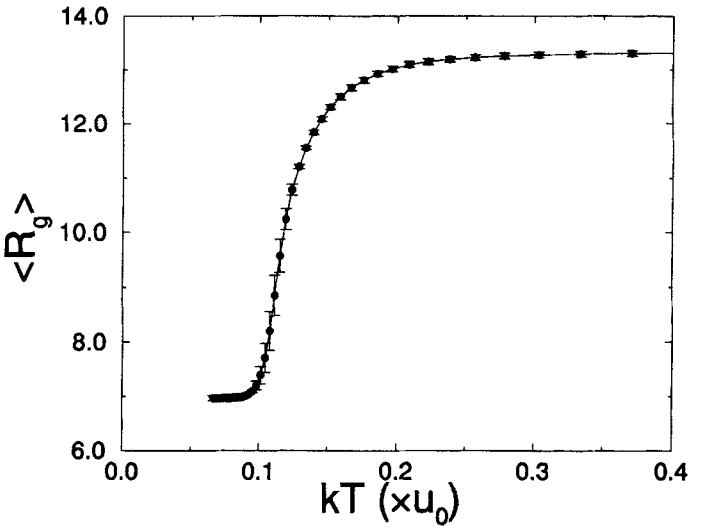

FIGURE 2 The temperature dependence of the radius of gyration.

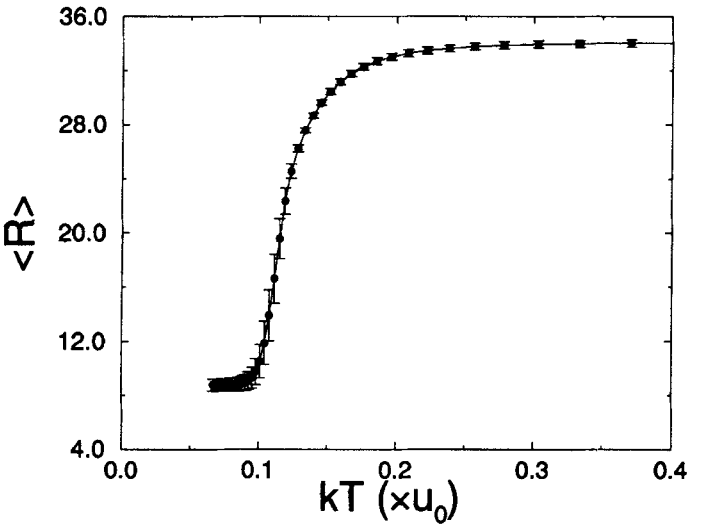

FIGURE 3 The temperature dependence of the end-to-end distance.

dependence of the end-to-end distance, and the results are similar to those of the radius of gyration.

We also investigated the distribution of the radius of gyration. In the case of a chain with only self-avoiding interactions between monomers, the

distribution function of the radius of gyration has the following form; [13, 14]

$$P(R_g, N) = \exp\left[- A_1 \left(\frac{N^v}{R_g}\right)^{\alpha d} - A_2 \left(\frac{R_g}{N^v}\right)^{\delta} - A_3 \right], \tag{7}$$

where

$$\alpha = (vd - 1)^{-1}, \quad \delta = (1 - v)^{-1}. \tag{8}$$

Here, A_1, A_2 and A_3 are fitting parameters, d is the space dimension, and v denotes the Flory exponent. For two dimensional self-avoiding walk, $v = 0.75$, and this distribution function corresponds to the case of $\beta = 0.0$ in our simulation.

In Figure 4 we show the distribution of the radius of gyration at infinite temperature, $\beta = 0.0$. The solid line in this figure is a fit to Equation (7). The fitting parameters A_1, A_2, and A_3 are shown in Table I. We can see that our simulation data is in agreement with Equation (7).

In Figure 5 we show the distribution of the radius of gyration at $\beta = 0.0$, $9.0/u_0$ and $12.0/u_0$. In our previous study [8] of the model with stickers interacting only between pairs, the distribution of the radius of gyration had

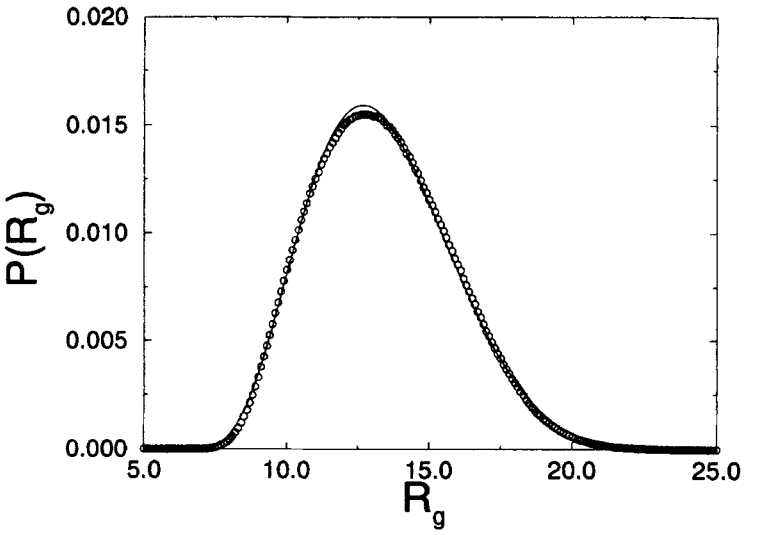

FIGURE 4 The distribution of the radius of gyration at $\beta = 0.0$. The solid line is a fit to Equation (7).

TABLE I Results for A_1, A_2, A_3 from a fit to Equation (7)

A_1	A_2	A_3
0.3874 ± 0.0002	1.2752 ± 0.0004	2.7348 ± 0.0007

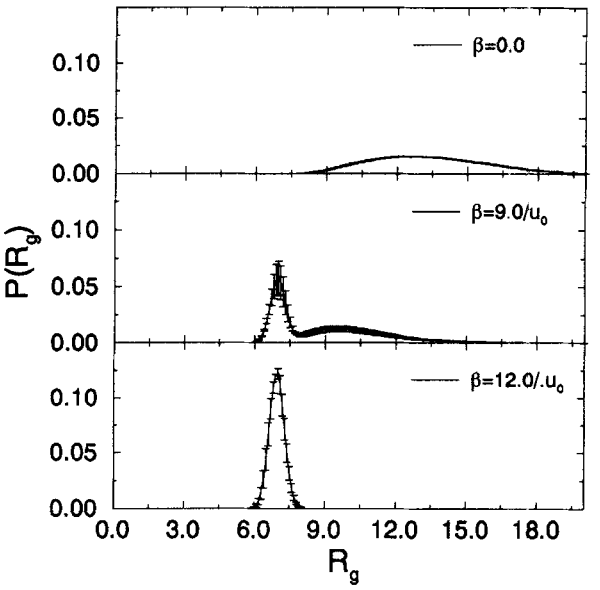

FIGURE 5 The distributions of the radius of gyration at $\beta = 0.0$, $9.0/u_0$, and $12.0/u_0$.

one peak at all temperautre. In contrast to that, with our present model, the distribution of the radius of gyration has two peaks at an intermediate temperature.

In Figure 6, we show the time dependence of the radius of gyration. We calculated the values of the radius of gyrations for every 10 MCS at $\beta = 0.0$, $9.0/u_0$, and $12.0/u_0$ with the Metropolis method. At $\beta = 0.0$ and $12.0/u_0$, the distribution of R_g has one peak, and R_g takes the values around the peak. At $\beta = 9.0/u_0$, where the distribution of R_g has two peaks, we can observe intermittent jumps of the value of R_g.

We call the peak with larger R_g in Figure 5 peak L and the peak with smaller R_g peak S. In Figure 7 we show the peak positions of the radius of gyrations as functions of temperature. The value of R_g for peak L decreases as the temperature is decreased. But the position of peak S is independent of the temperature, and is at $R_g = 7.0$. At the temperature $kT = 0.10\ u_0 \sim 0.15u_0$,

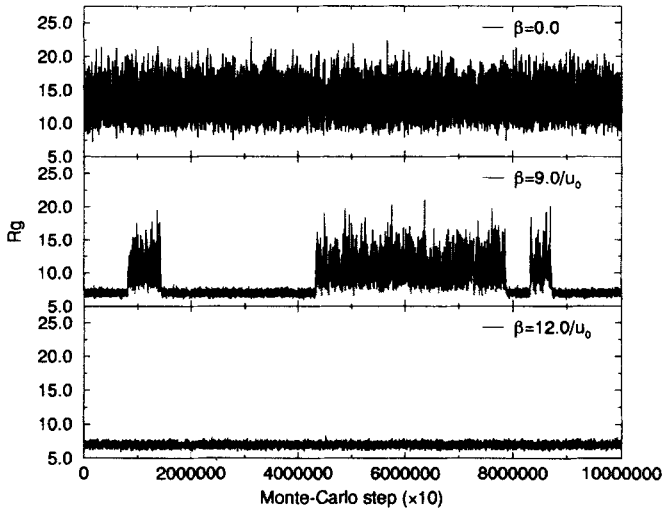

FIGURE 6 The MCS dependence of radius of gyration $\beta = 0.0, 9.0/u_0$, and $12.0/u_0$.

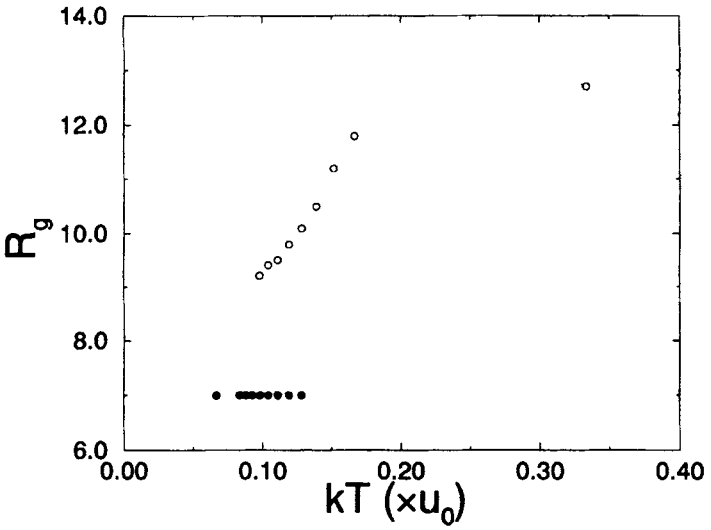

FIGURE 7 The temperature dependence of the peak of the distribution of the radius of gyration. ○ and ● denote peak L and S, respectively.

the peak L and the peak S coexist, and the distribution of the radius of gyration has two peaks. We can see that the structure of the chain changes at the temperature $kT = 0.10u_0 \sim 0.15u_0$.

Next, we investigated the typical configuration of the chain at different temperatures (Fig. 8). At the temperature $\beta = 0.0$, the stickers exist separately as shown in Figure 8(a). At $\beta = 9.0/u_0$, the configurations of the chain would be the two states like Figure 8(b) and (c). In Figure 8(b), some stickers combine with each other, but the stickers do not gather all in one place. In Figure 8(c), the configuration of the chain is the state that all stickers gather in one place. At $\beta = 12.0/u_0$, the typical configuration would be the state like Figure 8(c). The structure of the chain changes from the state with separated stickers to the state with combined stickers at an intermediate temperature.

In Figure 9, we show the temperature dependence of the total energy and the specific heat of the chain. The total energy of the chain drastically changes at the temperature $kT = 0.10u_0 \sim 0.20u_0$, where the radius of gyration and the end-to-end distance drastically change. The specific heats calculated from the energy fluctuation and from the numerical derivative of the energy are equal within error bars. The specific heat has a peak between the temperature $kT = 0.10u_0$ and $0.15u_0$ where the distribution of the radius of gyration has two peaks.

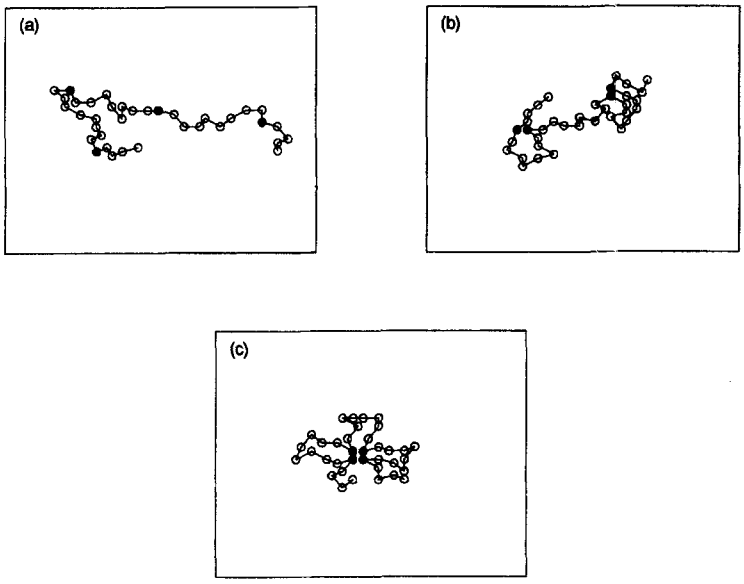

FIGURE 8 The typical configurations of the chain. Stickers are denoted by •, and non-stickers are denoted by ○.

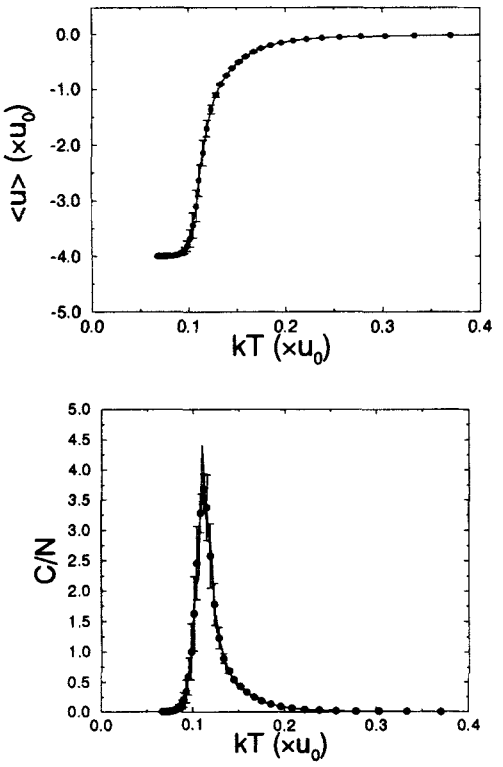

FIGURE 9 (a) The temperature dependence of the total energy of chain. (b) The temperature dependence of the specific heat, calculated from the energy fluctuation (● with errorbars) and the numerical differentiation (solid line).

5 SUMMARY AND FUTURE PROBLEMS

In this paper, we reported our results on our multicanonical Monte-Carlo simulation of a polymer with stickers. In our previous work, we have investigated the model where the stickers interacted only between pairing stickers. For that model, the distribution of the radius of gyration has only one peak at any given temperature. But in the present model, the distribution of the radius of gyration has two peaks at some temperature. At this temperature, the two states coexist. The stickers are separated at high temperature and combined at one place at low temperature. The transition is first-order like, and can be observed for finite chain length. It will be interesting to obtain the functional form of the distribution function of R_g for models with stickers.

In the future, one should study the behavior of the chain where the number of monomers is larger. The initial relaxation and the time spectrum are now under investigation.

Acknowledgements

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References

[1] Lundberg, R. D., Phillips, R. R. (1982). "Solution behavior of metal sulfonate ionomers. II. Effects of solvents", *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1143.
[2] Agarwal, P., Garner, R. T., Graessley, W. W. (1987). "Counterion and solvent effects on the dilute solution viscosity of polystyrene ionomers", *J. Plym. Sci., Part B: Polym. Phys. Ed.*, **25**, 2095.
[3] Duvdevani, J., Agarwal, P. K., Lundberg, R. D. (1982). "Blends of EPDM and sulfonated ethylene-propylene-diene (EPDM) rubber with polypropylene: structure, physical, and rheological properties", *Polym. Eng. Sci.*, **22**, 499.
[4] Cates, M. E., Witten, T. A. (1986). "Chain conformation and solubility of associating polymers", *Macromolecules*, **19**, 732.
[5] Witten, T. A., Cohen, M. H. (1985). "Cross-linking in shear-thickening ionomers", *Macromolecules*, **18**, 1915.
[6] Baljon-Haakman, A. R. C., Witten, T. A. (1992). "Architecture-controlled interaction between associating polymers", *Macromolecules*, **25**, 2969.
[7] Baljon, A. R. C. (1993). "Swollen conformations of associating polymer chains", *Macromolecules*, **26**, 4339.
[8] Urakami, N., Takasu, M. (1996). "Multicanonical Monte-Carlo simulation of a polymer with stickers", *J. Phys. Soc. Jpn*, **65**, 2694.
[9] Minagawa, K., Matsuzawa, Y., Yoshikawa, K., Khokhlov, A. R., Doi, M. (1994). "Direct observation of the coil-globule transition in DNA molecules", *Biopolymers*, **34**, 555.
[10] Carmesin, I., Kremer, K. (1988). "The bond fluctuation method: a new algorithm for the dynamics of polymers in all spatial dimensions", *Macromolecules*, **21**, 2819.
[11] Berg, B., Neuhaus, T. (1992). "Multicanonical ensemble: a new approach to simulate first-order transitions", *Phys. Rev. Lett.*, **68**, 9.
[12] Berg, B., Celik, T. (1992). "New approach to spin-glass simulations", *Phys. Rev. Lett.*, **69**, 2292.
[13] Lhuillier, D. (1988). "A simple model for polymeric fractals in a good solvent and an improved version of the Flory approximation", *J. Phys. France*, **49**, 705.
[14] Victor, J. M., Lhuillier, D. (1990). "The gyration radius distribution of two-dimensional polymer chains in a good solvent", *J. Chem Phys.*, **92**, 1362.