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Properties of star-branched and linear chains in confined space. A Monte-Carlo study

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Abstract We have studied the properties of simple models of linear and star-branched polymer chains confined in a slit formed by two parallel impenetrable walls. The polymer chains consisted of identical united atoms (homopolymers) and were restricted to a simple cubic lattice. Two macromolecular architectures of the chain: linear and regular stars with three branches of equal length, were studied. The excluded volume was the only potential introduced into the model and thus the system was athermal. Monte-Carlo simulations with the sampling algorithm based on the chain's local changes of conformation were carried out for chains with different lengths as well as for different distances between the confining surfaces. We found that the properties of model chains differ for both macromolecular architectures but a universal behavior for both kinds of chains was also found. Investigation of the frequency of chain-wall contacts shows that the ends of the chains are much more mobile than the rest of the chain, especially in the vicinity of the branching point in star polymers.

Keywords Confined chains · Lattice models · Monte-Carlo simulations · Polymer structures · Star branched polymers · Confined polymers

Introduction

The problem of the confinement of molecules not only has an important meaning for theoretical considerations but also practical consequences in such fields as materials science and engineering [1]. The confinement in which we are interested takes place when the size of the

molecules is comparable with the size of the confined space. In such a case the effects caused by a significant reduction of the configuration space can be observed. The confinement affects both the static and dynamic properties of the system. The geometrical confinement 'squeezes' the molecules and changes their dimensions. Also the confinement can be treated as steric obstacles and its presence strongly changes the freedom of the molecules' motions. One can find many examples of confined polymer chains in such systems as biological microstructures, systems of lubricants and adhesives, problems of liquid flow, capillary electrophoresis, and corrosion-protective coatings. The properties of linear polymer chains in layers, in microstructures, and in biosystems were studied recently theoretically [2–10]. The major conclusions of these studies were that the properties of polymer chains depend mainly on the ratio between the dimensions of the molecule and the dimensions of the confinement. One has to remember that substantial changes of polymer properties can be caused by the presence of a repulsive, adsorbing or patterned surfaces. Theoretical investigations of this problem on the basis of the Scheutjens-Fleer mean-field model were used successfully for the case of polymer adsorption on a surface [11, 12]. A scaling analysis of the polymer near the surface system was given by de Gennes [13] with special interest paid to the structure of the polymer film. They found that there were two regimes in density profiles. The segment density decays exponentially in the vicinity of the wall, whereas the decay was slower for longer distances from the wall.

Since the majority of the work described above was devoted to confined linear polymer chains, we decided to start investigations on the behavior of branched chains in a confined space. Such objects sometimes exhibit properties different from their linear counterparts. The simplest model of a non-linear chain is a star-branched polymer that contains three chains (branches) emanating from a common origin. Such polymer chains can also be synthesized and experimental studies can be performed [14, 15]. The differences between the linear and branched

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molecules are mostly caused by the different distributions of monomers in the coil.

In the last two decades, simple lattice models of star-branched chains were constructed and studied by means of Monte-Carlo simulations [16–19]. It was shown that even simple and coarse-grain models can give results showing the structure of a star-branched polymer chain. In our previous paper, we presented a study of the dimensions of confined star-branched polymer chains in a slit formed by two impenetrable surfaces [18, 19]. It was possible to describe the behavior of the chain's size with one universal 'master' curve, which was valid for all chain lengths and all sizes of the slit. Some dynamic properties of star-branched chains were also studied. We showed that the self-diffusion coefficient did not change monotonically with the distance between the confining surfaces. A possible explanation of this fact was that the mechanism of motion changes on going from a three-dimensional to two-dimensional polymer chain. Since an influence of confinement on the properties of macromolecules is observed, one can try to compare the presence of confinement on polymers of different architecture, namely the linear and star-branched chains. Refs. [18, 19] were devoted entirely to star-branched polymers and these studies were focused on the dynamic properties of the systems.

In this paper, we investigate polymer chains of different macromolecular architecture in order to determine the influence of the chain's topology on differences in static properties. Previous such comparative studies were successful in showing the impact of the macromolecular architecture on the coil-globule transition [20]. This paper is organized as follows. We describe the model and present the method of simulation used. In the next section, the results are presented and discussed. Finally, the main conclusions are presented.

The model and the algorithm

We studied properties of two different polymer-chain topologies; linear and star-branched chains. Linear chains consisted of a sequence of N connected beads, while star polymers were built of $F=3$ linear chains (arms) of equal length n emanating from a common origin called the branching point. Therefore, in the latter case the total number of beads in the chain was $N=F(n-1)+1$. Each polymer bead can be treated as a united atom representing some monomers of a real macromolecular chain. The model chains were built on a simple cubic lattice in order to make the simulations more efficient. This simplification is sufficient for our studies as we studied properties of the chain as a whole. The excluded volume was the only interaction included in the model. The polymer chains were confined to a slit formed by two impenetrable walls. These confining surfaces were purely repulsive and there was no chain adsorption and thus the influence of the walls had only entropic character. The absence of the polymer-wall and

polymer–polymer interactions (see e.g. Ref. [21]) was intentional and we therefore modeled infinitely diluted macromolecules at good solvent conditions. The idea of the model studied is shown in Fig. 1. The orientation of the surfaces was chosen to be parallel to the xy -plane. The edge of the Monte-Carlo box was large enough to study longer chains ($L=200$). Periodic boundary conditions were imposed in the x and y directions only [16, 19].

A series of the Monte-Carlo simulations was carried out to calculate the properties of the model chains. The conformation of a chain was modified by a set of random local moves typical for a Metropolis-like algorithm. The procedure of preparation and equilibration of the initial chain conformation has been described in detail elsewhere [18, 19]. The following set of micromodifications was used for this purpose. One-bond chain-end motion, two-bond chain-end motion, two-bond kink motion, three-bond kink motion and three-bond 90° crankshaft motion. For star-branched chains, an additional branching point collective motion was employed [16]. The production simulation run consisted of 10^7 – 10^8 cycles. For each chain length and the size of the slit, the simulations were repeated 20–30 times starting from quite different initial conformations. In this paper, we present the mean values of parameters calculated from simulations and averaged over all runs—the relative errors did not exceed 5%.

Results and discussion

Linear polymer chains studied consisted of $N=50, 100, 200,$ and 400 beads. For star-branched polymers the lengths of the arms were varied between $n=17, 34, 67,$ and 134 beads, making the total number of beads in the chain $N=49, 100, 199,$ and 400 , respectively. In our previous work, we showed that this range of chain lengths was sufficient to study the chain's scaling properties on a cubic lattice [18]. The size of a slit, i.e. the distance between the confining surfaces was between $d=3$ (corresponding to the shortest possible distance for which the sampling algorithm can move the chain) up to $d=60$, where even long chains were not affected (squeezed) [18].

The size of a polymer chain is usually described by the mean-squared radius of gyration $\langle S^2 \rangle$ regardless of its internal architecture. In Fig. 2, we show the changes

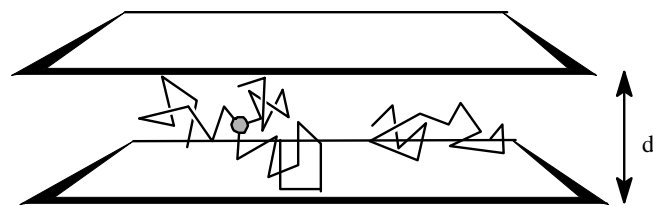


Fig. 1 The scheme of a star-branched (*left*) and a linear (*right*) chain located between two parallel impenetrable surfaces

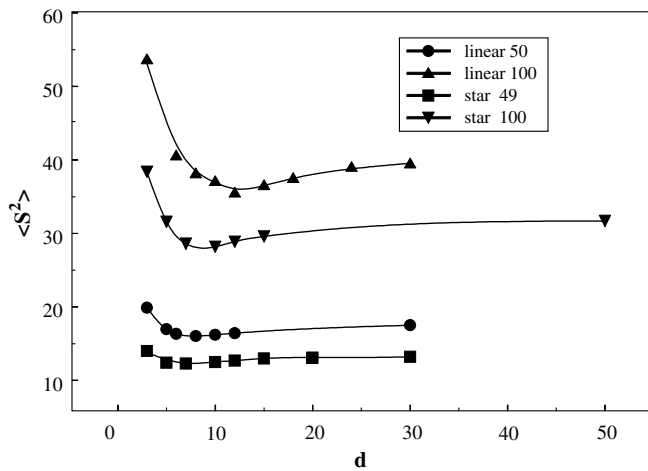


Fig. 2 The mean-squared radius of gyration $\langle S^2 \rangle$ as a function of the distance between surfaces d . The chain lengths and the type of macromolecules are given in the *inset*

of this parameter with the distance between the confining surfaces d for some chain lengths. The changes of both macromolecular architectures are qualitatively the same. Reducing the distance d led initially to a slight reduction of the chain's size. Further reducing of the size of the slit caused an increase of the radius of gyration. This behavior can be explained by the fact that the chain undergoes a transition from a three-dimensional structure to a flat, almost two-dimensional one. This transition can be confirmed by an analysis of the scaling behavior of the mean-squared radius of gyration $\langle S^2 \rangle$. The scaling exponent is 1.19 ± 0.01 for both architectures of unconfined chains. For the strongest confinement ($d=3$) it reaches 1.46 ± 0.01 for star molecules and 1.50 ± 0.01 for the linear chains, close to the predicted value $3/2$. This confirms the two-dimensional behavior of the system under strong confinement.

It was shown previously that one can introduce a reduced parameter in order to compare the behavior of polymer chains in the confinement regardless of their length and the size of the slit [2, 18]. The reduced distance between the surfaces d^* defined as:

$$d^* = \frac{d}{\sqrt{2 \cdot \langle S^2 \rangle_0}} \quad (1)$$

where $\langle S^2 \rangle_0$ stands for the mean-square radius of gyration of the unconfined (free) entire star-branched chain. Now the size of the chain will be described by the ratio $\langle S^2 \rangle / \langle S^2 \rangle_0$. The universal behavior of star-branched chains was recently shown. The plots of reduced size versus the reduced distance d^* were located on the same curve regardless of the chain length and the size of the slit [18]. The question arises if this master curve as presented is valid for both chain topologies, i.e. linear and star-branched chains. In Fig. 3, we show the ratio $\langle S^2 \rangle / \langle S^2 \rangle_0$ as a function of the reduced distance d^* for the chains under consideration. One can observe that data for the linear and star polymers are located along

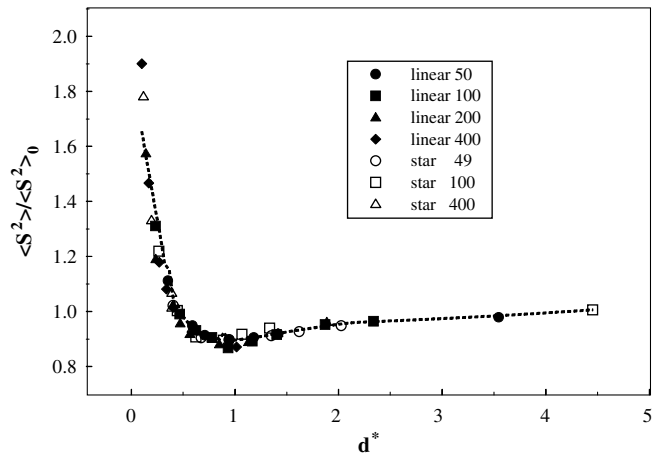


Fig. 3 The reduced radius of gyration $\langle S^2 / S_0^2 \rangle$ as a function of the reduced distance between surfaces d^* . The chain lengths and the type of macromolecules are given in the *inset*

the same master curve. This means that, despite the different chain architectures, the changes of size can be treated as universal in terms of reduced parameters. The shape of the master curve is similar to those in Fig. 2, i.e. for unreduced parameters. The longest chains show slight deviations from this universal behavior.

Additional information about the changes of the size and the structure of confined polymer chains can be found by an analysis of the ratios of some parameters describing the size of a chain [22]. At first, we consider the ratio of the mean-squared radius of gyration $\langle S^2 \rangle$ to the mean-squared center-to-end distance $\langle D^2 \rangle$ (the distance between the branching point and the end of an arm). Theoretical considerations give the values of this ratio: 0.389 and 0.393 for chains without and with excluded volume, respectively [23]. In Fig. 4, one can observe changes of this ratio with the reduced size of the slit d^* . For the sake of comparison, we also show the ratio calculated for confined linear chains. For the latter case, we calculated this ratio by treating the linear chain as a star-branched macromolecule consisting of two arms with the branching point located at the middle bead. One can observe that the ratio remains almost constant (with some slight shift for $d^* < 1$) in the case of linear (around 0.35) and star-branched (at the level 0.42) chains. The difference between the two cases is due to the different architectures of the macromolecules, i.e. this ratio describes a single arm (or half of a linear chain). This behavior suggests that squeezing a star-branched chain changes the conformation of its arms in similar way as halves of linear chains. Below $d^*=1$, the ratio decreases rapidly despite of the increase of the radius of gyration (see Fig. 2).

The next ratio we considered was earlier a frequent measure of the dimensions for linear chains: $\langle S^2 \rangle$ divided by the mean-squared end-to-end distance $\langle R^2 \rangle$. This ratio takes the values 0.167 and 0.157 for free (unconfined) linear chains without and with excluded volume, respectively [23]. For star-branched chains, the

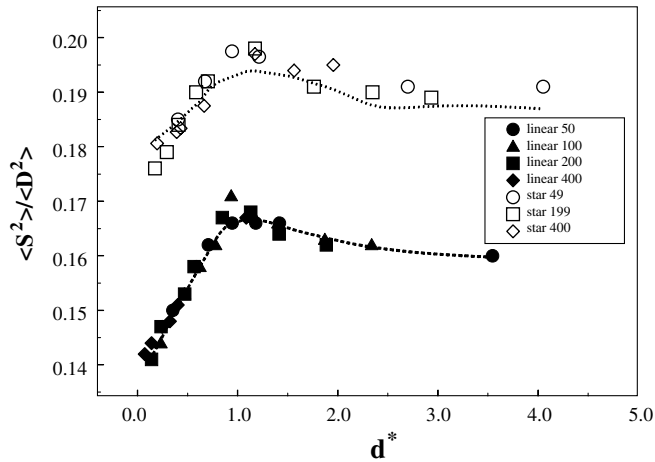


Fig. 4 The ratio $\langle S^2/D^2 \rangle$ as a function of the reduced distance between the surfaces d^* . The chain lengths and the type of macromolecules are given in the inset

parameter $\langle R^2 \rangle$ can be calculated as the mean-square distance between a pair of ends of arms. However, one has to remember that calculating this parameter we ‘forgot’ the presence of the third arm and, therefore, we treated the star-branched chain as if it were the linear structure. Obviously, the presence of the third arm was visible as we compared the numerical results shown in Fig. 5. The curves shown for the linear and star-branched cases are qualitatively very similar. One can clearly distinguish the two regimes, one for $d^* < 1$, where the ratio increases linearly along with d^* , then the maximum is observed at $d^* = 1$. An analysis of both ratios (Figs. 4, 5) clearly shows that the center-to-end distance grows faster than the end-to-end distance. This suggests that pairs of arms (and halves of linear chains) are rather not extended in opposite directions but still remain coiled and inter-entangled.

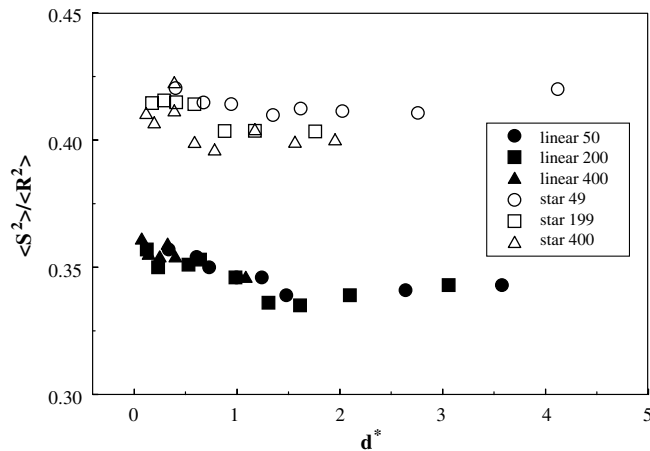


Fig. 5 The ratio $\langle S^2/R^2 \rangle$ as a function of the reduced distance between the surfaces d^* . The chain lengths and the type of macromolecules are given in the inset

The structure of a polymer chain in a slit was also analyzed by investigation of the number of contacts between polymer segments and the impenetrable surfaces, which can be considered a measure of the pressure the chain exerted on the walls. It can also be treated as a measure of the exposure of parts of the chain to the confining walls. Therefore, one can establish the frequency of these contacts with respect to the different parts of a macromolecule. One can expect that, at least for the moderately squeezed chains, the most frequent contacts of polymer beads with the walls take place for the polymer segments not hidden in the middle part of the polymer film but for those exposed in the outer surface of the coil. The frequency f_i was defined as the number of polymer-surface contacts of the i -th bead of the chain per time unit. Following the idea of emphasizing the similarity in behavior of chains having different lengths, we recalculated the frequencies f_i as follows [19].

$$f_i^* = \frac{f_i}{\langle f \rangle} \quad (2)$$

where the reduced frequency of contact of the i -th bead f_i^* was obtained by normalization of the frequency f_i by the mean value $\langle f \rangle$. The result is comparable for all chain lengths under consideration. This quantity is shown as a function of the reduced bead number i/n . The calculations of the frequency were performed for each polymer bead number i separately. The numbering of beads started from the branching point (bead# 1), ended at the arm’s end (bead# n) and was averaged for all arms. Figure 6 shows the mean reduced frequency of polymer-surface contacts for star-branched chains as a function of the reduced bead number i/n . A similar procedure was used for the linear chains. In order to compare the behavior of star-branched and linear chains, we treated the linear chain as a star-branched chain having only two branches ($F=2$) with the branching point located in the middle bead of the chain ($\# n/2$). Following this idea, the numbers of beads were counted starting from bead# $n/2$ and ending at beads# 1 and# n (the results were then averaged over two branches). Figure 7 also shows the frequencies of polymer-surface contacts for linear chains. The two plots are similar and form a universal master curve that is independent of the chain length and the distance between the confining surfaces. However, one can easily find some differences, as will be discussed later. For star-branched chains, one can distinguish three regions in the plot: (i) the branching point vicinity (for the reduced bead number $i/n < 0.1$) in which the frequency grows with the bead number but was visibly lower than for other parts of the chains, (ii) the main part of the chain (for i/n between 0.1 and 0.9) for which a plateau was observed (some fluctuations were present) and (iii) the terminal region (for $i/n > 0.9$), where the frequency rose sharply with the bead number. A similar behavior was found for the linear chains. However, there are only two regions in

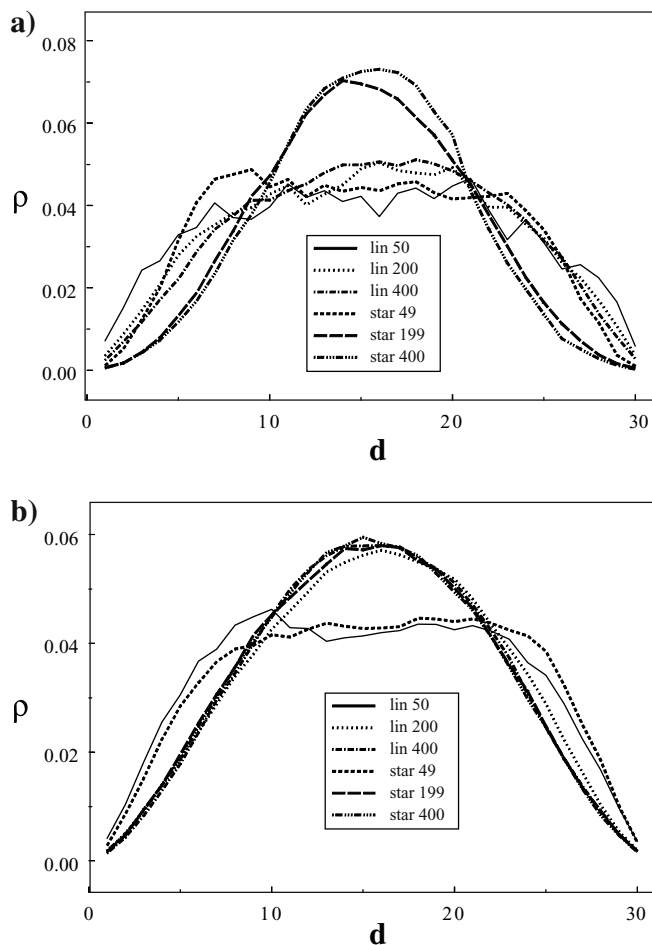


Fig. 6 Density profiles of the core (a) and the middle section (b) of chains (see text for details). The chain lengths and the type of macromolecules are given in the *inset*

the plot: (i) the plateau for $i/n < 0.8$, (ii) the terminal region with a rising frequency of contacts for $i/n > 0.8$. Construction of one common curve embedding the wide range of chain lengths and the distances between the surfaces revealed the internal structure of confined star-branched chains and the linear ones. The presence of the branched structure results in a relatively dense core of the molecule in the vicinity of the branching point [24]. The size of that core can be estimated by an analysis of the frequency of the wall-polymer contacts. From Fig. 7 we can estimate that roughly 10% of the chain's beads (counted from the branching point) form a core region of the chain in confined space. On the other hand, the terminal 10% of beads are the most mobile and flexible part of the chain. In the case of the linear chains, the presence of the core of the molecule is not evident. However, one can observe that the most flexible and mobile part of the chain consists of the roughly 15–20% terminal beads.

In order to confirm the above conclusions, we analyzed the density profiles for the parts of the chains embedding the core and middle of the chain,

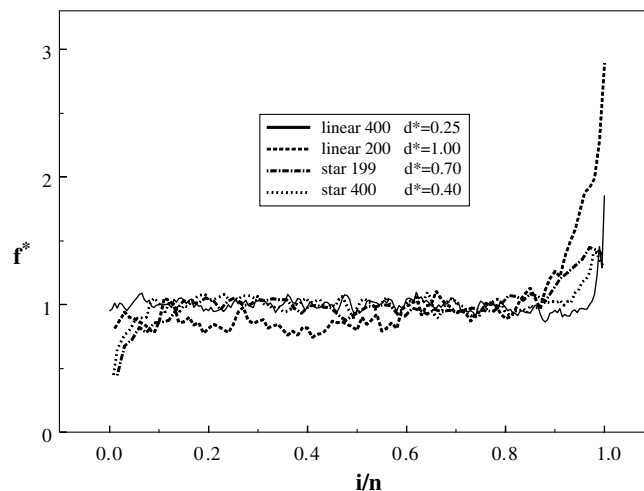


Fig. 7 The reduced frequency of contacts f^* as a function of the bead reduced number i/n . The chain lengths, the type of macromolecules and distances d^* are given in the *inset*

respectively. The core of the star-branched chains was taken as 10% of the inner beads. The same analysis was used in the case of the linear chains. We show the density profiles taken for 10% of the inner beads (counted from the middle bead of the chain). One has to remember that there was no core region found in the linear chain case. The calculations are performed for the sake of comparison with the star chains only. The density profiles of the beads for whom the plateau shown in Fig. 7 was obtained (middle part of the chain—as defined above—were also calculated. The density profiles are shown in Fig. 6a, b for core and middle of the chains, respectively. Note that for star-branched chains a Gaussian-type curve is obtained with a well defined maximum. On the other hand, the density profiles for linear chains exhibit wide plateaus. This is additional evidence for the lack of the core in the linear chain systems. The middle part of chain's density profiles (Fig. 6b) show that there is no distinction between the star and linear chains—the longer chains form parabolic profiles. The short chains give the plateau region caused by the relatively small size of the chain if we compare it with the distance d .

Conclusions

We have studied simple models of linear and star-branched polymers confined by two parallel impenetrable walls. We employed a simple cubic lattice model of polymer chains with excluded volume interactions only (good solvent conditions). This model was studied by means of the Monte-Carlo simulation method in order to determine its average structural properties.

Comparison of confined linear and star-branched chains shows some differences in spite of some similarities. Their size holds a universal behavior and both linear and star-branched chains undergo a transition

from three-dimensional state to almost two-dimensional. Analysis of contacts between polymer beads and the surfaces reveals that the terminal parts of the chains are mostly exposed to the walls while the center of a macromolecule remains hidden away from the walls. This effect is more pronounced for star polymers, i.e. the size of this screened part called 'core' is larger. These differences in the chains' structure were confirmed by an analysis of the density profiles. The differences between the linear and star-branched chains are also seen in plots showing the ratios of the dimensions of the molecules. The course of these dependencies is similar in both cases. However, two separate curves are observed for each chain architecture.

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