Molecular dynamics simulations of polystyrene brushes in dry conditions and in toluene solution

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The properties of polystyrene brushes in dry conditions and in toluene solution are studied as a function of grafting density using molecular dynamics simulations. Both, individual brushes and double layers of opposing brushes are considered, the structural properties of which were found to be similar. The density profiles show very pronounced density oscillations which extend up to approximately 1.8 nm and fall into two groups of three peaks each. These features are observed regardless of grafting density and solvent conditions. In the absence of solvent, the chains undergo a transition from an oblate to a spherical shape as the grafting density increases. In contrast, in good solvent, the chains remain spherical independent of the grafting density. Solvation also increases the extension of the polystyrene chains roughly by a factor 2.5. Isotropic and two-dimensional radial distribution functions are used to characterize the structure of the polystyrene brushes. Toluene is observed to form up to four layers at the base of the grafted chains irrespective of grafting density.

I. Introduction

Polymers play a key role in many important problems in chemistry as well as in biology and surface science.^{1,2} For example, properties of objects can be altered dramatically by applying thin polymer coatings to the surface of materials, as they allow control of the interaction of a material with its environment. Systems in which polymer chains are attached at one end to a solid substrate are called polymer brushes. Polymer brushes are of interest from both fundamental and technological^{3–5} points of view because they exhibit conformations and dynamics different from those of the corresponding bulk systems, and these properties can be controlled by the grafting density. Of particular importance is the response of polymer brushes in solutions since the structure of a given polymer brush is critically dependent on solvent interactions. In the absence of a solvent the polymer chains typically prefer to curl up at the surface, while addition of a "good" solvent causes stretching of the chains. There are energetic and entropic contributions to the free energy governing this transition, including the chain configuration entropy and the free energy of solvation (which again has potential energy and entropy contributions).⁶ At high grafting density, the molecules will therefore be stretched away from the surface and can attain a molecular shape far from the self avoiding coil conformation that polymer molecules assume in solution.^{7,8}

The properties of polymer brushes have been intensively investigated theoretically. The earliest studies^{9–11} employed scaling arguments and considered a Flory-type model to determine the free energy balance between contraction and stretching of the chains. In this model the monomers are described as blobs with a constant diameter which—in the

Department of Chemical Engineering and Materials Science, University of California Davis, Davis, California 95616, USA simplest approximation—is given by the average distance between grafting points, $\sigma^{1/2}$, where σ is the grafting density. This picture implies that the monomer density profile perpendicular to the surface is a step function. In spite of its simplicity the blob theory proved to be extremely useful and enabled *e.g.*, to identify the regimes in which polymer brushes can exist depending on solvent conditions and to predict the principle dependencies of chain conformation on grafting density and chain length. It also provides scaling rule for the dependence of the brush height *h* on the degree of polymerization (or "chain length") *N* and the grafting density σ

$$h \propto N \sigma^{2/3}$$
. (1)

Later work using self-consistent field theory focused on obtaining more realistic density profiles as well as end-to-end distance distributions.^{6,12,13} Specifically, these studies predicted a parabolic density profile

$$\rho(z) = \rho_0 - \alpha z^2, \tag{2}$$

where $\rho \propto \sigma^{2/3}$ and $\alpha \propto N^{-2}$. This expression is obtained under the assumption of long chains, and is applicable in bad or mediocre solvent conditions and surface densities which are sufficiently high to induce stretching. While analytic theories are appealing due to their generality, they represent a coarse approximation to the actual chemical interactions. The next level of description therefore consists of studying the behavior of model polymers using molecular dynamics¹⁴ or Monte-Carlo simulations.^{15–17} These investigations revealed *e.g.*, density variations at the surface ("layering") and a "round-off" zone¹⁴ near the top of brush. They also provided scaling expressions for various length scales, specifically the size of the "final blob" and the chain diameter perpendicular to the chain.¹⁶ Since early models have been chemically unspecific, a further refinement of modeling polymer brushes requires force fields designed to describe the properties of "real" polymers and the incorporation of specific solvents. This avenue is pursued in the present work.

In the past the majority of simulation studies has been conducted on single brushes due to the smaller computational burden. The objective of the present work is to investigate polystyrene single and double brushes with different grafting densities, in dry conditions and in toluene solutions, and, eventually to establish a connection to experiments. This is done through a detailed investigation of the structural properties of the polystyrene chains and toluene molecules in equilibrated brush configurations, as well as the toluene diffusivity. The calculated radial distribution functions and corresponding structure factors are quantities that can be obtained in for example neutron scattering experiments. In section II we describe the setup of the initial cells, and the parameter sets used in our simulations. In section III the results of our simulations are presented and the importance of our results in comparison with experiments and the relevance of our findings for future studies on this subject are discussed.

II. Method

All molecular dynamics simulations were carried out using the GROMACS simulation package.^{18,19} The polystyrene model used in some of our earlier studies^{20–22} was adopted to describe the inter- and intramolecular interactions. Bond lengths were constrained using the linear constrained solver (LINCS) algorithm.²³ The temperature and, for the unconstrained melt, the pressure were controlled using the weak-coupling scheme introduced by Berendsen *et al.*,²⁴ using time constants of 0.1 and 1 ps for the temperature and pressure control, respectively. The Coulombic interactions were treated using the particle mesh Ewald method²⁵ with a real-space cutoff of 2.5 nm.

A Non-grafted polystyrene melts

First, we constructed 48 atactic polystyrene chains, each containing 15 monomer units and equilibrated the system at a temperature of 450 K and a pressure of 1 bar for 1 ns using a timestep of 1 fs. Subsequently, the melt was enclosed between two graphene surfaces, each consisting of two graphite sheets. The graphene sheets were fixed in place and only served to spatially confine the polystyrene melt. The graphene walls were impenetrable for the polystyrene chains. The interaction between the chains and the wall was described using a Lennard-Jones potential,

$$V(r_{ij}) = \frac{C_{ij}^{(12)}}{r_{ij}^{12}} - \frac{C_{ij}^{(6)}}{r_{ij}^{6}},$$
(3)

with the following combination rules

$$C_{ij}^{(6)} = (C_{ii}^{(6)} \times C_{jj}^{(6)})^{1/2},$$
(4)

$$C_{ij}^{(12)} = (C_{ii}^{(12)} \times C_{jj}^{(12)})^{1/2},$$
(5)

where the parameters $C_{ii}^{(6)}$ and $C_{ii}^{(12)}$ are atom type specific. They have been taken from the Gromos Forcefield.²⁶ The system dimension was 7.2 \times 8.3 nm in the x-y plane, and the initial distance between the two surfaces was chosen to be large enough to contain the melt droplet taken from the unconstrained simulations. For comparison, the radius of gyration obtained for PS chains in a bulk melt is about 0.7 nm. The melt-surface system was then equilibrated for about 1 ns. Then the separation of the two graphite surfaces was reduced in a sequence of steps. At each step the system was equilibrated for 1.0 ps, after which the distance of the graphite sheets was reduced by 0.03 nm. The systems corresponding to five intermediate compressions were further equilibrated for 2 ns to calculate average properties as a function of compression. The melt was confined in the density range between 300 kg m⁻³ and 700 kg m⁻³.

B Grafted polystyrene melts

The construction of polymer brushes with various grafting densities began with the extraction of polystyrene chains from the bulk melt. The curled chains were stretched by carrying out a series of molecular dynamics simulations in which the outermost carbon atoms of each chain were sequentially moved outwards using position restraints. This procedure was carried out for each polymer chain in the original melt in order to preserve the correct tacticity.

Arrays of stretched polystyrene chains were then grafted onto a graphite surface in order to construct polymer brushes with different grafting densities.

The end-grafting was achieved by restraining the position of one end of the chain both laterally and vertically at a short distance (0.25–0.30 nm) above the graphite layer. Systems with 3×3 , 4×4 , 5×5 , and 6×6 polystyrene chains, corresponding to grafting densities ranging from $1.5-6.0 \times 10^{13}$ chains cm⁻², were created. The corresponding opposing double brush configurations were created in an equivalent manner with the distance between opposite graphite layers set to 12 nm. The dimension of the simulation cell perpendicular to the graphite surfaces was set to 50 nm in order to avoid interactions between the periodic images in this direction. This also enables us to calculate spherical averages without problems. We verified this cell size to be sufficient by carrying out test simulations with cell dimensions of up to 200 nm in the direction perpendicular to the graphite surfaces. Additional simulations with graphite surface separations of down to 6 nm were carried out in order to investigate possible overlap of chains. We will report on these results in an additional paper.

In order to investigate the effect of a good solvent, toluene molecules were added to the simulation cells until the solution reached a homogeneous density of $\sim 800 \text{ kg m}^{-3}$. The final numbers of toluene molecules in all simulations are summarized in Table 1. A united-atom toluene model, where both the C–H parts and the CH₃ part are treated as pseudo atoms, was used.²⁷ Stable profiles for pressure and potential energy are obtained after ~ 10 ns for single brushes and after ~ 5 ns for double brushes. All systems

Table 1 Total number of toluene molecules, n_{toluene} , in the single and double brush configurations, where $n_{\text{PS chains}}$ is the total number of polystyrene chains in each brush configuration

Single brush		Double brush	
$n_{\rm PSchains}$	n _{toluene}	n _{PS chains}	n _{toluene}
9	3624	18	2871
16	3269	32	2768
25	3008	50	2494
36	2977	72	2262

were equilibrated for a total of 20 ns to collect sufficient statistics.

III. Results and discussion

A Non-grafted polystyrene melts

We first consider the non-grafted polystyrene melt confined between two graphene layers. This system was subjected to a series of more than 100 compression steps. For layer separations of 5.9 and 2.9 nm confined polystyrene melts with densities of 300 and 700 kg m⁻³ were obtained.

To characterize the structure of the melt we computed a two-dimensional radial distribution functions (2D-RDF). For the purpose of characterizing the PS–PS monomer distribution, we consider the 2D-RDF function which is defined as follows

$$g_{2D}^{\text{PS}}(r,z) \propto \frac{1}{r^2 N^2} \sum_{ij} \delta(r - r_{ij}) \delta(z - \Delta z_{ij})$$
(6)

where

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2}$$
 (7)

$$\Delta z_{ij} = z_i - z_j, \tag{8}$$

and x_i , y_i , and z_i denote the coordinates of particle *i*. The 2D-RDF defined by (6) measures the correlation between particles that are separated within the x-y plane by a distance r_{ij} and have an out-of-plane separation of z_{ij} . For simplicity, we do not consider correlations between all atom types but only between the center of the monomer units comprising the chains. For consistency with the coarse-grained model to be developed based on this study and the coarse-grained model for PS described in ref. 28 the center of the monomer unit was taken as the carbon atom in the backbone at which the phenyl ring is attached. The 2D-RDFs in this work were calculated as averages over the last 2 ns of the simulations.

For the smaller compression [see Fig. 1(a)] the 2D-RDF shows spherical symmetric rings which indicates a nearly isotropic pair correlation. For the larger compression [see Fig. 1(b)] these rings remain spherical but reveal an intensity decrease along the circumference as the out-of-plane separation increases. In addition, there is a notable increase in the 2D-RDF for large in-plane out but small out-of-plane separations. This behavior implies an increase in the in-plane correlation at distances $\gtrsim 1$ nm due to confinement.



Fig. 1 2D-Radial distribution functions of equilibrated confined melt systems at densities of ~300 and ~700 kg m⁻³. Δz is the separation between the graphite surfaces.

The corresponding structure factors, which may be measured by neutron scattering experiments, are shown in Fig. 2. The structure factor is defined as

$$S(k) = 1 + 4\pi\rho \int_0^\infty r^2 \frac{\sin kr}{kr} g(r) \, \mathrm{d}r,$$
 (9)

where g(r) is the spherically averaged radial distribution function.²⁹ The main feature of the structure factors is the periodicity of the fringes, which reflects the interlayer separation. Note that these plots are primarily relevant in comparison with the structure factors calculated for the polystyrene brushes to be discussed in the following section.

B Grafted polystyrene chains

We now describe results of our simulations of grafted polystyrene chains. Equilibrated configurations of simulated dry single brushes as well as single brushes in toluene solution are shown in Fig. 3. For comparison, the brushes with the lowest (3×3) and the highest (6×6) brush densities are shown. In vacuum the polystyrene chains contract and curl up. In contrast, in toluene the brushes are clearly more stretched out. This behavior is investigated in greater detail in the following subsection.



Fig. 2 Structure factors calculated for the equilibrated confined melt system. Δz is the separation between the graphite surfaces. The curves are shifted for clarity.



Fig. 3 Side views of equilibrated dry (a), (b) polymer brush configurations with 3×3 and 6×6 polymer chains and the equilibrated configurations in toluene solution (c), (d). For clarity, only the part of the simulation cell containing the polystyrene chains is shown.

1. Density profiles of polystyrene chains. The density profiles obtained for single brushes under dry conditions and in toluene solution are shown in Fig. 4. In all cases, one observes strong density oscillations near the surface. This "layering" effect is not predicted by the self-consistent field (SCF) theory of polymer $brushes^{6,12,13}$ but similar structures have been observed in Monte Carlo^{15–17} and molecular dynamics¹⁴ simulations of model polymers. In those studies the oscillations occur very regular about a roughly constant value and decay after about three to four periods. In comparison, in the present case, the density oscillation display a somewhat different pattern. For all cases, we find three initial oscillations with strongly decaying amplitude. In dry conditions, for the lowest grafting density studied, the density profile decays to zero after these three peaks, exhibiting a small shoulder at a distance of about 0.8 nm from the surface. Still in dry conditions, as the grafting density increases a fourth $(\sim 0.8 \text{ nm})$, fifth $(\sim 1.3 \text{ nm})$, and even sixth oscillation $(\sim 1.8 \text{ nm})$ can be identified. The period of these oscillations is clearly longer than the three rapid oscillations near the



Fig. 4 Polystyrene density profiles obtained for single brushes under (a) dry conditions and (b) in toluene solution. The gray bar indicates the positions of the last carbon atoms of the PS chains which are restrained to mimic the attachment of the chains to the surface.

surface and the peaks are consequently broader. Also it is noteworthy that while the amplitude decreases from the first to the third oscillations, the amplitude of the fourth oscillation is markedly larger than the third and a pronounced minimum can be seen between the two corresponding peaks.

Even without explicit comparison, it is clear from Fig. 4(a) that in dry conditions none of the density profiles can be described by the parabolic profile suggested by SCF theory. Since in the present work we consider rather short chains containing only 15 monomers and the SCF theory works best for long chains, the discrepancy is, however, not surprising.

If we focus on the profiles obtained in toluene solution, we find very similar patterns for the oscillations near the surface. The major difference is that due to the solvation effect of the toluene molecules the chains are more stretched out which allows the fourth and fifth oscillation to be observed even in the case of the 3×3 brush. To assess, whether the density profiles at distances larger than ~ 1.5 nm can be described by a parabola, we have plotted these profiles as a function of z^2 as shown in Fig. 5. In this plot a parabolic decay shows up as a straight line. In all cases, a part of the density profile can indeed be fitted by (2). However, the curvature α which should only depend on the chain length but not the grafting density shows a considerable variation going from the 3×3 to the 5×5 brush. Only for the two largest grafting densities the slope in Fig. 5 and thus the curvature α in (2) are independent of the grafting density. Again, we can attribute these



Fig. 5 Density profiles from Fig. 4(b) as a function of z^2 . The black dashed lines indicate fits to (2).

differences in the rate of density decay to the fact that SCF theory is most suitable for long chains while the PS chains considered in the present work are rather short. Also the different grafting densities may lead to different brush regimes.

The tails of the density profiles clearly deviate from the parabolic shape predicted by (2) showing a smooth instead of an abrupt decay to zero. This "round-off zone"¹⁴ has been observed in previous simulations of model polymers.^{14–17} It becomes smaller as the grafting density increases (and should also decrease for longer chains), approaching the limit described by the SCF theory.

As the chain density increases the PS chains occupy regions farther and farther away from the surface. To quantify this effect, it is not sufficient to just monitor the position of the monomer unit farthest away from the surface due to the "round-off zone". Instead, we define the "extension" (or height) of the brush to be the distance away from the surface below which 90% of the PS density can be found. For the lowest grafting density (3 × 3) this yields a value of 0.86 nm, whereas for the largest density (6 × 6) the limit is reached at 1.92 nm. The blob theory by Alexander and de Gennes predicts that the brush height should scale $\sigma^{2/3}$ which is nicely confirmed by our simulations as shown in Fig. 6.

3×3 5×5 6×6 4×4 2.4 2.0 Extension (nm) 1.6 1.2 ÷ SB w/o tol SB with tol 0 DB w/o tol 0.8 $\Delta z = 0.178 + 0.151 * \sigma^{2/3}$ DB with tol 0.3 0.4 0.5 0.6 0.7 Grafting density $\sigma^{2/3}$ (nm^{-4/3})

Fig. 6 Chain extension ("height") as a function of grafting density.

Double brush density profiles are found to be very similar to the results for the single brushes and are therefore not shown. Fig. 6 demonstrates that the dependence of the brush height on the chain density is also similar. In fact, as shown by the straight lines in Fig. 6 the data for single and double brushes can be fit jointly by two linear functions for dry and good solvent conditions, respectively.

2. Topology of polystyrene chains. To quantify the effect of grafting density and solvent quality on the topology of the polystyrene chains we computed various parameters. The most common tool for analyzing the conformational changes of polymers is the gyration tensor. It is obtained for an ensemble of N particles with coordinates $\vec{r}^{(i)}$ as

$$R_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{N} r_{\alpha}^{(i)} r_{\beta}^{(i)}, \qquad (10)$$

where α and β indicate the Cartesian directions. Since this tensor is symmetric by definition, it can always be diagonalized. It is therefore convenient to consider only its three principal components, λ_{α} . Here, we adopt the convention, $\lambda_1 \geq \lambda_2 \geq \lambda_3$. The principal components provide information about the spatial extent of a given polymer chain and its approximate geometrical shape.

From our analysis we observe that for dry brushes, irrespective of the specific conditions, the two larger principal components of the gyration tensor are roughly equal, whereas the third one is notably smaller, $\lambda_1 \approx \lambda_2 > \lambda_3$. This indicates that the grafted polystyrene chains in poor solvent conditions adopt an oblate shape, which agrees with the visual inspection of our systems. The ratio

$$\frac{\lambda_1 + \lambda_2}{2\lambda_3} \tag{11}$$

measures the aspect ratio of these oblate ellipsoids. As shown in Fig. 7, in the absence of solvent molecules, the aspect ratio displays a characteristic dependence on the grafting density. While for the smallest density (3×3) the ratio is about 2:1, it drops to about 3:2 for the largest densities considered $(5 \times 5, 6 \times 6)$. In stark contrast, the ratio is virtually independent of the grafting density in toluene solutions.



Fig. 7 The ratio of principal components λ_1/λ_2 of the gyration tensor.



Fig. 8 2D-Radial distribution functions of equilibrated systems. For comparison, the configurations with the smallest (a), (b) and largest (c), (d) fraction of polymer surface coverage are shown, for both single and double brushes in dry conditions and in toluene solution.

The radial distribution functions (RDF) provide additional insight. The conventional (isotropic) RDF was computed using the familiar expression²⁹ and was obtained by averaging over the last 2 ns of the equilibrated trajectories. The first peak at ~ 0.45 nm corresponds to the nearest neighbor separation of carbon atoms along the backbone of the polystyrene chains. It is extremely sharp since in our model this bond length is constrained to a constant value. The second peak at approximately 0.65 nm corresponds to the second neighbor C–C separation and its small spread reflects the stiffness of the C-C-C bond angles. In all cases, peaks up to the third neighbor shell can be distinguished but a clear pattern does not emerge. This is largely due to the 2D-nature of the present system which results from grafting the polymer chains. A more suitable measure is therefore the two-dimensional radial distribution function (2D-RDF) computed as introduced in section IIIA. For illustration, the 2D-RDFs for the 3×3 and 6×6 single brushes are shown in Fig. 8.

In the case of the 3×3 brush without toluene, Fig. 8(a) shows that the PS chains occupy only a small region of about 4 Å above the surface and display hardly any structure parallel to the surface. In contrast, in the case of the 6×6 brush, the PS chains occupy a region up to about 12 Å above the surface. The second neighbor ring at a distance of about 4 Å shows its maximum intensity perpendicular to the surface which indicates that the chains are predominantly stretching away from the surface instead of extending parallel to the wall. This feature also corresponds nicely with the second peak in the density profiles shown in Fig. 4. In addition, one can observe a reduction in the intensity at in-plane distances between 5 and 7 Å and (much weaker) at about 20 Å indicating the range of in-plane correlations between different PS chains.

The 3×3 brushes in dry conditions and in toluene solution [Fig. 8(a) and (b)] behave markedly different. In toluene solution the PS chains are strongly stretched and sample the region up to 15 Å above the surface. They also exhibit rather long ranged correlations in the direction perpendicular to the surface while the in-plane correlations reveal a pronounced minimum between 10 and 12 Å corresponding to the distance between nearest-neighbor chains. The toluene molecule fill up the region between the chains and effectively screen their interaction. This interpretation also corresponds with the snapshots shown in Fig. 3.

For the 6×6 brushes the comparison of dry conditions and toluene solution, reveals similar differences which are less pronounced than in the case of the 3×3 brush. This is largely due to the higher density of the brush which prevents the chains from collapsing onto the surface also in the absence of toluene. The most notable observation is that for the 6×6 brush in solution weak in-plane correlations up to the third nearest PS chain (20–30 Å) can be identified.

The corresponding structure factors, which in principle allow a direct comparison with experimental data, are shown in Fig. 9. For the single brushes [Fig. 9(a) and (b)] there is very little structure. In the case of the double brushes, the structure factors show characteristic oscillations, the period of which corresponds to the inverse spacing of the double brushes. Comparison of Fig. 9(c) and (d) reveals that the range of these periodic oscillations, depends sensitively on the amount of toluene in the system. In the absence of solvent molecules the periodic oscillations extend up to the largest Q-values considered. If, however, toluene molecules are added to the system, the oscillations are strongly damped.



Fig. 9 Structure factors calculated for the equilibrated single and double brush systems, with and without toluene solution. The curves have been shifted for clarity.

3. Toluene layers. We now consider the details of the distribution of toluene molecules. In all cases considered, toluene molecules were found to form layers at the surface. In Fig. 10, which shows the toluene densities of equilibrated configurations of single brushes, the first toluene enriched layer appears as a sharp peak in the density profiles at approximately 0.35 nm. The second layer at about 0.55 nm is weaker but the third peak at about 0.7 nm is again very pronounced. It is even possible to distinguish a fourth layer which appears as a shoulder at about 0.85 nm.

To further illustrate this behavior we calculated the mixed 2D-RDFs between the centers of the polystyrene monomer units and the toluene molecules, which is defined as follows

$$g_{2D}^{\text{PS-TOL}}(r,z) \propto \frac{1}{r^2 N^2} \sum_{ij} \delta(r - r_{ij}) \delta(z - \bar{z}_{ij})$$
(12)

where

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2}$$
(13)

$$\bar{z}_{ij} = (z_i + z_j)/2.$$
 (14)

Note that this definition is different from the 2D-RDFs considered in sections IIIA and IIIB2.



Fig. 10 Toluene densities per polystyrene chain calculated for the equilibrated single brush configurations. The gray bar indicates the positions of last carbon atoms of the PS chains which are restrained to mimic the attachment of the chains to the surface.

Fig. 11 exemplarily shows the result for the single 3×3 polystyrene brush. The 2D-RDF reveals a strong peak along the direction perpendicular to the surface due to the first toluene layer, and weaker correlations at larger distances



Fig. 11 2D-Radial distribution function between toluene and polystyrene of equilibrated 3×3 single brush system.

indicating a volatile second and third toluene layer. The 2D-RDF also shows that parallel to the surface the PS-TOL correlation is featureless beyond the exclusion range.

4. Toluene diffusivity. For the purpose of investigating the diffusivity of toluene molecules in our systems, we have calculated the mean square displacement (MSD) of the molecules in the two Cartesian directions parallel to the surface. Because of the lack of periodic boundary conditions perpendicular to the surface we cannot compute reliable diffusivities along this direction. Fig. 12 shows the MSDs of the 5×5 single brush system. From the slope of the MSD curves we can extract the in-plane diffusivity of toluene

$$D_{\parallel} = D_{xx} + D_{yy}. \tag{15}$$

We obtain values between 11 to 21×10^{-5} cm² s⁻¹ but our data do not show a clear correlation between D_{\parallel} and the grafting density. These values are in reasonable agreement with the experimental diffusivity for pure toluene at 450 K which has been measured as 55×10^{-5} cm² s⁻¹.^{30,31}

IV. Conclusions

Using molecular dynamics simulations we have successfully determined the properties of polymer brushes under dry conditions and in toluene solution.



Fig. 12 Mean square displacement of the toluene molecules in the 5×5 polystyrene simulation system.

We find that the density profiles are dominated by very distinct oscillations which extend up to ~1.8 nm above the surface and fall into two groups of three peaks each. These features are observed independent of grafting density and solvent conditions. The density fluctuations near the surface are similar to earlier simulations of model polymers^{14–17} but they are more pronounced and exhibit a less regular structure. The parabolic density decay predicted by SCF theory^{6,12,13} and the scaling of the associated parameters can only be observed in a certain distance range for the two largest grafting densities. These differences are not surprising as the SCF expression is most suitable for long chains. The smooth decay of the density toward zero is expected due to the relatively short PS chains.

By combining analysis of the gyration tensor with visual inspection of the configurations, we found that in the absence of a solvent, the chains undergo a transition from an oblate to a more spherical shape as the grafting density increases. In contrast, in the presence of a good solvent, the chains remain roughly spherical independent of the grafting density. Solvation furthermore increases the extension of the polystyrene chains roughly by a factor 2.5.

Conventional RDFs provide little insight into the chain structure, since they do not account for the 2D nature of the polymer brushes studied in this work. Instead, 2D-RDFs have been computed which provide a very clear picture of the average structure of the brushes. We also determined the corresponding structure factors which reveal pronounced differences between single and double brushes structure with and without toluene and in principle allow for a direct comparison with scattering experiments.

Our simulations provide valuable insight into the interaction of polymer chains, solvent molecules, and graphite surfaces which are very difficult to resolve experimentally. Specifically, for both the single and double brush arrangements, toluene molecules are found to form up to four layers at the base of the polystyrene chains regardless of the density of the brush. There is however no correlation parallel to the surface. The diffusivity of the toluene molecules ranges from 11 to 21×10^{-5} cm² s⁻¹ and is only weakly correlated with the chain density.

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