Computer Simulation of the Dynamic Behavior of Double Polymer Brush-Solvent Systems

K. Hałagan¹, M. Banaszak^{2,3}, J. Jung¹, P. Polanowski¹, A. Sikorski^{4*}

 Lódź University of Technology Department of Molecular Physics ul. Żeromskiego 116, 90-924 Łódź, Poland

² Adam Mickiewicz University Faculty of Physics ul. Uniwersytetu Poznańskiego 2, 61-614 Poznań, Poland

³ Adam Mickiewicz University NanoBiomedical Centre ul. Wszechnicy Piastowskiej 3, 61-614 Poznań, Poland

> ⁴ University of Warsaw Faculty of Chemistry ul. Pasteura 1, 02-093 Warsaw, Poland E-mail: sikorski@chem.uw.edu.pl

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Abstract: Opposing polymer brush systems were investigated by computer simulations. In a coarse-grained model, chains were restricted to a face-centered cubic lattice with the excluded volume interactions only. The macromolecules were grafted onto two parallel impenetrable surfaces. The dynamic properties of these systems were studied by means of Monte Carlo simulations. The Dynamic Lattice Liquid model and a highly efficient parallel machine ARUZ were employed, which enabled studying large systems at long time scales. The influence of the surface grating density on the system dynamic was shown and discussed. It was demonstrated that the self-diffusion coefficient of solvent depended strongly on the grafting density.

Key words: dynamic lattice liquid, lattice models, Monte Carlo method, polymer brushes, polymer dynamics

I. INTRODUCTION

Polymer brushes are built of chains terminally attached to a surface. Brushes were the subject of various experimental techniques of synthesizing, as recently reviewed [1-5]. They were also studied theoretically but owing to their complexity many questions are still not fully answered [1-3].

Understanding the factors that influence the properties of brushes is therefore important for designing useful and intelligent polymeric systems [6]. The properties of brushes were studied by means of Molecular Dynamics and Dissipative Particle Dynamics [7–9], Monte Carlo simulations [8, 10–18], scaling theory, and self-consistent-field theoretical considerations [17, 19–22].

Opposing polymer brushes are systems that consist of two parallel surfaces, both grafted with chains, i.e. they consist of a pair of brushes. They were also a subject of interest [23]. The theoretical treatment mainly concerned the compression of such brushes [24–27]. Computer simulations were found to be a useful tool for studying opposing polymer brushes: structure, interaction, and friction between a pair of brushes (neutral and charged) were recently investigated [26, 28–33]. The latest studies revealed the structure of such brushes at very high grafting densities and for relatively long macromolecules showing surprisingly small interpenetration and different scaling behavior of short and long chains [18].

In this paper, we focus on solvent and polymer dynamics in opposing polymer brushes. Both brushes were synthesized simultaneously using a 'grafting from' procedure, where the polymerization of each chain started from a surface. Because of the complex molecular architecture, great lengths of chains and high polymer concentration, these systems had to be studied employing coarse-grained models. The representation of macromolecules was therefore highly reduced, and polymers consisted of interconnected statistical segments that were embedded to nodes of a face-centered cubic (FCC) lattice. Chains were firmly grafted by one end to an impenetrable planar surface and a pair of surfaces formed a slit. The model system was studied at good solvent conditions, where all non-bonded interactions were the same in the whole system under consideration, and thus assumed equal to zero. The excluded volume was the only potential implemented directly into the model. In the simulations, we employed a realistic probability of polymerization per algorithm time step (10^{-6}) . A long relaxation time, up to 10^9 Monte Carlo steps (total simulation time), allowed reaching equilibrium states of the confined dense polymer brushes. Dynamic Monte Carlo simulations of the presented model were carried out by means of the Dynamic Lattice Liquid (DLL) model dynamics [34, 35]. This effective simulation algorithm provides the proper dynamics and reproduces the molecular transport in dense systems. It has already been successfully used to study various polymerization processes and other dynamical phenomena in soft matter systems [36-38].

II. THE METHODOLOGY

The DLL model used in the present simulations is based on the concept of strictly cooperative motion of objects in a dense system. The objects represent coarse-grained fragments of matter, which in our case means polymer segments and solvent molecules. For simplicity, the positions of objects are limited to the nodes of a quasi-crystalline face centered cubic lattice with the coordination number q = 12. It has been assumed that the system has some excess volume, so each object has enough space to vibrate around its position like in real dense liquid. This position is, however, defined by a lattice node. In contrast to many other lattice models, DLL allows studying of systems with all lattice sites occupied by objects, i.e. at the highest density. One object can occupy one lattice node, which implies the introduction of the excluded volume potential. All remaining longdistance interactions were assumed to be the same and thus were not taken into consideration, and the model was strictly athermal, that is, at good solvent conditions. The objects cannot move over a longer distance because all lattice sites in the system are occupied by other polymer segments and solvent molecules. A long-range motion can take place as a cooperative rearrangement having a form of a closed loop of displacements involving at least three neighboring objects. The DLL model described above has been implemented as a dynamic Monte Carlo simulation and the single simulation time step consisted of the following stages:

- The generation of random vector field of motion attempts. A unit vector, pointed towards one of the nearest-neighboring lattice sites was associated with each lattice site. It represents the direction along which the object attempted to move.
- 2. The identification of groups of vectors forming closed loops indicated the ways of possible cooperative rearrangements of objects in space. The rest of the objects is immobilized at the given time step. Additionally, if the movement realized in a given loop would lead to break a bond between segments in a polymer chain or to cross a chain, then the loop is immobilized.
- 3. Rearrangement of objects along these loops by displacing them to neighboring sites according to the vector generated in step (1).

A discussion of the detailed balance and ergodicity of the DLL algorithm was presented elsewhere [34]. Time was assumed to be a discrete variable for which the positions of all objects were attempted to be updated simultaneously. Compared to real experiments, one time step in DLL corresponds to 6×10^{-13} s for systems consisting of low-weight molecules [39] up to 3×10^{-12} s in the case of macromolecular systems [13].

The model system under consideration contained fully flexible chains immersed in a solvent. The simulation procedure consisted of two steps. In the first step, polymer chains grafted to a pair of parallel surfaces were virtually synthesized. Polymer brushes in real experiments can be obtained using two different methods: by tethering the chains that were previously polymerized and by growing chains from initiators anchored on the surface [40–43]. The second method enables to obtain highly grafted brush. Moreover, in computer simulations it is the only way to obtain properly equilibrated highly grafted macromolecular systems [4, 13]. Therefore, the second method was chosen for this study.

During the first part of the simulation, the entire simulation box was filled with a monomer while the initiator was randomly placed on both surfaces with an assumed grafting density. The controlled living irreversible radical polymerization was chosen, and the process of attachment of monomers to a growing chain was assumed to be irreversible with the reaction rate of this polymerization $p = 10^{-6}$. This choice was previously justified [13, 18, 44]. The chains grew until they reached the desired number averaged degree of polymerization DP_n value. It has to be underlined that this criterion of polymerization termination leads to the generation of polydisperse systems, which much better reflects properties of real brush systems [13]. After the reaction was stopped, the unreacted monomer was replaced by inert solvent molecules. The second step was a production run. Fig. 1 presents the scheme of the DLL model applied to this simulation.

The model system was a slit built by a pair of parallel impenetrable surfaces with width 2d = 142. The edge of the Monte Carlo box directions parallel to the surfaces was set as L = 144. Therefore, there were 1 492 992 FCC lattice nodes in the system. Periodic boundary conditions were applied both in x- and y-direction. The end of each chain was immobilized on one of the surfaces while the grafting positions were randomly selected. The synthetized systems were polydisperse and, therefore, we describe them using the averaged degree of polymerization. The number averaged degree of polymerization DP_n is defined as usual $DP_n = \sum_{i=1}^{2N} n_i m_i / \sum_{i=1}^{2N} n_i$, where 2N is the total number of chains in the system, m_i is the number of polymer segments of $i^{\rm th}$ chain and n_i is a number of chains with length m_i . The grafting density of each brush was defined as the number of chains grafted to one surface to the number of lattice nodes forming a surface. The grating density was always assumed to be the same for both surfaces. The following grafting density σ was studied: 0.2, 0.25, 0.3, 0.35 and 0.4.



Fig. 1. The scheme of the DLL algorithm. The 2D case is presented for simplicity

As the number of objects in the system under consideration exceeded 10^6 (the simulation box was composed of $72 \times 144 \times 144$ lattice nodes, with more than 8000 polymer chains), it was impossible to study a large number of time steps using a typical computer cluster or supercomputer running a DLL algorithm [45]. Therefore, the usage of the dedicated computing hardware appeared to be inevitable.





(b)

Fig. 2. Photos of the dedicated machine ARUZ. (a) Power system and (b) interconnection cables between electronic circuits

We employed the Analyzer of Real Complex Systems (Polish: Analizator Rzeczywistych Układów Złożonych – ARUZ) [45-47]. This dedicated machine was designed and constructed using the Technology of Real Systems Analyzers (Polish: Technologia Analizatorów Układów Rzeczywistych - TAUR) developed at Łódź University of Technology [48]. The machine is located in the BioNanoPark Łódź (Poland). It is composed of almost 26 000 reconfigurable Field Programmable Gate Arrays (FPGAs) interconnected in a 3D network - see Fig. 2. ARUZ is a scalable, fully parallel data processing system equipped with low-latency communication channels, dedicated to simulation of dense systems containing a huge number of elements interacting locally. ARUZ can perform DLL simulations for systems with several millions of objects with 10^9 time steps performed in just a few days (this corresponds to ca. 200 days on a HPC node using multithreading [45]). This was the first time this timescale was reached for the DLL algorithm for the simulation box of the described size.

III. RESULTS AND DISCUSSION

The studies concerning the influence of the grafting density were carried out for systems where $DP_n = 110$, where both brushes interpenetrate [18]. The previous studies showed that grafting density $\sigma = 0.3$ for single brushes and for opposing brushes was located near the value of transition from the so-called 'mushroom regime' to the real brush regime [18]. This value corresponds to 0.35 chains/nm² in a system where a polymer bead represents the MMA



Fig. 3. Configuration of an opposing polymer brush system. The case of $DP_n = 70$ and grafting density $\sigma = 0.3$. Solvent molecules are not shown here for clarity. Chain ends are marked as red

monomer unit [13]. Fig. 3 shows a snapshot of the opposing brush system under consideration for $DP_n = 70$ and for $\sigma = 0.3$.

The dynamic behavior of soft matter systems is usually studied by means of mean squared displacement (MSD), which is defined as $\Delta r^2(t) = \frac{1}{N} \sum_{i=1}^{N} \left[(\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 \right]$, where $\mathbf{r}_i(t)$ are coordinates of i^{th} object (a polymer bead or a solvent molecule) at time t and N is the total number of a given kind of object in the system. In general, the dependency of the mean-squared displacement vs time can be written as $\Delta r^2 \sim t^{\alpha}$. If diffusion follows the Einstein relation with the exponent $\alpha = 1$, it is called normal, while the case $\alpha < 1$ corresponds to a sub-diffusive (anomalous) motion. The latter is expected to appear in complex macromolecular systems [49]. Fig. 4 presents the MSD/t for polymer beads and solvent molecules as a function of time in a double logarithmic plot. MSD was divided by time in order to



Fig. 4. MSD/t as functions of time of polymer beads (top) and of solvent molecules (bottom). The case of degree of polymerization $DP_n = 110$. The grafting densities σ are given in the insets

better capture the phenomenon of anomalous diffusion: normal diffusion corresponds to fragments of plots parallel to the time axis while sub-diffusion corresponds to fragments where MSD/t decreases. Regions where normal diffusion is present are clearly observed for a very short time in the case of polymer beads while for longer times a sub-diffusive behavior was found. This behavior was expected, as the motion of grafted chains was limited. The influence of the grafting density was rather weak. The diffusion of solvent molecules is anomalous at the beginning and the end of trajectory. For intermediate times a sub-diffusive motion appears. The density of polymer in the system is apparently above the static percolation threshold but, despite this, the motion of solvent is not limited at a longer time scale. It can be explained by the fact that polymer chains are also mobile; it was previously shown that the percolation threshold do not exist for mobile obstacles [50–51].

Identification of regions with anomalous diffusion using MSD function is not an easy task as changes of the exponent α are rather small. Therefore, we calculated the exponent α as a logarithmic derivative of MSD: $\alpha = \frac{d(\log(\Delta \hat{r^2}(t)))}{\alpha}$ α as a logarithmic derivative of MSD: $\alpha = \frac{1}{\alpha(\log(t))}$. Fig. 5 presents the dependency of the exponent $\alpha - 1$ (i.e. deviations from a normal diffusion) vs time for various grafting densities σ . The deviations from the value $\alpha = 1$ were found at a time between $10^1 - 10^4$ (the first minimum) and for considerably longer times between 10^4 and 10^8 (the second minimum). The depth of the first one approaches the value 0.17. The same behavior was observed for the second minimum, although the changes in depth were smaller while the shift was considerably larger. It has already been proved that the first minimum can be related to the presence of an opposing polymer brush while the second is apparently caused by the presence of a pair of impenetrable surfaces [18, 52]. The grafting density does not influ-



Fig. 5. The parameter $\alpha - 1$ calculated for solvent molecules (see the text for details) as a function of time. The case of $DP_n = 110$. The values of grafting densities are given in the insets

ence the shape of $\alpha(t)$ curves but the higher σ , the deeper the minimum on an $\alpha(t)$ curve. The next visible influence of grafting can be found in the location of maxima on $\alpha(t)$ curves: the increase of σ shifts the minima on curves towards longer times. The depth of the second minima is almost not affected.

The mobility of solvent was calculated as the ratio of the number of performed moves in a given lattice node (when it was occupied by the solvent) to the total time units in a simulation run and averaged over the given plane xy. The reduced mobility was calculated dividing mobility by the mobility calculated for a pure solvent 0.0588 [53]. Fig. 6 presents the changes in the reduced mobility of solvent molecules





Fig. 6. Solvent mobility as a function of the position across the slit. The degree of polymerization $DP_n = 110$

in the brush across the slit for two grafting densities: in the 'mushroom regime' and in the brush regime. In the case of the 'mushroom regime', the reduction in solvent mobility is of the order of magnitude across the slit when going from the middle of the slit to the surfaces. In the brush regime, the changes of mobility are not significant.

The dynamics of chains in the opposing polymer brush systems takes place in cooperation with solvent molecules. The motion of the entire polymer is restricted because of its anchoring and, therefore, the motion of chain fragments. Fig. 7 presents the mean-squared displacement of selected beads in chains as a function of time in a double logarithmic plot. We chose beads number 25, 50 and 100 counting from the surface. Two regimes can be distinguished for each curve. The increase of distance from the grafting surface to a given bead along the chain contour makes the bead more mobile. In each regime, all chains exhibit the same scaling behavior regardless of the degree of polymerization: short time regime (below 10^2 time units), where $\Delta r^2 \sim t^1$ and a regime where the scaling changes between $t^{0.4}$ and $t^{0.5}$. The latter regime corresponds to a limited motion. Simulation within the frame of the same model for a solution of monodisperse free polymer chain a different scaling was found: t^1 the short time regime and $t^{0.3}$ (short chains) and $t^{0.4}$ (long chains) for longer times [39]. Recent simulation studies of single brushes based on the Bond Fluctuation Model and with lower grafting density ($\sigma = 0.11$) showed the scaling with time like $t^{0.5}$ (at longer time) but then flattens out [54].



Fig. 7. The mean square displacement of inner polymer beads (see the text for details). The degree of polymerization $DP_n = 110$. The grafting densities and the number of polymer beads are given in the inset

The long-time-scale dynamics of solvent in the opposing brush systems can be characterized by the self-diffusion coefficient D_{self} calculated from MSD as $D_{\text{self}} = \Delta r^2/6t$.

The values of the diffusion coefficient were determined in time windows where the diffusion was normal, i.e., where $\Delta r^2 \sim t^1$. Such regions can be found for all systems under consideration at the longest times. Fig. 8 presents the reduced self-diffusion coefficient D/D_0 , i.e. normalized by the value determined for a system containing solvent molecules only as a function of grafting density σ . The decrease in solvent mobility is strong, and one can describe it as an exponential: $D/D_0 \sim \exp(-\sigma)$. We compared our results with the Yasuda theory [55] based on free volume because it turned out that this theory was also useful for polymer systems studied using the DLL model [52] $\frac{D}{D_0} = \exp\left(B\frac{\Phi_p}{1-\Phi_p}\right)$, where B is a constant depending on free volume. One can observe that the fit is satisfactory.



Fig. 8. The reduced self-diffusion coefficient of solvent D/D_0 as a function of grafting density σ (top axis) and the polymer concentration $\Phi_p/(1-\Phi_p)$ (bottom axis). The case of $DP_n = 110$. The fit to the Yasuda theory was also marked

IV. CONCLUSIONS

Dynamics of a system consisting of opposing polymer brushes immersed in a good solvent were studied using a Monte Carlo simulation algorithm based on the Dynamic Lattice Liquid (DLL) with a cooperative movement concept. In this model, cooperative rearrangements on a lattice (face-centered cubic lattice) have the form of closed loops of displacements with all lattice sites of the systems occupied by polymers and solvent molecules. Simulations were performed using the Analyzer of Real Complex Systems (ARUZ), unique hardware – a fully parallel data processing system equipped with low-latency communication channels.

The main conclusions of this paper are related to the dynamic properties of opposing polymer brushes, and the focus was placed on the motion of solvent molecules in such a complex system. The appearance of anomalous diffusion was shown, with a recovery of normal diffusion, satisfying Einstein's law, for all systems studied. The mobility of solvent molecules depended on the distance from a grafting surface and reflected the distribution of polymer beads. It was also shown that the long-time self-diffusion coefficient was strongly dependent on the grafting density. The changes in the self-diffusion coefficient with the polymer concentration showed that it could be described by the free volume theory. On the basis of the deviation from normal diffusion of solvent in different layers of the slit, a possibility of capture changes of this mobility was shown.

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Krzysztof Hałagan received his MSc in Physics in 2006 and his PhD degree in Chemical Technology in 2013, both from Łódź University of Technology. His main fields of interest are computer simulations of molecular systems using Monte Carlo methods, molecular dynamics and quantum calculations. His main research area includes application of the Dynamic Lattice Liquid algorithm to various physicochemical problems like diffusion, polymerization kinetics and simulation of soft matter, polymer systems and complex liquids. He is interested in hardware-related issues, accompanying computer modelling, like dedicated computing devices based on FPGAs and GPUs.



Michał Banaszak graduated in Theoretical Physics from the Adam Mickiewicz University in Poznań in 1985. He received his PhD degree in Physics in 1991 from Memorial University in St. John's, Canada, specializing in Polymer Physics. From 1992 to 1995 he worked as postdoctoral fellow in Exxon Research & Engineering Co. in Annandale, New Jersey, USA, working on theory and modeling of polymer solutions. From 1995 to 1997 he worked in the Chemistry Department of UMIST in Manchester, UK, as a research associate, specializing in large-scale computer simulations of ionic copolymers. In 1997 he joined the Adam Mickiewicz University, obtaining his DSc degree (habilitation) in 2004 in Physics (specialization: Soft Matter Physics and Computer Simulations), and later professorship in Physics. His main interest is in developing new models and theories for nanoscale self-assembly of various polymer systems. He also collaborates with experimentalists, using large-scale computing. Since 2020 he has been serving as Vice-rector of the Adam Mickiewicz University for Digitalization and Business Cooperation.



Jarosław Jung received his MSc degree in Physics in 1987 from the University of Łódź and in Electronics in 1990 from Łódź University of Technology. He received his doctorate in Chemistry at Łódź University of Technology in 2001 and postdoctoral degree in Electronics in 2016. He works at the Department of Molecular Physics, Łódź University of Technology. His interests include the study of organic semiconductors and photoconductors, organic electronic devices, construction of electronic devices, as well as the design of state machines dedicated to the parallel simulation of dense molecular systems.



Piotr Polanowski received his MSc degree in Physics in 1987 from Łódz University. He earned the PhD in Chemistry from Łódz University of Technology in 2002 and the postdoctoral degree (habilitation) in Physics from the Adam Mickiewicz University in Poznan. Currently he works at Łódź University of Technology in the Department of Molecular Physics. His fields of interest cover simulations of complex molecular and macromolecular systems with saving proper dynamic behavior, parallel computing (hardware and software) in application to complex molecular systems, and simulation software development.



Andrzej Sikorski graduated from the Department of Chemistry, University of Warsaw. He completed his PhD thesis in Chemistry in 1986 in the same Department. In 1987/89 and 1990/91, he worked as a postdoc and visiting professor in Washington University in St. Louis and in The Scripps Research Institute in La Jolla. In 1995, he obtained his DSC degree in Chemistry. His main scientific interests are: theory and simulations of polymers at interfaces and in confined geometries and molecular transport in a crowded environment.