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PROPERTIES OF CONFINED STAR-BRANCHED AND LINEAR CHAINS. A MONTE CARLO SIMULATION STUDY *

Piotr Romiszowski and Andrzej Sikorski

Department of Chemistry, University of Warsaw
Pasteura 1, 02-093 Warszawa, Poland

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A model of linear and star-branched polymer chains confined between two parallel and impenetrable surfaces was built. The polymer chains were restricted to a simple cubic lattice. Two macromolecular architectures of the chain: linear and star branched (consisted of $f = 3$ branches of equal length) were studied. The excluded volume was the only potential introduced into the model (the athermal system). Monte Carlo simulations were carried out using a sampling algorithm based on chain's local changes of conformation. The simulations were carried out at different confinement conditions: from light to high chain's compression. The scaling of chain's size with the chain length was studied and discussed. The influence of the confinement and the macromolecular architecture on the shape of a chain was studied. The differences in the shape of linear and star-branched chains were pointed out.

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1. Introduction

The confinement of macromolecules in a slit is interesting because the presence of the impenetrable surfaces changes dramatically most of the properties of such polymers when compared with the free (unconfined) chains in solution. This problem is also interesting due to its practical applications like lubrication, production of thin polymer films, colloidal stabilization [1]. The properties of polymer under confinement were extensively studied by means of the computer simulation. Van Vliet and ten Brinke carried out Monte Carlo simulations of lattice models of polymer chains [2]. They found that the size of a polymer chain exhibits a universal behavior disregarding its

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length. They also discussed the problem of orientation of the chain between the squeezing walls. Milchev and Binder built an off-lattice model of a polymer chain and studied it by means of the Monte Carlo method [3]. Besides, the results concerning the size of a chain they also calculated the polymer density profiles inside the slit. Recently, some intensive simulations concerning lattice models of single star-branched polymers were done [4–7]. It was shown that besides the universal behavior of the polymer size, the similar results were found for the short-time (relaxation processes) and long-time (self-diffusion) dynamic properties. The possible changes in the mechanism of a chain motion during the squeezing of the walls were discussed there. In this paper we studied models of single linear and star-branched polymers in a slit formed by two parallel and impenetrable walls. We have investigated the dependence of the size, the shape and the structure of the polymer systems as a function of the slit size and the chain length.

2. Model and simulation algorithm

Single linear polymer chains which correspond to an infinitely diluted solution were studied. We studied two different types of polymer chains having different macromolecular architecture: linear chains and star-branched chains. A star-branched polymer consisted of three linear chains starting from a common origin (the branching point). The locations of polymer segments were restricted to vertex of a simple cubic lattice. In the model system there was no long-distance interaction potential between polymer segments what implied that the system was athermal. The forbidding of the double occupancy of lattice sites by polymer segments introduced the excluded volume what corresponds to good solvent conditions or high temperatures [7]. The model system was put into a Monte Carlo box with periodic boundary conditions set in x and y directions only. The surfaces that confined the polymer chain were parallel to the xy plane. Each surface was impenetrable for polymer segments. The distance between the surfaces was d lattice units.

In figure 1 we present a schematic representation of a linear and star-branched polymer chain trapped between two surfaces. The model polymer systems were studied by means of the Monte Carlo method. In the simulation algorithm the conformation of a polymer chain was randomly modified using the following set of micromodifications: 2-bond move, 2-bond move, 3-bond crankshaft move and chain's ends moves [5]. A number of attempts of all micromodifications per one polymer segment is defined as a time unit. A new conformation of the chain obtained as a result of such local move was accepted due to topological constraints and the excluded volume condition (double occupancy of lattice sites by polymer bead was forbidden and polymer chains were not allowed to cross the confining surfaces). Each Monte

Carlo simulation run consisted of 10^7–10^8 time units. The simulations for each model system was carried out 30 times starting from quite different conformations [7].

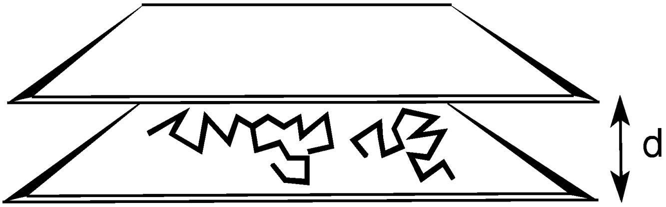

Fig. 1. The scheme of star-branched and linear polymers located between two parallel impenetrable walls.

3. Results and discussion

The Monte Carlo calculations were performed for star-branched and linear chain models that contained the same number of beads. We studied star-branched chains with $n = 17, 34, 67, 134$ and 267 beads in one arm, which corresponded to the total number of beads $N = 49, 100, 199, 400$ and 799, respectively. Linear chains under consideration consisted of $N = 49, 100, 199, 400$ and 799 beads in order to make the results comparable for both types of chains. We studied properties of our model chains for distances between the two parallel impenetrable surfaces from $d = 3$ to $d = 80$. The first one is the smallest possible distance for which the micromodifications of polymer conformations are possible while the second one was much higher than the mean diameter of the longest chains under consideration and therefore chains were here almost unaffected by the presence of the confinement [7, 8]. The size of a polymer chain was described by its radius of gyration. Figure 2 presents the log-log plot of the mean-square radius of gyration $\langle S^2 \rangle$ *vs.* the total number of polymer segments N. The presented cases are linear and star-branched chains, and two distances between the surfaces: $d = 3$ and $d = 10$. One can observe that for longer chains (for $N > 199$) the radius of gyration scales as $\langle S^2 \rangle \sim N^{\gamma}$. For larger distances ($d = 10$) the scaling exponent of the star-branched chain was $\gamma = 1.346 \pm 0.008$, for linear chain the scaling exponent was found to be $\gamma = 1.388 \pm 0.006$. From the point of view of the fractal systems one can notice that the fractal dimension d_{f} of the object can be determined from the relation $d_{\mathrm{f}} = 1/\frac{1}{2}\gamma$ [9, 10]. We obtained the following values of d_{f}= 1.49 and 1.44 for star-branched and linear chains, respectively. Both these scaling exponents were considerably higher than those for the free chain, where $\gamma = 1.19$ [10]. This behavior can be explained by the fact that longer chains are in the transition between three-dimensional and two-dimensional chains.

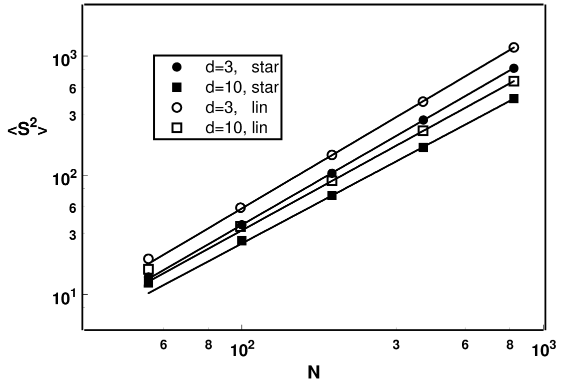

Fig. 2. The mean-square radius of gyration $\langle S^2 \rangle$ as a function of the total chain length N. The distances between the surfaces d and macromolecular architecture are given in the inset.

For the distance between the surfaces $d = 3$ which is the smallest possible to be simulated in our model [7] the scaling behavior of the radius of gyration is quite different. For star-branched chains $\gamma = 1.459 \pm 0.011$, while for linear ones it was $\gamma = 1.496 \pm 0.008$. The obtained values of the scaling exponents are very close to $\frac{3}{2}$ which was characteristic for all two-dimensional polymer chains [10]. This result was rather expected as the chains squeezed by two surfaces to the distance $d = 3$ are almost two-dimensional. The fractal dimensions for this confinement was found $d_{\mathrm{f}} = 1.37$ and 1.34 for the star-branched and linear chains, respectively. These values are smaller than for less confined systems what also confirms that the highly squeezed molecules become almost two-dimensional. The differences between size of linear and branched polymer chains are usually expressed in terms of the factor g defined as:

$$g = \frac{\langle S^2 \rangle_{\mathrm{bra}}}{\langle S^2 \rangle_{\mathrm{lin}}}\,, \tag{1}$$

where subscripts 'bra' and 'lin' denote branched and linear chains, respectively. The theoretical considerations [10] led to the following simple formula for random-flight unconfined chains (with no excluded volume):

$$g_{\mathrm{theor}} = \frac{3f - 2}{f^2}\,, \tag{2}$$

what implies that for chains with three arms of equal length $g_{\mathrm{theor}} \approx 0.778$.

Figure 3 presents the factor g calculated for our model chains as a function of the reciprocal of the total chain length $1/N$. One can observe that relatively short chains ($N < 199$) remain almost constant for both distances d under consideration: for $d = 10$ $g \approx 0.75$ while for $d = 3$ $g \approx 0.71$. For longer chains the g parameter evidently decreases. Simulations of unconfined chains within the frame of the same model gave g between 0.786 (short chains) and 0.744 (longer chains) while this parameter extrapolated towards the infinitely long chain was 0.730 [7]. The decrease of the g parameter along the diminishing size of the slit indicates that the squeezing of star-branched chains led to more compact structures when compared to their linear counterparts.

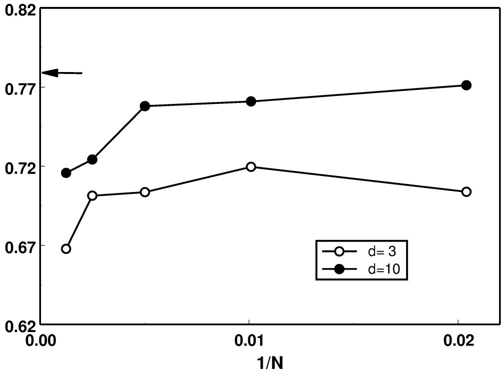

Fig. 3. The g factor *versus* the $1/N$. The distances between the surfaces d are given in the inset. The theoretical value of g is indicated by the arrow.

The analysis of the radius of gyration gives information about the mean spatial distribution of polymer segments only. More insight into the structure of a confined chain can be obtained from the polymer density profiles inside the slit. In figure 4 we present polymer segment density profiles of linear and star-branched chains for $d = 3$ and $d = 30$. As one can notice, for both values of N the profiles for star-branched and linear molecules are almost identical, what means that they are independent on the architecture of the polymer. For a small distance between surfaces ($d = 3$), where polymer chains were the most squeezed: there is no difference in density profiles for different chain lengths. For polymers that were only slightly deformed ($d = 30$) the distribution of polymer segments was different. For the case of longer chains ($N = 799$) when $2\langle S^2\rangle^{1/2} \gg d$ the density profiles were parabolic as for $d = 3$. For shorter chains ($2\langle S^2\rangle^{1/2} < d$) a plateau appeared in the middle part of the slit. This is caused by the fact that chains can migrate between the walls. The width of the plateau region is the same for linear and star-branched chains and roughly equals $d - 4\langle S^2\rangle^{1/2}$. This means that in the center of the space between the walls the short chain is not affected by the confinement. The deformation of the short chain by the walls is visible at the distance equal to the diameter of the coil.

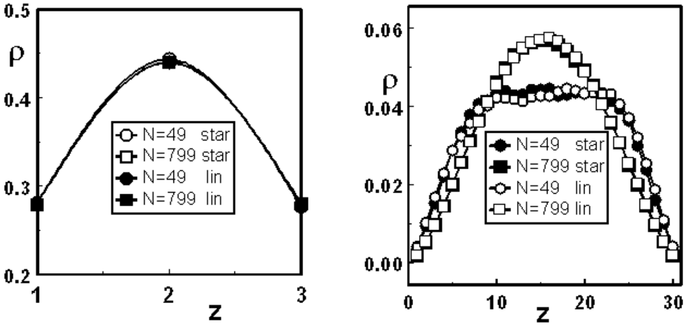

Fig. 4. The distribution of polymer segments ρ *versus* the distance from a wall z for the distances $d = 3$ (left) and $d = 30$ (right). The values of chain lengths N and macromolecular architecture are given in the inset.

The above results can be compared with findings of Milchev [11] for diluted solution of linear chains, where the presence of the plateau was also noticed. Further information about the differences in the structure between star-branched and linear chains in a slit can be found from the analysis of the shape of the chain. The eigenvalues of the tensor of gyration called L_1^2, L_2^2, L_3^2 correspond to the three main axes of the equivalent ellipsoid. In order to determine the instantaneous shape of a chain we calculated the asphericity factor δ^* defined originally by Rudnick and Gaspari [12]:

$$\delta^* = \frac{\left\langle \sum\limits_{i>j}^{3} \left(L_i^2 - L_j^2\right)^2 \right\rangle}{2\left\langle \sum\limits_{i=1}^{3} L_i^2 \right\rangle} . \tag{3}$$

This parameter takes the value 0 for a sphere and 1 for a one-dimensional rod.

In figure 5 we showed changes of the asphericity factor δ^* with the distance between the surfaces d for some chain lengths. For all chains under consideration δ^* is close to 0.4. For more squeezed chains the asphericity became larger. The changes of the chain's shape are not monotonic: there are shallow minima on all curves. This behavior can be explained by the fact that chains in larger slit are rather reoriented than deformed [5]. The principal axes of the chain are oriented predominately parallel to the walls. One has to remember that the theoretical predictions of the asphericity for single 'free' linear chains were found $\delta^* = 0.53$ and for star chains $\delta^* = 0.34$ [13].

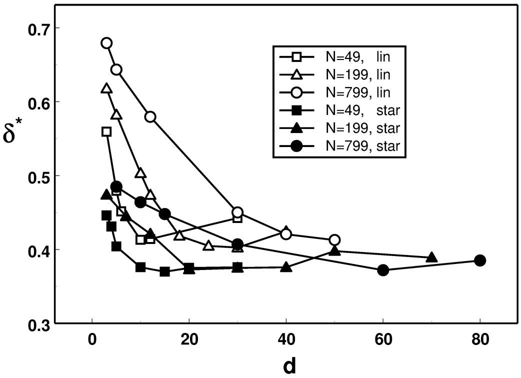

Fig. 5. The asphericity factor δ^* *versus* the distance between walls d. The chain lengths and macromolecular architectures are given in the inset.

4. Conclusions

We studied the properties of a simple model of polymers with different internal macromolecular architecture: linear chains and star-branched chains. Despite the simplicity of the model (simple cubic lattice, confinement in a form of an impenetrable surface) the results obtained enable one to conclude some interesting features of the system. The presence of a confinement has a major impact on polymer's size and shape. It is observed that the linear chains are less symmetric than their star-branched counterparts in the entire range of confinement. The shape of linear chains is more sensitive on confinement than that for branched polymer systems.

REFERENCES

[1] R. Eisenriegler, *Polymers near Surfaces*, World Scientific, Singapore 1993.
[2] J.H. van Vliet, G. ten Brinke, *J. Chem. Phys.* **93**, 1436 (1990).
[3] A. Milchev, K. Binder, *Eur. Phys. J.* **B3**, 477 (1998).
[4] A. Kolinski, M. Vieth, A. Sikorski, *Acta Phys. Pol. A* **79**, 601 (1991).
[5] A. Sikorski, *Macromol. Chem. Theory Simul.* **2**, 309 (1993).

[6] P. Romiszowski, A. Sikorski, *Comput. Theor. Polym. Sci.* **11**, 129 (2001).

[7] A. Sikorski, P. Romiszowski, *J. Chem. Phys.* **116**, 1731 (2002).

[8] A. Sikorski, *Acta Phys. Pol. A* **103**, 339 (2003).

[9] *On Growth and Forms: Fractal and Non-Fractal Patterns in Physics*, ed. H.E. Stanley and N. Ostrowsky, Martinus Nijhoff Publ., Dordrecht 1985.

[10] P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY 1979.

[11] A. Milchev, *Eur. Phys. J.* **E8**, 531 (2002).

[12] J. Rudnick, G. Gaspari, *J. Phys. A* **19**, L191 (1986).

[13] G. Zifferer, *J. Chem. Phys.* **109**, 3691 (1998).