COMPUTER SIMULATIONS OF ADSORBED POLYMER CHAINS*

Andrzej Sikorski and Piotr Romiszowski

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

(Received March 10, 2005)

Dedicated to Professor Andrzej Fuliński on the occasion of his 70th birthday

The simple cubic lattice model of polymer chains was used to study the properties of adsorbed macromolecules with different internal architectures: linear chains and star-branched chains with 3 arms of equal lengths. The polymer chains were modeled with the excluded volume interactions only, *i.e.* in good solvent conditions. The chains were placed on an impenetrable surface and a contact potential between polymer segments and this surface was assumed. The strength of this potential was chosen to emulate the conditions of a weak adsorption regime. The Metropolis-like sampling Monte Carlo algorithm was used to determine the properties of the adsorbed polymer film. The size and the internal structure of adsorbed chains were described. The size, distribution and lifetimes of structural elements such as tails, loops and trains were also determined. The differences between the structure of films consisting of star-branched and linear chains were described and discussed.

PACS numbers: 07.05.Tp, 61.25.Hq, 83.10.Nn

1. Introduction

The adsorption of polymer chains on a solid surface is a very important phenomenon in material science due to practical applications such as colloidal stabilization, glueing, lubrication *etc.* [1]. It is possible to study such polymer systems experimentally using techniques like quasi-elastic light scattering, induced fluorescence and small angle neutron scattering and measurements of forces between polymers adsorbed from the dilute solutions and the surface [2-4]. The adsorption of polymers usually was performed up

* Presented at the XVII Marian Smoluchowski Symposium on Statistical Physics, Zakopane, Poland, September 4–9, 2004.

to the saturation of the adsorbed layer, what means, that the real experiments concerning isolated polymer chains (infinitely diluted systems) are difficult. Recently, Maier and Radler have studied DNA molecule adsorbed on a lipid bilayer by the means of fluorescence microscopy, while Granick and Frantz studied adsorbed polyethylene glycol [5-6]. The polymer adsorption is also interesting from the theoretical point of view because the presence of the attractive surface distorts the properties of the adsorbed chains when they are compared to free chains in solution or in the melt. One of the important questions concerns the influence of the internal architecture of macromolecules on the properties of adsorbed polymer chains. Experiments concerning the adsorption of polymer chains having the internal architecture different from linear have also recently been carried out. Yerushalami *et al.* studied cyclic polystyrenes in cyclopentane located between two mica surfaces [7]. They found that in solvent conditions at which chains were adsorbed they were different for both architectures. Stratouras and Kosmas explained this behavior from the theoretical point of view and showed that rings were significantly more adsorbed than linear chains [8]. The structure of an adsorbed polymer can be described in the terms of trains, loops and tails. A train is formed by adjacent beads, which are adsorbed, a loop is simply a connection between a pair of trains (the connection formed by not adsorbed beads only) while a tail is a sequence of not adsorbed beads at the end of a chain. Fig. 1 presents a scheme of these structural elements.

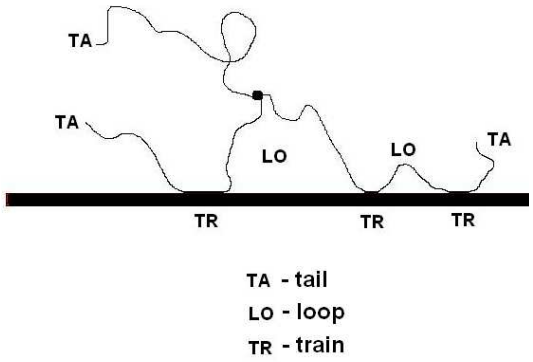


Fig. 1. A scheme of an adsorbed star-branched chain and its structural elements.

Experimental works are still not able to study the detailed structure of the adsorbed chain, *i.e.* trains, loops and tails. The number and mean length of trains, loops and tails was given in the mean field lattice theory of Scheutjens and Fleer that originated from the Flory–Huggins theory of polymer solutions [9–10]. They also showed that for shorter distances from the adsorbing surface segment density decays exponentially but for longer

distances this decay is much slower. Binder and co-workers carried out Monte Carlo simulations of single adsorbed short polymers on a diamond lattice [11]. They determined the temperature at which the adsorption of chains changed from weak to strong. They also studied some properties of chains in these both regimes. Tirrell *et al.* studied the irreversible adsorption of lattice linear chains using the Monte Carlo simulations [12].

Properties of branched chains were found in general to be different from their linear counterparts [13]. Therefore, the comparison of properties of polymers with different internal architectures seems to be interesting from the theoretical point of view. Kosmas *et al.* developed a theory of adsorbed polymer chains with no excluded volume [14]. They found that the difference in adsorption of star-branched polymers consisting of a few arms and linear chains were almost negligible. For stars with $f = 3$ arms the adsorption appeared to be 6% higher than of linear chains. The increase of the number of arms caused the higher adsorption of a polymer. This was explained by the fact that a polymer had a more compact structure than a linear one. These results were confirmed recently by Joanny and Johner [15]. Halperin and Joanny performed a scaling analysis of adsorbed star-branched chains [16]. They found that in the case of a weak adsorption the chains retained their spherical shapes and scalings characteristic of free polymers. Binder and Ono studied star-branched polymers, which were adsorbed to impenetrable surfaces using the scaling theory and the renormalization group method [17–19]. They showed that scaling exponents of density profiles depended on the number of arms. Recently, we built a simple lattice model for the simulation of the isolated polymer chains adsorbed on an attractive surface and for studying the influence of the chain architecture on the degree of adsorption [20–22]. It was shown that ring chains were about 50% more adsorbed than linear and star-branched chains. The transition from a weakly to a strongly adsorbed chain was found to take place at the same temperature for all chain architectures. Besides the Metropolis sampling method other Monte Carlo algorithms like the configurational bias Monte Carlo (CBMC) algorithm (which is, in fact, a modified Rosenbluth–Rosenbluth method) were used. Binder *et al.* studied the transition from a weak to strong adsorption by this method [23]. The adsorption of a copolymer on patterned surfaces was investigated by Semler and Genzer also by means of CBMC [24]. Some dynamic properties of the adsorbed polymer systems were also investigated by a Monte Carlo method [22, 25, 26].

In this paper, we compared the properties of polymers having different macromolecular architecture: linear and star-branched chains. For the purpose of this study we designed simple models of polymers using two approximations — a united atom and a lattice representation. The properties of these model chains were determined using the dynamic Monte Carlo sim-

ulations — the simulation algorithm is explained in the following section. The detailed analysis of the internal structure of chains was presented and the differences between linear and star-branched polymers were pointed out.

2. Model and the simulation algorithm

We studied models of two different macromolecular architectures: linear chains and star-branched chains. In both cases we suppressed all the atomic details and polymers were represented by united atoms [20, 27]. It was shown that the reduced models can be used for studying structural properties of polymer systems assuming that we were not interested in very fast processes and in the atomic structure. Linear chains consisted of the sequence of identical beads (homopolymers). The star-branched model chains consisted of $f = 3$ arms. Each arm emanated from the same origin (the branching point) and consisted of n identical beads. Therefore, the total number of beads in the star-branched chain was $N = f(n-1)+1$. The second assumption was that the positions of polymer beads were restricted to vertices of a simple cubic lattice. The polymer chains were studied in good solvent conditions. The excluded volume interaction was introduced into the model by forbidding the double occupancy of lattice sites by polymer beads. We studied the structure of adsorbed single chains, *i.e.* infinitely diluted systems.

The chains were put into the Monte Carlo box with periodic boundary conditions imposed in x and y directions only. The size of the Monte Carlo box was chosen large ($L = 200$) to minimize the influence of its size on the results. Additionally, in the plane $z = 0$ we placed the surface which was impenetrable for polymer beads. The adsorption of chains on that surface was realized by the introduction of an attractive contact potential between the surface and polymer beads. This potential had the form of square well commonly used in lattice models:

$$V(z_i) = \begin{cases} 0 & \text{for} \quad z_i > 1\,, \\ \varepsilon & \text{for} \quad z_i = 1\,, \\ \infty & \text{for} \quad z_i < 1\,, \end{cases} \tag{1}$$

where z_i is a distance between i-th polymer bead and the surface while ε is a negative constant. The reversed potential could be treated as a usual measure of the temperature of the system $T^* = 1/\varepsilon$. As we studied the case of the weak adsorption the problem how to keep the chain in contact with the surface appeared. The properties of model adsorbed chains were studied by means of the Monte Carlo method and the simulation algorithm was based on the Metropolis scheme [27]. The initial conformation of the chain underwent a series of local changes of its conformation. The set of these micro-modifications presented in Fig. 2 was the following: (a) two-bond

motion, (b) three-bond motion, (c) three-bond crankshaft motion, (d) ends reorientations, and (e) branching point collective motion (for star-branched chains only). All the local moves were selected randomly along the chain

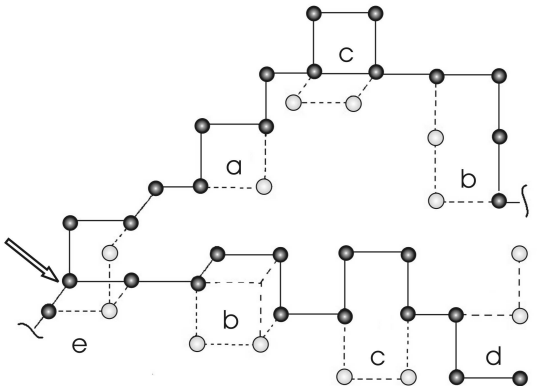


Fig. 2. The set of micro-modifications of the chain-light beads show new positions (see text for details). An arrow shows the branching point.

during the simulation. It was shown that one can define a time unit as an average attempt of every micro-modification per one polymer bead. The transition from an old to a new conformation was accepted according to the Metropolis criterion with the following probability:

$$P_{\text{old}\to\text{new}} = \min\left\{1,\, \exp\left(\frac{E_{\text{new}} - E_{\text{old}}}{kT}\right)\right\}, \tag{2}$$

where E_{old} and E_{new} were the energies of old and new chain conformations, respectively, k was the Boltzmann constant and T was the temperature. The randomly chosen chain conformation underwent a series of local motions, usually in the order of 10^7–10^8 time units. For each set of parameters (macromolecular architecture and the chain length N) 30–40 different and independent long simulation runs were performed.

Since the aim of this work was to study equilibrium properties of the system one had to be sure that the state of equilibrium had been reached. In order to provide that we performed the simulations according to the following procedure: the system in its initial random conformation was equilibrated for a long time. The equilibration runs lasted for at least 10^6 time units, depending on the size of the system. At equal time intervals the control parameters were obtained. These were: the mean dimensions of the system, the mean energy of the system and their fluctuations. The equilibration runs were performed until the probe results were reasonably stable and independent of different sampling periods. After the equilibration was

achieved the main simulation runs begun. Calculated parameters were averaged over many independent simulation runs and one can estimate the standard errors of these parameters on the level of 2–3%.

3. Results and discussion

The calculations were made for the chains consisted of $N = 50$ to 1200 beads (linear polymers) and of $N = 49$ to 1201 beads (star-branched polymers). The potential of interaction between polymer beads and the surface was chosen to be $\varepsilon = -0.3$ because it was shown that this potential corresponded to the reduced temperature T^* located just above the transition from a weak to a strong adsorption regime [20].

Some information about the structure and local mobility of adsorbed polymers can be obtained from the analysis the elementary changes of chain conformation. In Fig. 3 we present the fraction of elementary motions accepted due to the Metropolis criterion as a function of the distance from the adsorbing surface for star-branched chain with $N = 199$ beads. The analogous fractions for linear chain with $N = 200$ beads were almost the same so we do not present them. In the vicinity of the adsorbing surface all the motions were less effective. This can be explained by the fact that the adsorbing surface was an obstacle for modifications. Moreover, the density of polymer beads was in this region considerably larger (see the discussion below). For longer distances (above 5 lattice units) the acceptance fraction of these all types of motion remained on the steady level. In the outer part of the polymer film, *i.e.* for z close to 40 the fraction of the acceptance fluctuated. The main conclusion was that the mobility of the entire adsorbed

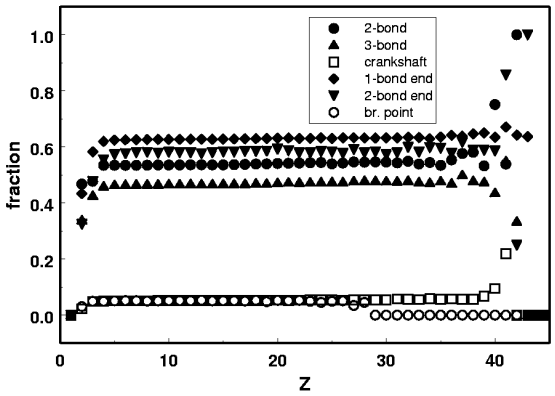


Fig. 3. The fraction of accepted local moves as a function of the distance from the adsorbing surface. Types of moves are given in the inset. The case of a star-branched chain for $N = 199$.

linear and star-branched chain was rather constant with the exception of the thin layer located directly on the adsorbing surface. One has to remember that the motion of the entire adsorbed polymer chain in the very long time limit had to be the same for all distances z because of the chain connectivity. The above results could be treated as complementary to the results of Baschnagel and Binder showing the difference in the perpendicular and parallel motion of adsorbed chains [28]. Real experiments suggest that this distribution was different for different molecular architectures [16]. In Fig. 4 we present the density profile of polymer beads ρ *versus* the distance from the attractive surface z for two pairs of linear and star-branched chains of the same length. The density was calculated as the number of beads at a given distance from the surface divided by the total number of polymer beads N. One can observe that, surprisingly, differences between density profiles of linear and star-branched chains were rather small. The only difference was that the segment density for shorter distances from the

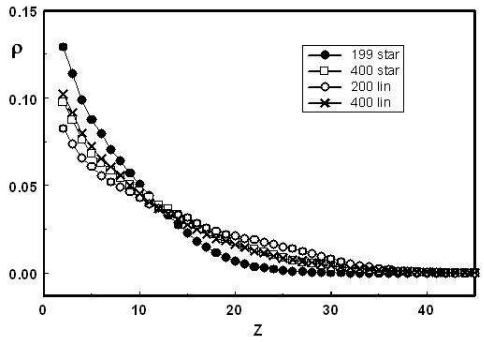


Fig. 4. The density of polymer beads as a function of the distance from the adsorbing surface z. The chain length and the architecture of chains are given in the inset.

adsorbing surface was larger for star-chains while for longer distances the star density was smaller. This can be explained by the fact that near the branching point the segment density was always larger than in the middle of linear chain. The shape of these density profiles did not depend strongly on the chain length. The increase of the chain length led to almost the same segment density. Density profiles predicted theoretically for chain without the excluded volume scaled as $\rho \sim \exp(-az)$. For chains in good solvent conditions, *i.e.* with the excluded volume the scaling was $\rho \sim z^{-1/2}$ (but in good solvent conditions polymers had high tendency to dissolve rather than to adsorb [29]). Density profiles obtained in our simulations were quite different from those obtained for chains located between two walls ("double confinement" regime) [30].

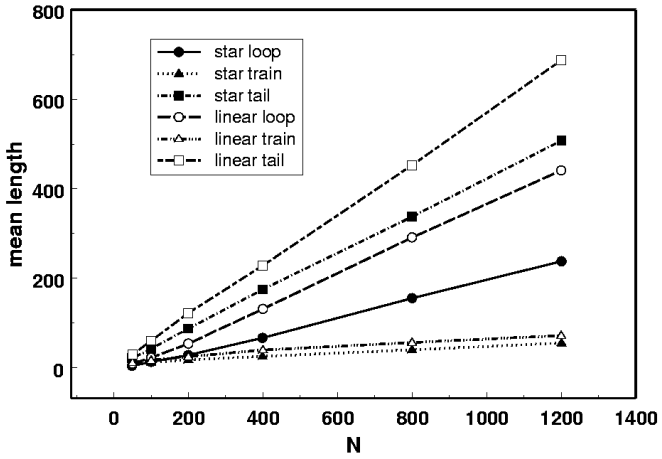


Fig. 5. Mean length of loops, trains and tails as a function of chain length N.

The structure of an adsorbed chain was usually described in terms of trains, loops and tails (see Fig. 1). Fig. 5 shows the plot of the mean length of these structural elements as a function of the total chain length N. One can observe that all these dependences are linear. The length of the trains was relatively small comparing to the length of tails and loops. It means that for the weak adsorption the majority of chain remained away from the surface and thus the chain was only slightly deformed comparing to the free chains. Considering chains with different internal architecture it was especially interesting to study the frequency of the appearance of trains, loops and tails along the chain.

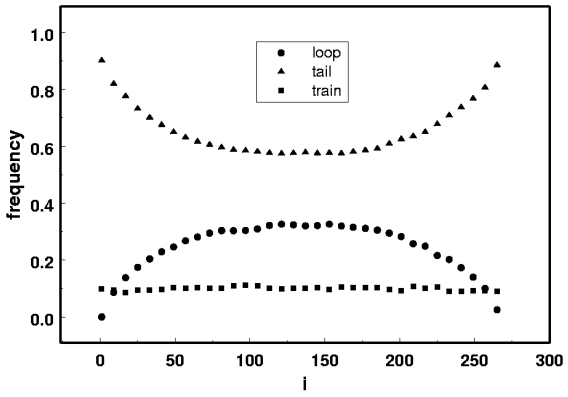


Fig. 6. Frequencies of the appearance of a structural elements as a function of a bead number. The case of a star-branched chain with $N = 400$.

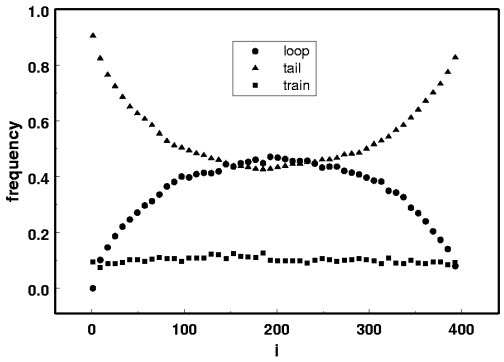


Fig. 7. Frequencies of the appearance of a structural elements as a function of a bead number. The case of a linear chain with $N = 400$.

Figs. 6 and 7 present such frequencies for linear and star-branched chain. One can uniquely define these structural elements for star-branched chains when stars were treated as the set of three linear chains consisted of pairs of star's arms. The bead numbering was here different for both chain architectures. For linear chains beads number grew from one end to another.

For star-branched chains the numbering went from one end of an arm through the branching point towards the end of the other arm. One can observe that for linear and star-branched chains the frequency of trains was almost constant for all beads and very low (on the level of 0.1). This is obvious as weakly adsorbed chains had only few contacts with the surface [20]. The formation of loops was more probable near the middle point of linear chains and near the branching point in star polymers. The formation of tails was the highest for end beads and the lowest for the middle part of chains. The main difference between linear and star-branched chains was that the frequency of loops was higher in the inner part of arms and in the vicinity of the branching point. On the other hand, the formation of tails in these parts of stars was less frequent. The stability of the above mentioned structural elements of the adsorbed chain was also studied. Figs. 8 and 9 present the mean lifetimes of trains, loops and tails for both polymer architectures. The bead numbering was the same as described in the previous paragraph. One can see that the lifetimes of trains were almost constant along the chain contour and close to 1 what implied that, in average, in every time unit a train disappeared. The lifetimes of loops depended on the position of the beads — the shortest lifetimes were observed at the ends of chains. The lifetimes of tails were the longest and almost constant for the beads located in the middle of chains. At the ends of chains the lifetimes of tails increased rapidly. In general, for both cases of chain architecture the lifetimes were very similar.

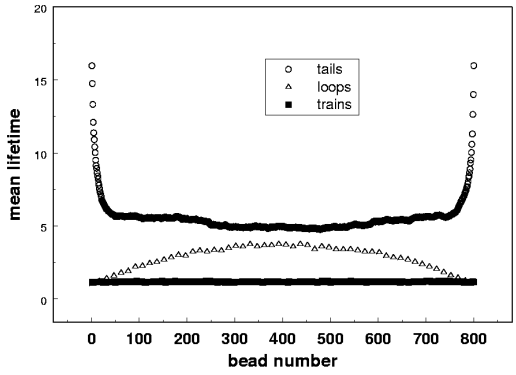


Fig. 8. Lifetimes of structural elements as a function of a bead number. The case of a linear chain with $N = 800$.

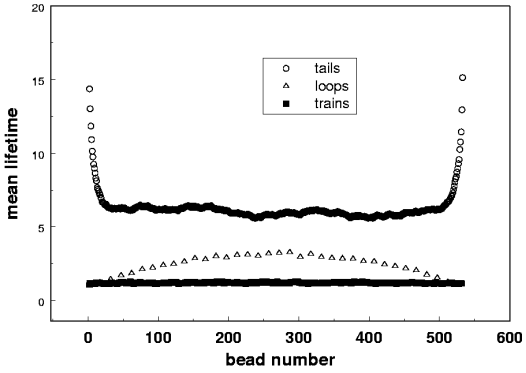


Fig. 9. Lifetimes of structural elements as a function of a bead number. The case of a star-branched chain with $N = 799$.

4. Conclusions

In this paper we made an elementary analysis of structure of weakly adsorbed linear and star-branched chains. The density profiles, as well as the structure of polymer films, were investigated. The dynamic behavior of structural elements of adsorbed chains like trains, loops and tails was analyzed and the differences were pointed out and discussed. It was shown that in spite of different macromolecular architecture the structures of adsorbed chains were rather similar while bulk properties of such chains were quite different.

REFERENCES

[1] R. Eisenriegler, *Polymers near Surfaces*, World Scientific, Singapore 1993.

[2] M. Kawagushi, H. Yu, *Macromolecules* **20**, 2732 (1981).

[3] D. Aussere, H. Herret, F. Rondelez, *Phys. Rev. Lett.* **54**, 1948 (1985).

[4] K.G. Barnett, T. Cosgrove, B. Vincent, A.N. Burgess, T.L. Crowley, T. King, J.D. Turner, Th.F. Tadros, *Polymer* **22**, 283 (1981).

[5] B. Maier, J.O. Radler, *Phys. Rev. Lett.* **82**, 1911 (1999).

[6] P. Frantz, S. Granick, *Phys. Rev. Lett.* **66**, 899 (1991).

[7] R. Yerushalami-Rozen, B.J. Hostetter, L.J. Fetters, J. Klein, *Macromolecules* **23**, 2984 (1990).

[8] G. Stratouras, M. Kosmas, *Macromolecules* **25**, 3307 (1992).

[9] J.M.H.M. Scheutjens, G.J. Fleer, *J. Phys. Chem.* **83**, 1619 (1979).

[10] J.M.H.M. Scheutjens, G.J. Fleer, *J. Phys. Chem.* **84**, 178 (1980).

[11] E. Eisenriegler, K. Kremer, K. Binder, *J. Chem. Phys.* **77**, 6296 (1982).

[12] K. Konstadinidis, S. Prager, M. Tirrel, *J. Chem. Phys.* **97**, 7777 (1992).

[13] G.S. Grest, L.J. Fetters, J.S. Huang, *Adv. Chem. Phys.* **94**, 67 (1996).

[14] M.K. Kosmas, *Macromolecules* **23**, 2061 (1990).

[15] J.F. Joanny, A. Johner, *J. Phys. II (France)* **6**, 511 (1996).

[16] A. Halperin, J.F. Joanny, *J. Phys. II (France)* **1**, 623 (1991).

[17] K. Ono, K. Binder, *J. Stat. Phys.* **64**, 781 (1991).

[18] K. Ono, K. Binder, *J. Chem. Phys.* **95**, 5444 (1991).

[19] K. Ono, K. Binder, *J. Chem. Phys.* **95**, 5459 (1991).

[20] A. Sikorski, *Macromol. Theory Simul.* **10**, 38 (2001).

[21] A. Sikorski, *Macromol. Theory Simul.* **11**, 359 (2002).

[22] A. Sikorski, *Macromol. Theory Simul.* **12**, 325 (2003).

[23] S. Metzger, M. Muller, K. Binder, J. Baschnagel, *Macromol. Theory Simul.* **11**, 985 (2002)

[24] J.J. Semler, J. Genzer, *Macromol. Theory Simul.* **13**, 219 (2004)

[25] A. Milchev, K. Binder, *Macromolecules* **29**, 343 (1996)

[26] R.B. Pandey, A. Milchev, K. Binder, *Macromolecules* **30**, 1194 (1997)

[27] A. Sikorski, P. Romiszowski, *J. Chem. Phys.* **104**, 8703 (1996).

[28] J. Baschnagel, K. Binder, *J. Phys. I (France)* **6**, 1271 (1996).

[29] S.S. Patel, M. Tirrel, *Annu. Rev. Phys. Chem.* **40**, 597 (1989).

[30] A. Sikorski, P. Romiszowski, *Acta Phys. Pol. B* **35**, 1535 (2004).