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The influence of the macromolecular architecture on adsorption of polymer chains on a solid surface**)

Summary — Computer simulations of a simple model of adsorbed polymer chains were performed with the dynamic Monte Carlo method. The coarse grained chain representation was used and model macromolecules were confined to vertices of a simple cubic lattice. The chains were modeled with excluded volume only, *i.e.* at good solvent conditions. The polymers interacted with an impenetrable surface *via* an attractive potential, which was varied to cover both weak and strong adsorption regimes. Three different chain architectures were studied: linear and star-branched with three and four arms. It was found that size of chains obeys the scaling law with exponential characteristics for two- and three-dimensions for the weak and strong adsorption regime respectively. The transition temperatures between these regimes were also determined. The structure of adsorbed polymers was found similar for all architectures especially for the case of strong adsorption.

Key words: polymer adsorption, Mote Carlo method, lattice models, branched polymers.

WPŁYW ARCHITEKTURY ŁAŃCUCHA NA ADSORPCJĘ CZĄSTECZEK POLIMERU NA POWIERZCHNI CIAŁA STAŁEGO

Streszczenie — Za pomocą symulacji komputerowej metodą Monte Carlo (wykorzystano algorytm Verdiera-Stockmayera) przeprowadzono badania właściwości zaadsorbowanych łańcuchów polimerowych. Makrocząsteczki modelowano korzystając z uproszczonych modeli, w których rzeczywisty nieprzecinający się łańcuch był przybliżony sekwencją jednakowych segmentów. Założono, że modelowe łańcuchy tworzą pseudo-krystaliczną sieć regularną. Polimery umieszczono w szczelinie, której ściany oddziałują potencjałem przyciągającym na segmenty łańcucha. Zbadano trzy modele makrocząsteczek o różnej architekturze wewnętrznej: łańcuchy liniowe oraz gwiaździście rozgałęzione zawierające 3 lub 4 ramiona. Zbadano wpływ podstawowych parametrów układu na strukturę zaadsorbowanych łańcuchów. Wykazano, że łańcuchy w temperaturach wyższych (słaba adsorpcja) skalują się jak trójwymiarowe, a w niższych (silna adsorpcja) jak dwuwymiarowe, i to niezależnie od architektury łańcucha. Wyznaczono parametry przejścia słaba adsorpcja → silna adsorpcja oraz pokazano, że zwłaszcza w przypadku silnej adsorpcji, struktura zaadsorbowanej warstwy polimerowej słabo zależy od architektury łańcucha.

Słowa kluczowe: adsorpcja polimerów, metoda Monte Carlo, modele sieciowe, polimery rozgałęzione.

The adsorption of polymer chains on a solid surface is an important phenomenon due to its practical applications like colloidal stabilization, lubrication *etc.* [1, 2]. Many experimental techniques are used for studying the polymer adsorption: quasi-elastic light scattering, induced fluorescence and small angle neutron scattering and measurements of forces between polymers and the surface [3—9]. But experimental studies of isolated polymer chains are rather difficult and, therefore, the computer simulation is a proper tool to study such systems. Moreover, the adsorption is also interesting from the theoretical point of view because the presence of the attractive surface usually changes the properties of the adsorbed chain dramatically, when compared with a free chain in solution. It is also well known that polymers of different macromolecular architecture like rings or stars exhibit different static and dynamic properties [10, 11]. Thus the question appears, what these changes for a macromolecule near a surface would be.

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Theoretical works concerning adsorbed polymers were based on mean field approximation [12—16]. The theory of adsorbed random-flight chains with nonlinear architecture like ring, star, and comb was developed recently by Kosmas [17]. Similar mean field studies were recently carried out by Joanny and Johner [18]. These theories predict that the adsorption of ring polymers is considerably higher than the linear ones. The adsorption of stars is also higher and increases with the increase of the number of arms. This difference in the behavior of star-branched macromolecules was explained by the compactness of the star polymer compared with the linear one. Computer simulations showed that for certain temperature an adsorbed polymer chain changes from a three-dimensional to a two-dimensional structure [19—21]. The details of this structure (trains, loops and tails) and the dynamics of adsorbed linear, ring and star-branched chains were also studied recently [22]. The scaling analysis was also applied to adsorbed star-branched polymers [23—25]. The dilute and semidilute polymer solutions were studied with this method [26—28].

In this study we carried out a series of Monte Carlo simulations of simple model of star-branched polymer chains. The adsorbed macromolecules were regular stars embedded in a simple cubic lattice and located near an impenetrable and attractive planar surface. It was shown that the lattice models can be used for studies of the properties of polymer systems assuming that we are not interested in very fast processes and in the structure on the atomic level [11]. The analysis of the applicability of such models for free single chains, dense polymer melts and chains adsorbed on a surface was made elsewhere [11, 29]. The macromolecules were studied at good solvent conditions (excluded volume only, no attractive segment-to-segment interactions) what was usually more difficult for theoretical considerations. The Monte Carlo algorithm employed a Verdier-Stockmayer type local chain motions. The influence of the temperature on the static properties and the structure of chains were also studied. The influence of the internal macromolecular chain architecture on its adsorption was investigated and discussed.

THE MODEL AND THE CALCULATION METHOD

Macromolecules were represented as sequences of beads, *i.e.* all the atomic details were suppressed. Chains were built on a simple cubic lattice, *i.e.* polymer segments connecting beads were approximated by vectors of the type [±1, 0, 0]. The excluded volume was introduced by forbidding the double occupancy of lattice sites by polymer beads. This resembled good solvent conditions where the excluded volume was not compensated by the attraction between polymer beads. The calculations were carried out for single chains, *i.e.* in the case of infinitely diluted solution. Three different chain architectures were studied: linear chains and star branched chains with $f = 3$ and $f = 4$ arms. Linear chains consisted of N beads while in star macromolecules each arm was of the same length n and thus, the total number of beads in the chain was:

$$N = f \cdot (n - 1) + 1 \tag{1}$$

The model chain was put into the Monte Carlo box with periodic boundary conditions in x and y directions only. We chose the size of the Monte Carlo box large enough ($L = 200$) to minimize the influence of its size on the results. It was assumed that at $z = 0$ a surface impenetrable for polymer segments was located. The adsorption of polymer on that surface was realized by introduction of the attractive contact potential between the surface and polymer beads. This potential had a form of a square well:

$$V(z_i) = \begin{cases} 0 & \text{if } z_i > 1 \\ \varepsilon & \text{if } z_i = 1 \end{cases} \tag{2}$$

where: z_i — *distance between* i^{th} *polymer bead and the surface*, ε — *contact energy and* $\varepsilon < 0$.

The reduced temperature of the system (T^*) can be defined *via* the potential of interaction (ε):

$$T^* = 1/\varepsilon \tag{3}$$

The simulation algorithm was based on the Metropolis scheme. The initial conformation of the chain underwent a series of local micromodifications. The proper set of these micromodifications was designed and described previously in detail [30, 31]:

— one-bead motion,
— two-bead motion,
— two-bead crankshaft motion,
— end reorientations,
— branching point collective motion (for star-branched polymers).

All the above micromodifications were selected at random during the simulation. It was shown that this set of moves is efficient assuming that the temperature was not too low ($T^* \geq 1$) [30—32]. The time unit was defined as one attempt of every micromodification per one polymer segment. A new chain conformation was accepted due to the chain connectivity and the excluded volume with the probability proportional to its Boltzmann's factor as found in the Metropolis scheme. The protocol of the simulation was as follows. A randomly chosen conformation of the chain underwent an initial series of micromodifications (the equilibration run usually consisted of 10^7 time units) in a high temperature. Then, the production run (of order 10^8—10^9 time units) was performed. In the next step the temperature is slightly lowered and this procedure is repeated until the lowest temperature is reached. The simulation was repeated 20—25 times starting from different initial conformations in order to provide the proper sampling of the conformational space. At lower temperatures a thermalization procedure was used additionally in order to avoid the trapping of the system in the deep local minima.

RESULTS AND DISCUSSION

The Monte Carlo simulations were performed for linear chains consisting of N = 50, 100, 200, 400 and 800 beads and stars with n = 17, 34, 67, 134, 267 and n = 13, 26, 51, 101, 201 for f = 3 and f = 4 arms respectively. The temperature T^* was changed in the range between 10 and 1, because it was previously found that it should cover the case of the weak and strong adsorption of the chain [30]. The weak adsorption occurs where the interaction between a single polymer bead and the surface is weak, *i.e.*, $\varepsilon << kT$. But other parts of a long polymer chain interact with the surface with many beads and, therefore, the total adsorption energy $E = \nu\varepsilon >> kT$, where ν is a number of polymer beads interacting with the surface. Thus, in spite of the fact that a single polymer bead interacts with the surface very weakly the process of adsorption of the entire chain is rather irreversible. Weak adsorption of a polymer chain on an attractive surface is a theoretically tractable case [10].

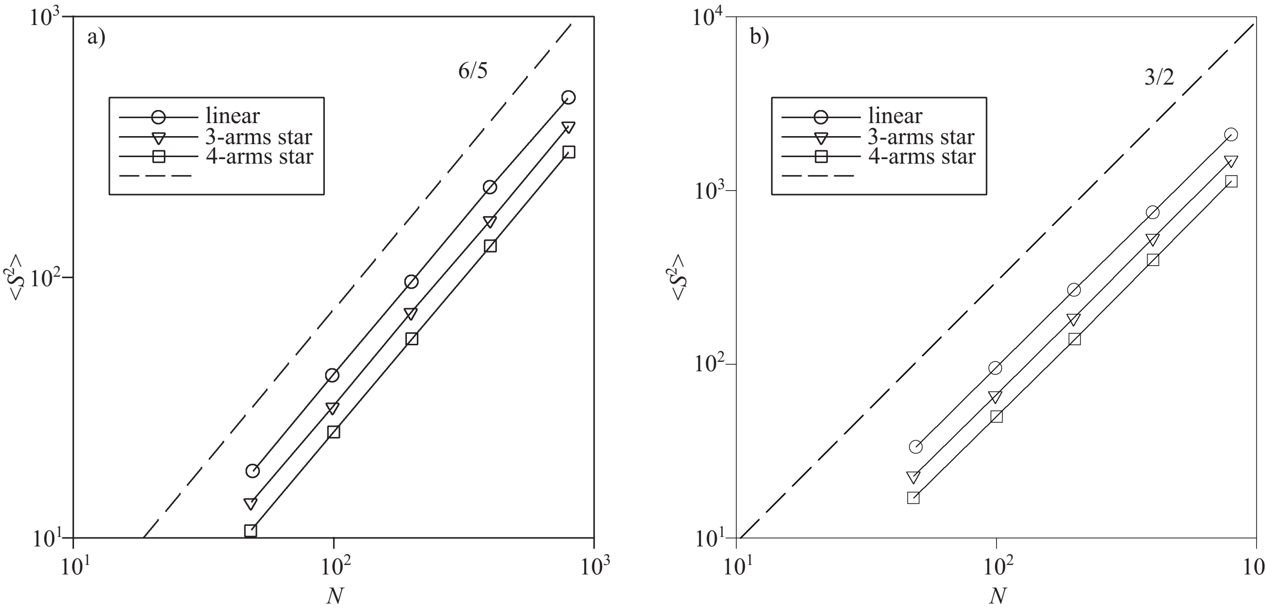

Fig. 1. The log-log plot of the mean-squared radius of gyration (< S^2 >) versus the total number of polymer beads (N) for different chain architectures at reduced temperatures: a) T^* = 3.33, b) T^* = 1.0

The influence of the internal macromolecular architecture of the chain on the process of the polymer adsorption is the first problem addressed. The size of the chain is usually described by means of the mean-square radius of gyration. Figure 1 shows the dependence of the mean-squared radius of gyration < S^2 > on the chain length N in the case of a weak adsorption (at the temperature T^* = 3.33) and in the case of a strong adsorption (at the temperature T^* = 1). The size of the chain decreases with the increase of the number of arms what is similar to the behavior of non-adsorbed chains macromolecules and it is in good agreement with theoretical predictions [10]. One can observe that for all macromolecular architectures under consideration the polymer size scales with the chain length: $< S^2 > \sim N^{\gamma}$. The scaling exponents for the high temperature (T^* = 10) were found to be γ = 1.160 ± 0.009, 1.193 ± 0.007 and 1.192 ± 0.002 for linear chains, stars with f = 3 and f = 4 arms respectively. One can observe that the exponents characterizing the adsorbed chains are very close to those for free chains in good solvent conditions, where γ = 6/5 [31, 33]. Thus, the size and shape of chains are changed when compared with isolated free chains in a solution but the universal scaling remains unaffected. In Fig. 1b the mean-square radius of gyration at the temperature T^* = 1 is plotted versus the number of polymer beads N in the case of a strong adsorption. The size of macromolecules also decreases with the increase of the number of arms but it is considerably larger when compared to the previous case. Scaling exponents of the radius of gyration at that temperature are: γ = 1.486 ± 0.002, 1.500 ± 0.002 and 1.506 ± 0.002 for linear chains, stars with f = 3 and f = 4 arms respectively. These values are very close to the theoretical predictions for two-dimensional systems [1, 10] where γ = 3/2 and to two-dimensional simulation results where γ = 1.49 [1, 34, 35].

Figure 2 shows the mean-squared radius of gyration $<S^2>$ versus the reduced temperature T^* for linear and both star-branched chains. One can observe that for higher temperatures (T^* > 2.5) the size of all adsorbed chains does not change significantly. Further annealing leads to the more pronounced changes of the chain conformations: the size of all types of chain starts to grow very rapidly. This growth takes place because the chain

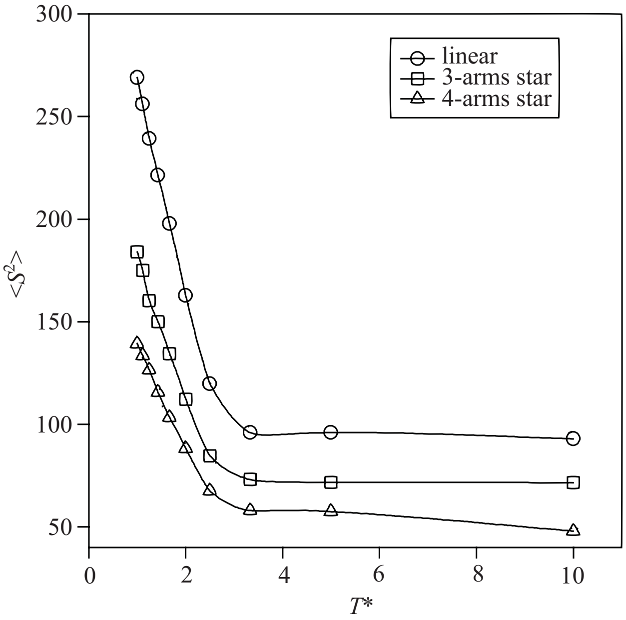

Fig. 2. The mean-squared radius of gyration (<S^2>) versus the reduced temperature (T) for the chain consisting of N = 200 beads and for different chain architectures*

tends to maximize its number of contacts with the surface. This increase of the chain size at lower temperatures strongly suggests that a transition to a fully adsorbed chain took place and polymers became almost two-dimensional structures. In other words, a transition from the weakly to the strongly adsorbed regime took place at the temperature somewhere near $T^* = 2$. The behavior of such chains was studied in real experiments [36] as well as in computer simulations [34, 35, 37]. The above findings showing that at low temperatures almost the entire chain interacts with the surface and, thus, forms a two-dimensional structure can by verified by the analysis of the *z*-contribution to the mean-square radius of gyration $\langle S^2\rangle_z$. In the Figure 3 we present the changes of this parameter with the temperature for all kinds of chains under consideration. One can observe that in the region of weakly adsorbed chains $\langle S^2\rangle_z$ decreases slightly for branched chains but increases for linear chains. Further annealing leads to the significant decrease of the chain size along the direction perpendicular to the adsorbing surface. The thickness of the polymer layer for the strong adsorption case is independent of the chain length what is in good agreement with other simulation results [21].

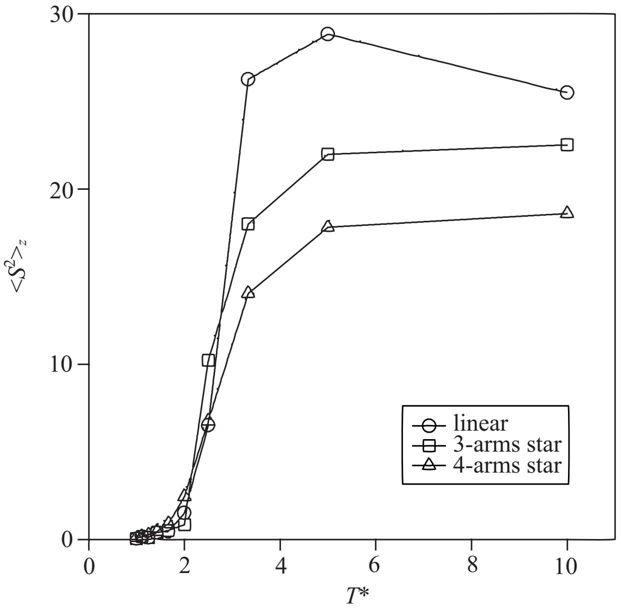

Fig. 3. The z-contribution to the mean-square radius of gyration (<S^2>$_z$) as a function of the reduced temperature (T) for the chain consisting of N = 200 beads and for different chain architectures*

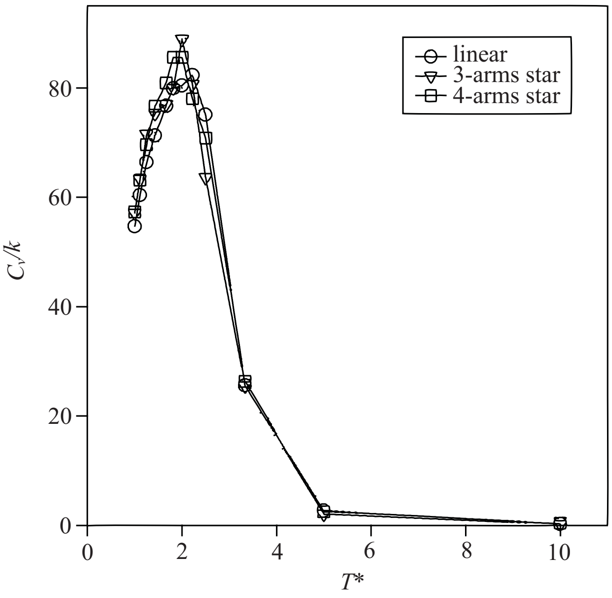

Fig. 4. The heat capacity (C_v/k) of the polymer chain versus the reduced temperature (T) for the chain consisting of N = 200 beads and for different chain architectures*

Confirmation of the existence of the transition from the weakly to the strongly adsorbed chain in the vicinity of the temperature $T^* = 2$ can be observed in Fig. 4 where the heat capacity C_v is plotted versus the reduced temperature T^*. The heat capacity was calculated according to the fluctuation theorem, *i.e.*:

$$C_v/k = \left(\left\langle E^2\right\rangle - \left\langle E\right\rangle^2\right)/k^2T^2 = \left(\left\langle \nu^2\right\rangle - \left\langle \nu\right\rangle^2\right)(T^*)^2 \qquad (4)$$

where: *k — the Boltzmann's constant, E — total energy of the chain, ν — number of polymer-surface contacts*.

All C_v/k curves show maxima conditions, although the transition temperature for linear chain occurs at the highest temperature and it decreases with the increase of the number of arms: T_C (linear) = 2.3, T_C (f = 3) = 2.0, T_C (f = 4) = 1.9. It should be also pointed out that the transition from the weakly adsorbed chain to the strongly

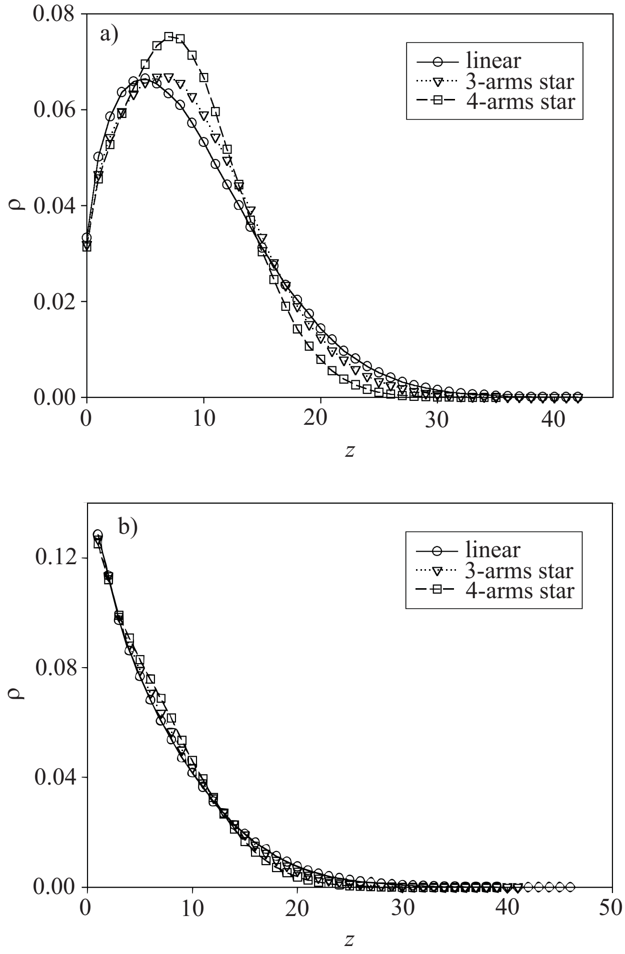

Fig. 5. The density of polymer beads (ρ) versus a distance from the attractive surface z for the chain consisting of N = 200 beads, for different chain architectures at the temperature: a) T = 10, b) T* = 2*

adsorbed chain took place at the temperature close to the temperature of the coil-to globule transition of a free chain [31].

The next important question concerns the spatial distribution of polymer beads as experiments suggest that this distribution is different for different molecular architectures [18]. In Figure 5 we present the density of polymer beads (ρ) as a function of the distance from the attractive surface *z* at two different temperatures and thus, for different adsorption regimes. The density is the number of beads at a given distance from the surface divided by the total number of polymer beads *N*. In the region of weakly adsorbed chains, *i.e.* at the temperature *T** = 10 (Fig. 5a) the distribution functions take the maximum values at the distance of 4—6 lattice units and this maximum shifts towards longer distances with the increase of the number of arms in the star. For longer distances from the surface the density functions are smooth and decay exponentially [$\rho \sim \exp(-z)$] as it was suggested by analytical theories [10]. These differences between the thickness of the polymer layer formed by linear and branched chains at high temperatures are apparently caused by the internal architecture of a polymer chain. For the case of stars usually one arm (or one arm plus a part of the second one) is adsorbed and the remaining part of a chain is rather free. In the vicinity of the transition from weakly to strongly adsorbed chain a rearrangement of the entire macromolecule takes place and non-adsorbed parts of chain (non-adsorbed arms of the star) look for the non-covered surface what usually requires movement of parts of the chain in *z* direction. This behavior confirms predictions of scaling analysis [25]. The annealing of the system leads to a different shape of the density functions. On Fig. 5b we present functions ρ for the temperature *T** = 2. The density functions are almost the same for all kinds of chain architectures and decay exponentially but more rapidly than at high temperature. The thickness of the polymer layer is therefore considerably smaller than that at high temperatures and almost the same for all architectures under consideration.

CONCLUSIONS

In this work the analysis of the structure of adsorbed linear and star-branched polymer chains was made. It was shown that weakly adsorbed macromolecules had rather properties of three-dimensional polymer chains regardless of the internal architecture. The crossover region from three-dimensional to two-dimensional chain was determined and the transition temperature appeared to be diminished with the number of arms of the star. The second important conclusion is that there are no essential differences in segment distribution for linear and star-branched chains. The differences can by found at high temperatures only, where the increase of arms shifts the maximum apart from the surface.

It was shown in real experiments that the adsorption of polymer chains depends strongly on their concentration [38]. Dense polymer systems with different macromolecular architecture and in different solvent conditions will be a subject of our further studies. Differences in the dynamic behavior of adsorbed and grafted linear, star and ring polymers will also be studied.

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