# Adsorption from Oligomer−Monomer Solutions on the Surfaces Modified with End-Grafted Chains

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ABSTRACT: A density functional theory has been applied to study adsorption from oligomer−monomer solutions on solid surfaces modified with end-grafted polymers. Chains are modeled as freely jointed tangent spheres. All spherical species interact via Lennard-Jones (12-6) potential. The grafted chains are not attracted by the surface. Fluid molecules interact with the substrate via Lennard-Jones (9-3) potential. It is shown how a shape of the relative excess adsorption isotherms depends on such parameters as the oligomer length, the grafting density, oligomer−substrate interactions, oligomer−grafted chains interactions, and oligomer−monomer interactions in the bulk solution. As attractive interactions between free and grafted chains strengthen, the relative excess adsorption isotherm can change from negative, through S-shaped with an adsorption azeotropic point, to positive in the whole concentration region. A change of oligomer−monomer interactions causes the opposite effects. For low grafting densities of attractive bonds, the relative excess of oligomers increases, reaches a maximum, and decreases. The structure of surface layers is also analyzed.
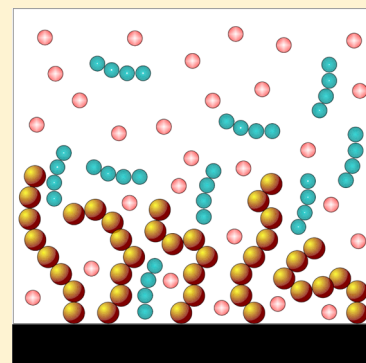
I. INTRODUCTION

Polymer-tethered surfaces find numerous technological applications, e.g., for stabilization of colloidal suspensions, chromatographic separations, lubrication, production of protective coatings, and biocompatible materials. From an academic point of view, the grafted chain layers are not only very important but also fascinating.

Many theoretical approaches have been utilized to describe thermodynamic properties of end-grafted chain layers. Among these are scaling theories,[1,2] classical self-consistent field methods,[3−10] single-chain mean-field methods,[11−13] density functional theories,[14−24] and computer simulations.[25−41] The structure of chain layers immersed either into an explicit solvent or into a solvent treated as a continuous medium that moderates molecular interactions has been investigated. It has been shown that the surrounding fluid may considerably modify the brush. The studies of tethered polymers have been a subject of several reviews.[9,42−46]

Adsorption of fluid molecules on solid surfaces covered by grafted chains has been less intensively studied. Although the behavior of small molecules,[20−24] polymers, proteins, peptides, and lipids[41,47−51] near such surfaces has been investigated, our understanding of the adsorption mechanism still remains unsatisfactory.

In our previous paper[23] we have discussed adsorption from binary solutions of small, spherical molecules on polymer-tethered surfaces. We found that, depending on the parameters of the model, relative excess adsorption isotherms had different shapes. The theoretical predictions were in accordance with the results of computer simulations and experimental measurements. However, numerous liquid mixtures used in analytical and technological applications of polymer brushes consist of molecules having different sizes. It is therefore important to know how the size and shape of particles affect their adsorption. One of the most interesting problems is adsorption of chain molecules on modified solid surfaces.

In this work we employ the density functional theory in order to explore adsorption of short linear molecules dissolved in a monomeric solvent on chemically bonded phases. We consider the penetration of the grafted chain layers by chains of the same chemical nature and length, as well as, by chemically different free polymers. Sometimes this process is treated as absorption of molecules in the brush[41] or their partitioning between the surface region and the bulk phase.[53] In our approach changes of the densities in the whole inhomogeneous system are taken into account. The equilibrium density distributions result from an intriguing interplay between the entropic and enthalpic effects. We present here a systematic study of the adsorption competition between different species. Adsorption of chain molecules gives rise to a marked alteration in the interfacial properties of the system. This phenomenon is the driving force behind separation of molecules of different sizes in liquid chromatography.

Our manuscript is arranged as follows. In the next section we introduce the model and describe the computational scheme. Then, we present and discuss the results of our calculations carried out for different parameters characterizing the system. Finally, the last section summarizes the main conclusions of the paper.

II. THEORY

We consider a monomer−oligomer mixture in contact with the surface covered by the end-grafted chains. We introduce a simple system model that we have utilized previously.[22] The system consists of the tethered polymers, P, free chains (indexed as 1) and spherical molecules (indexed as 2).

The chains consists of M_k tangentially jointed segments. The connectivity of segments belonging to a given molecule is forced by the potential, V_B

$$\exp[-\beta V_B(\mathbf{R})] = \prod_{i=0}^{M_k-1} \delta(|\mathbf{r}_{i+1} - \mathbf{r}_i| - \sigma^{(k)})/4\pi(\sigma^{(k)})^2 \tag{1}$$

where $\mathbf{R}_k \equiv (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{M_k})$ is the vector specifying positions of segments, the symbol δ denotes the Dirac function, $\sigma^{(k)}$ is the polymer segment diameter and $\beta^{-1} = k_B T$ ($k = P,1$).

All species (polymer segments and monomeric molecules) interact with other segments by means of a truncated Lennard-Jones potential

$$u^{(kl)}(r) = \begin{cases} 4\varepsilon^{(kl)}[(\sigma^{(kl)}/r)^{12} - (\sigma^{(kl)}/r)^6] & r < r_{cut}^{(kl)} \\ 0 & \text{otherwise} \end{cases} \tag{2}$$

where $\varepsilon^{(kl)}$ is the parameter characterizing interactions between species k and l, $\sigma^{(kl)} = 0.5(\sigma^{(k)} + \sigma^{(l)})$ ($k = P, 1, 2$), r is the distance between interacting spherical segments and $r_{cut}^{(kl)}$ is the cutoff distance. In this work $r_{cut}^{(kl)} = 3\sigma^{(kl)}$.

The chains P are permanently pinned to the surface. The interactions of the first segment of each chains with the substrate describe the following potential

$$\exp[-\beta v_{s1}^{(P)}(z)] = C\delta(z - \sigma^{(P)}/2) \tag{3}$$

where z is a distance from the surface and C is a constant. Note, that according to our model the surface-binding segments are located at the distance $z_0 = \sigma^{(P)}/2$, but they can move within the xy plane. The remaining segments of the grafted chains interact with the surface via the hard-wall potential. In other words, they are inert with respect to the substrate. However, the segments of free molecules interact with the surface via the potential of the Lennard-Jones (9-3) type.

$$v^{(k)}(z) = 4\varepsilon_s^{(k)}[(z_0^{(k)}/z)^9 - (z_0^{(k)}/z)^3] \tag{4}$$

In the above equation $\varepsilon_s^{(k)}$ characterizes the strength of interaction between the k-th component and the adsorbent ($k = 1,2$) and $z_0 = \sigma^{(k)}/2$.

We use the version of the density functional theory described in the papers.[21−23] In the following we outline only basic steps of the computation scheme, which involves (i) the construction of the free energy functional, (ii) the minimization of the thermodynamic potential of the system, and (iii) a numerical solution of a set of Euler−Lagrange equations for density profiles of the components. We apply the Weeks−Chandler−Anderson method[54] and divide the Lennard-Jones potential (2) into the repulsive (reference)

$$u_{rep}^{(kl)}(r) = \begin{cases} \infty & r < \sigma^{(kl)}/2 \\ 0 & \text{otherwise} \end{cases} \tag{5}$$

and attractive (perturbation) part

$$u_{att}^{(kl)}(r) = \begin{cases} -\varepsilon^{(kl)} & r < 2^{1/6}\sigma^{(kl)} \\ u^{(kl)}(r) & r \geq 2^{1/6}\sigma^{(kl)} \end{cases} \tag{6}$$

Then, we express the free energy functional as the following sum: $F = F_{ex} + F_{id} = F_{hs} + F_c + F_{att}$. The ideal part, F_{id}, can be calculated exactly.[55] The excess free energy connected with hard-sphere interactions, F_{hs}, follows from the fundamental measure theory of Rosenfeld.[56] The chain connectivity contribution, F_c, results from the first-order perturbation theory of Wertheim.[57] One can find the suitable expressions in ref 22 [see eqs 7, 10, and 12]. The excess free energy due to interactions between different segments is calculated in the framework of the mean-field approximation

$$F_{att} = \frac{1}{2} \sum_{k=P,1,2} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \rho_s^{(k)}(\mathbf{r}_1)\rho_s^{(k)}(\mathbf{r}_2)u^{(kk)}(\mathbf{r}_{12})$$
$$+ \sum_{k,l=P,1,2; k\neq l} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \rho_s^{(k)}(\mathbf{r}_1)\rho_s^{(l)}(\mathbf{r}_2)u^{(kl)}(\mathbf{r}_{12}) \tag{7}$$

where $\rho_s^{(k)}$ the local density of segments of the k-th component

$$\rho_s^{(k)}(\mathbf{r}) = \sum_{i=1}^{M_k} \rho_{s,i}^{(k)}(\mathbf{r}) = \sum_{i=1}^{M_k} \int d\mathbf{R} \, \delta(\mathbf{r} - \mathbf{r}_i)\rho^{(k)}(\mathbf{R}) \tag{8}$$

and where $\rho^{(k)}$ is the local density of the k-th molecules and $\rho_{s,i}^{(k)}$ is the density of the ith segment, $\rho_s^{(2)} = \rho^{(2)}$.

In our model the grafting density is fixed

$$\int dz \rho_{s,i}^{(P)}(z) = \rho_P \tag{9}$$

Under the above constraint, the thermodynamic potential is given by

$$Y = F[\rho^{(P)}(\mathbf{R}_P), \rho^{(1)}(\mathbf{R}_1), \rho^{(2)}(\mathbf{R}_2)]$$
$$+ \int d\mathbf{R}_P \, \rho^{(P)}(\mathbf{R}_P)v^{(P)}(\mathbf{R}_P)$$
$$+ \sum_{k=1,2} \int d\mathbf{R}_k \, \rho^{(k)}(\mathbf{R}_k)(v^{(k)}(\mathbf{R}_k) - \mu^{(k)}) \tag{10}$$

The minimization of the thermodynamic potential leads to the set of equations [see eq 17 in ref 22] that we solve using the standard numerical iterative method. In this way, we obtain the segment density profiles of all the components, which, according to our model, are functions only the distance from the surface, $\rho_s^{(k)} = \rho_s^{(k)}(z)$.

Next we can evaluate different quantities that characterize the extent of adsorption. The excess adsorption isotherms of individual components are defined as

$$\Gamma^{(k)} = \int (\rho_s^{(k)}(z) - \rho_{sb}^{(k)}) \, dz \tag{11}$$

and the total excess adsorption isotherm of the fluid is given by

$$\Gamma^{(F)} = \int (\rho_s^{(F)}(z) - \rho_{sb}^{(F)}) \, dz \tag{12}$$

where $\rho_s^{(F)} = \rho_s^{(1)} + \rho_s^{(2)}$ is the total density of the fluid and $\rho_{sb}^{(F)}$ is the total fluid density in the bulk phase.

In this work, however, we concentrate on adsorption of dense fluids. Because of considerable incompressibility of liquids the excesses, $\Gamma^{(F)}$, are close to zero.[21,23] Adsorption from liquids has a competitive character. Therefore, we calculate the relative excess adsorption isotherms that are usually used in the theory of adsorption from solution[58−67]

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$$N_k^e = \int (x^{(k)}(z) - x_b^{(k)}) \, dz \tag{13}$$

where

$$x^{(k)} = \frac{\rho_s^{(k)}(\sigma^{(k)})^3}{\rho_s^{(1)}(\sigma^{(1)})^3 + \rho_s^{(2)}(\sigma^{(2)})^3} \quad k = 1, 2 \tag{14}$$

is the local volume fraction of the k-th component and $x_b^{(k)}$ is its value in the bulk phase. Note that $N_2^e = -N_1^e$.

The relative excess adsorption N_k^e can be directly compared with experimental data. This quantity is proportional to the difference in the bulk solution composition after and before establishing the adsorption equilibrium, $\Delta x = x^{(k)} - x_0^{(k)}$.[58−67]

The aim of our study is to show how the selected parameters characterizing the system affect the adsorption isotherms of short chains. By adsorption isotherm we mean a plot of the relative excess adsorption as a function of the volume fraction of the oligomer in the bulk solution, $N_2^e = N_1^e(x_b^{(1)})$.

We treat the parameter $\varepsilon^{(PP)}$ as the unit of energy ($\varepsilon^{(PP)} = \varepsilon \equiv 1$) and the diameter $\sigma^{(P)} = \sigma \equiv 1$ as the unit of the length. The reduced temperature is defined as $T^* = k_B T/\varepsilon$.

The molecular interactions in the system can be also discussed using the Flory−Huggins type parameters $\chi^{(kl)} = -(\varepsilon^{(kl)} - 0.5(\varepsilon^{(kk)} + \varepsilon^{(ll)}))$. The parameters $\chi^{(Pk)}$ characterize the quality of both solvents with respect to the grafted chains. However, the parameter $\chi^{(12)}$ dictates the properties of the bulk liquid mixture.

III. RESULTS AND DISCUSSION

We have studied adsorption of short chain molecules from their solution in a monomeric solvent on the solid surface covered by end-grafted chains. The model described above involves a considerable number of parameters. In order to simplify the analysis we have limited the investigations to a special category of model systems. First, we have assumed that the diameters of monomers and diameters of free and bonded chains have the same size, $\sigma^{(kl)} = \sigma$. Second, we have chosen the length of the grafted chains taking $M_P = 8$. Third, we have fixed the following parameters: $\varepsilon_s^{(2)} = \varepsilon^{(PP)} = \varepsilon^{(11)} = \varepsilon^{(22)} = \varepsilon^{(P2)} = \varepsilon \equiv 1$. Notice that in the considered case $\chi^{(P2)} = 0$. The other parameters were varied. In particular, we have performed calculations for different lengths of free chains, M_1. We have also changed the parameter $\varepsilon^{(P1)}$ ($\chi^{(P1)}$) that characterizes interactions between free and grafted chains. Next, we have performed calculations for different interactions of the free chains either with the substrate ($\varepsilon_s^{(1)}$) or with the monomer ($\varepsilon^{(12)}$, i.e., also $\chi^{(12)}$) has been varied. Finally, we have changed the grafting density. Below we discuss how these parameters affect the adsorption isotherms of short chains and the structure of the surface layer.

The total bulk density of the fluid, $\rho_{sb}^{(F)} = \rho_{sb}^{(1)} + \rho_{sb}^{(2)}$, was fixed at $\rho_{sb}^{(F)} = 0.66$. The reduced temperature was equal to $T^* = 3$. Under assumed conditions the model fluids exhibit a complete mixing in the bulk phase. All of the results presented below, except for those displayed in Figures 6 and 7, have been obtained for the grafting density $\rho_P = 0.1$.

We want to show how the length of free chains and various interactions affect the shape of relative adsorption isotherms in the considered systems. A detailed classification of experimental excess adsorption from solution on solid surfaces into five categories was given by Schay an Nagy.[68] This classification was based on the isotherm shape. The excess adsorption isotherm

can have the same sign in the whole concentration region (the types I−III) or it changes its sign at a certain composition of the bulk solution (the types IV and V). The influence of different parameters on the shape of the relative excess adsorption isotherms from solutions consisting of small molecules has been discussed elsewhere.[23,58−60]

The effect of varying length of the free chains is illustrated in Figure 1 for different strengths of the free chain−brush
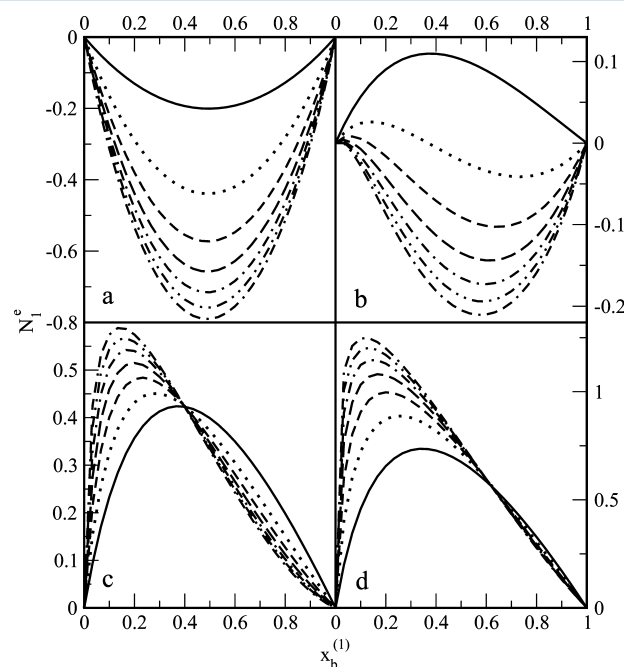

Figure 1. Relative excess adsorption isotherms for increasing strength of free chains−brush interactions: $\varepsilon^{(P1)} = 1.0$ (part a), 1.25 (part b), 1.5 (part c), and 1.75 (part d). Consecutive lines are for different lengths of oligomers, M_1: 2 (solid lines), 4 (dotted lines), 6 (dashed lines), 8 (long dashed lines), 10 (dotted-dashed lines), 12 (double dotted-dashed lines), and 14 (dotted-double dashed lines). The remaining energy parameters are $\varepsilon_s^{(k)} = \varepsilon^{(P2)} = \varepsilon^{(PP)} = \varepsilon^{(kl)} = 1.0$ ($k,l = 1,2$). The grafted chains are built of $M_P = 8$ segments. The grafting density is $\rho_P = 0.1$.

interactions, $\varepsilon^{(P1)}$. The remaining energy parameters are assumed to be the same and $\varepsilon^{(kl)} = \varepsilon^{(P2)} = \varepsilon_s^{(k)} = \varepsilon \equiv 1$, ($k,l = 1,2$). Part a shows the case when all energy parameters are the same. This means that also $\varepsilon^{(P1)} = \varepsilon = 1$ and $\chi^{(P1)} = 0$. For such systems the relative adsorption of chains is negative. There is more monomers than the oligomer segments in the surface layer (see the density profiles in Figure 3a). One sees that monomers are preferentially adsorbed from the considered solutions. A polymer molecule placed near the solid surface experiences reduction in the conformational entropy, and as a result, it tends to stay away form the surface. This effect is stronger in the presence of the grafted-chains because they form an additional barrier for free chains. In this case we see that as the length of free chains increases the relative excess adsorption, N_1^e, decreases. The same tendency has been reported for adsorption of polymers on impenetrable solid surfaces.[62] A comparison between adsorption on bare solid surfaces and on adsorbents modified with end-grafted chains has been presented in ref 22. These results are qualitatively consistent with the predictions of the self-consistent-field theory for adsorption of dilute polymers on brushes.[10]

The situation changes when the oligomer-brush interactions become energetically profitable (Figure 1b−d) Interesting results have been obtained for $\varepsilon^{(P1)} = 1.25$ (Figure 1b). In this case the relative excess adsorption of dimers is positive in the whole concentration range. The isotherms of 4-mers and 6-mers exhibit the adsorption azeotropy.[60] The azeotropic point (i.e., a point at which $N_1^e(x_b^{(1)}) = 0$) shifts toward lower oligomer concentrations with increasing M_1. The adsorption isotherms for longer chains are negative. In both cases considered above an increase of the length of free chains always causes a decrease of the relative adsorption N_1^e.

It is worthwhile to note that the adsorption azeotropy is often observed in real systems, either for nonmodified solid surfaces[58,59] or for polymer brushes.[63−67] As it has been already mentioned, the relative excess adsorption can be zero, $N_k^e(x_{az}^{(1)}) = 0$, for a certain composition of the solution. One can say also that at the azeotropic point the composition of the surface layer is the same as the composition of the bulk solution [see eq 13].

The isotherms exhibiting adsorption azeotropy are S-shaped. For solutions consisting of monomers, this phenomenon was studied in the framework of the lattice models.[60] It was shown that the adsorption azeotropy can occur for nonideal solutions in contact with energetically homogeneous surfaces and is a consequence of the tendency of like molecules to aggregate in non ideal solutions. The aggregation leads to enrichment of the dilute component in the surface layer. The azeotropic behavior is characteristic for mixtures, in which components have similar affinities to the substrate.[60] The adsorption azeotropy is also observed for ideal solutions adsorbed on heterogeneous surfaces.[59]

In previous paper[23] we have investigated adsorption from binary solutions consisting of small molecules on the surfaces modified with grafted chains using density functional theory. General conclusions concerning the evolution of the isotherm shapes with the values of the parameters characterizing the system are consistent with those formulated for the bare solid surface. Our theoretical predictions are in agreement with experimental results.[63−67] The physical origin of the adsorption azeotropy observed in Figure 1b is the difference in molecular sizes of mixture components. In the case of adsorption of oligomers, the adsorption equilibrium results from a balance between the entropic repulsion from the surface region, the attractive forces extorted by the substrate, and the grafted chains and the interactions in the bulk solution. The reduction in conformational entropy is greater for longer chains. Tetramers and hexamers are preferentially adsorbed from dilute solutions. However, for higher concentrations of oligomers the entropic repulsion prevails and adsorption of monomers becomes more profitable. One can say that the entropic effects lead to the azeotropic behavior.

So far the adsorption azeotropy has not been found for solutions, in which all intermolecular interactions are the same ($\chi^{(12)} = 0$). When the energy parameter $\varepsilon^{(P1)}$ is sufficiently high, oligomers are preferentially adsorbed (see Figure 1c ($\varepsilon^{(P1)} = 1.5$) and Figure 1d ($\varepsilon^{(P1)} = 1.75$)). There exists the bulk concentration, $x_b^{(1)}*$, at which the relative excess adsorption, N_1^e, is independent of the polymer length. With increasing attraction between free and grafted chains this point moves toward higher oligomer concentration. We have found that $x_b^{(1)}* = 0.40$ for $\varepsilon^{(P1)} = 1.5$, whereas for $\varepsilon^{(P1)} = 1.75$, $x_b^{(1)}* = 0.62$. In the region of high oligomer concentrations the influence of the parameter M_1 on the relative excess adsorption is the same as for the systems discussed above, i.e., the relative excess

decreases for longer chains. If $x_b^{(1)} < x_b^{(1)}*$ an inverse sequence of the isotherms is found, namely, longer chains exhibit higher adsorption.

In dilute solutions attractive interactions with the bonded phase dominate. Because longer chains provide more energetically favored contacts with segments of grafted chains, N_1^e increases. However, when the concentration of oligomers increases, the stronger entropic repulsion causes that the adsorption of longer chains is smaller. At the point $x_b^{(1)}*$ both these effects are balanced. Similar results have been reported[62] for adsorption of polymers on solid surfaces. In the case of $\varepsilon^{(P1)} = 1.75$ the impact of the length of free chain is almost negligible at high polymer concentrations. In general, the effect of polymer size M_1 on the relative excess adsorption diminishes as M_1 increases. This is particularly apparent, when the free molecules are longer than the grafted chains, $M_1 > M_P$.

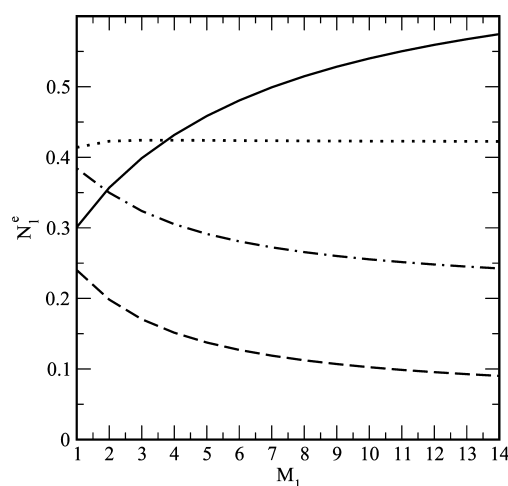For a better visualization of the impact of the size of free chains on their adsorption in Figure 2, we present the

Figure 2. Influence of the length of free chains on the relative excess adsorption, N_1^e, calculated for different values of the volume fractions $x_b^{(1)}$: 0.2 (solid line), 0.4 (dotted line), 0.6 (dotted-dashed line), and 0.8 (dashed line). The energy parameter $\varepsilon^{(P1)} = 1.5$. The remaining parameters are the same as in Figure 1.

dependences N_1^e vs M_1, estimated at different volume fractions $x_b^{(1)}$. All of the parameters are the same as in Figure 1c. For low oligomer concentration in the bulk mixture ($x_b^{(1)} = 0.2$), the relative excess considerably increases with an increasing chain length. At $x_b^{(1)} = 0.4$ the relative excess remains almost constant. For higher oligomer concentrations the function $N_1^e(M_1)$ decreases and achieves a plateau for $M_1 > M_P$ (see the curves plotted for $x_b^{(1)} = 0.6$ and $x_b^{(1)} = 0.8$). It is worthwhile to mention that a similar effect was observed in liquid chromatography. The retention of a given solute depends on its adsorption on (or absorption in) chemically bonded phase. The retention increases with an increase of chain length. However, it was reported that this increase is considerably weaker for homologues longer than organic ligands in the stationary phase.[69]

We have monitored the changes in the distribution of different molecules in the surface layer with the changes of the parameters by inspecting the local density profiles. Figures 3 and 4 show several examples corresponding to the adsorption isotherms discussed above. In Figure 3 we present the results for free chains considerably shorter than the grafted chains
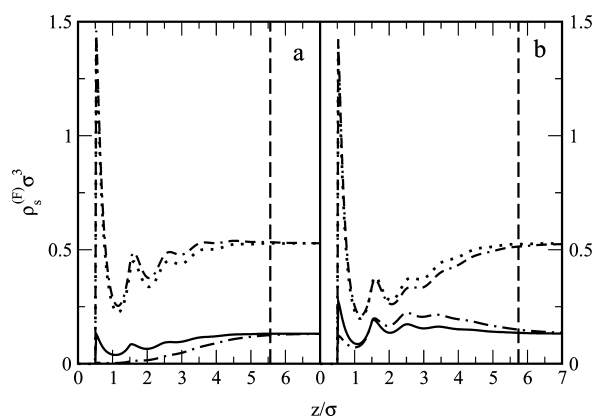
Figure 3. Density profiles of oligomers and monomers for two values of the parameter $\varepsilon^{(P1)}$ characterizing oligomer-brush interactions: 1.0 (part a) and 1.5 (part b). The volume fraction of oligomers in the bulk solution is fixed at $x_b^{(1)} = 0.2$. The remaining parameters are the same as in Figure 1. The solid line ($M_1 = 2$) and dotted-dashed line ($M_1 = 14$) are for the oligomers, whereas the dotted line ($M_1 = 2$) and dotted-double dashed line ($M_1 = 14$) are for monomers. The remaining parameters are the same as those in Figure 1.
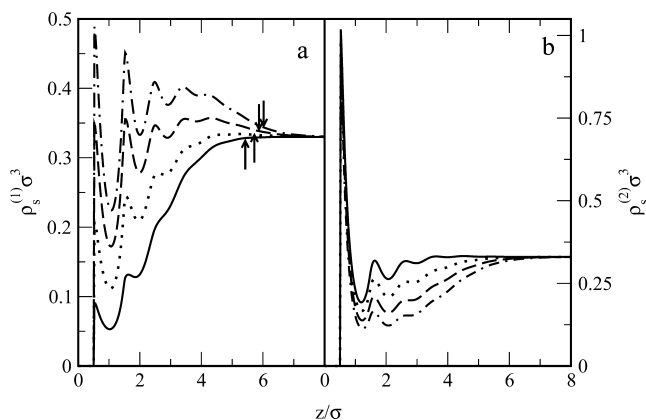

Figure 4. Density profiles of hexamers (part a) and monomers (part b) for different values of the parameter $\varepsilon^{(P1)}$ characterizing oligomer–brush interactions: 1.0 (solid lines), 1.25 (dotted lines), 1.5 (dashed lines), and 1.75 (dotted-dashed lines). The volume fraction of oligomers in the bulk solution is fixed at $x_b^{(1)} = 0.5$. The remaining parameters are the same as those in Figure 1.

(dimers) and for longer molecules (14-mers). We compare the density profiles calculated for weak (part a) and strong (part b) oligomer–brush interactions. These profiles correspond to relative excess adsorption isotherms displayed in parts a and c of Figure 1, respectively. The volume fraction of the chain molecules in the bulk phase, $x_b^{(1)}$, equals 0.2. The vertical line shows the brush edge, i.e., the distance from the surface at which the density of the grafted chains attains zero. In the scale used, the influence of solvent on the brush thickness cannot be displayed. One sees that small molecules more strongly penetrate the interior of the brush than bigger particles. The density of monomers in the interfacial layer are higher than the densities of chain molecules and exhibit several well-pronounced maxima near the surface. A similar structure is observed for dimers, whereas for longer chains the maxima are less visible.

Molecules of both components "compete for a room" within the brush. An increase of the local density of oligomer causes a decrease of the monomer density. When all energy parameters are the same (Figure 3a), the density of 14-mers is always lower than the density of dimers. Another relation is observed when the brush−oligomer contacts are energetically favored (Figure 3b): the oligomer density decreases with increasing oligomer length only very close to the surface. An opposite effect is observed within the outer part of the surface layer. Short chains are adsorbed, first of all, on the solid surface, whereas long chains are located mainly on "atop" of the brush. Likely, when free chains are longer than grafted chains, the dominating mechanism of adsorption changes.

Figure 4 illustrates the influence of oligomer−brush interactions on the structure of the surface layer for hexamer−monomer solution at the oligomer concentration in the bulk phase equal $x_b^{(1)} = 0.5$. We present here density profiles of hexamers (part a) and monomers (part b). One sees that the penetration of hexamers into the brush increases with an increase of the parameter $\varepsilon^{(P1)}$. For $\varepsilon^{(P1)} = 1.0$ and 1.25, the hexamer density in the brush is lower than in the bulk phase. However, if $\varepsilon^{(P1)} = 1.5$ and 1.75, hexamers cumulate in the surface region. Of course, an inverse relation for the density profiles of monomers is observed. The arrows in Figure 4a indicate the position of the brush edge. When the strength of oligomer-brush interactions increases, more molecules of the fluid penetrate the surface layer and they "push" the segments of grafted chains away from the wall. Therefore, the brush thickness slightly increases.

Next, we study the effects of other interaction in the system on adsorption. In Figure 5 relative adsorption isotherms, N_1^e, are plotted for different interactions of free chains with the substrate (part a) and with monomeric molecules (part b). The effect of the interaction with solid substrate is shown for rather weak all remaining interactions in the system, $\varepsilon^{(kl)} = 1$ ($k,l = P,1,2$). It is clear that with increasing affinity of the oligomers to
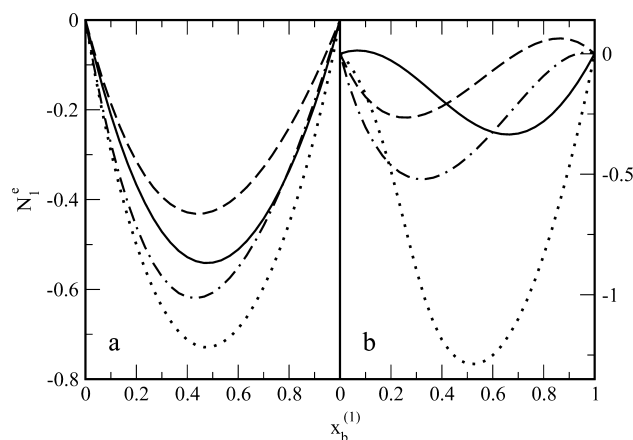

Figure 5. Influence of the strength of free chains−substrate interactions (part a) and the interactions between mixture components (part b) on the relative excess adsorption isotherms. In part a nomenclature of the lines is as follows. The solid line is for $M_1 = 6$ and $\varepsilon_s^{(1)} = 2$, whereas dashed line is for $M_1 = 6$ and $\varepsilon_s^{(1)} = 5$. The dotted line ($\varepsilon_s^{(1)} = 2$) and dotted-dashed line ($\varepsilon_s^{(1)} = 5$) are for longer free chains, $M_1 = 12$. The parameter controlling interactions in the bulk is $\varepsilon^{(12)} = 1$. In part b adsorption isotherms for different values of the energy parameter $\varepsilon^{(12)}$ are shown. Solid line ($\varepsilon^{(12)} = 0.8$) and dashed line ($\varepsilon^{(12)} = 1.5$) are for dimers, $M_1 = 2$. Dotted line ($\varepsilon^{(12)} = 0.8$) and dotted-dashed ($\varepsilon^{(12)} = 1.5$) line are for octamers, $M_1 = 8$. The remaining energy parameters are $\varepsilon_s^{(2)} = \varepsilon^{(Pk)} = \varepsilon^{(PP)} = \varepsilon^{(kk)} = 1.0$ ($k,l = 1,2$). The grafted chains are built of $M_P = 8$ segments. The grafting density is $\rho_P = 0.1$.

the substrate (i.e., for an increasing $\varepsilon_s^{(1)}$) their adsorption increases. This effect is relatively weak for the systems under study, because the layer of grafted chain constitutes a barrier against the penetration of free chains toward the wall. Then, we show how the monomer−oligomer interactions in the bulk mixture ($\varepsilon^{(12)}$) affect relative adsorption, N_1^e (Figure 5b). At low volume fractions $x_b^{(1)}$, the relative adsorption of oligomers increases with weakening monomer−oligomer interactions. An inverse relation is observed at high oligomer concentrations. The influence of interactions in a bulk solution on adsorption on solid surfaces has been already discussed in terms of the lattice model.[60−62] The arguments used in the above cited works are also applicable to our systems: due geometrical reasons a fluid molecule in the surface region has fewer fluid−fluid contacts than the same molecule in the bulk solution.

The role of interactions in the liquid mixture depends strongly on its composition. Let us consider of interactions of molecules of a chosen component, say the component 1. In a dilute solution their "contacts" are more likely to be of 1−2 type rather than of 1−1 type. A displacement of a molecule 2 in the surface region by a molecule 1 leads to a net change of a number of 1−2 contacts. Depending on the value of the parameter $\varepsilon^{(12)}$ this causes stabilization or destabilization of a dilute component in the surface layer. The opposite effects will be observed for concentrated solutions of the component 1 (such solutions are diluted with respect to the other component). Therefore, the adsorption azeotropy occurs for certain values of the parameter $\varepsilon^{(12)}$.

We proceed now to the discussion of the results for small molecules. When the strengths of interactions between all of the segments are the same ($\varepsilon^{(kl)} = 1$ (solid line in Figure 1a)), the relative adsorption of dimers is always negative. In this case the entropy dictates the adsorption equilibrium. For other systems considered above the S-shaped isotherms are found with the azeotropic point at $x_{b,az}^{(1)}$. When $x_b^{(1)} < x_{b,az}^{(1)}$ the relative adsorption N_1^e is positive for $\varepsilon^{(12)} = 0.8$ and negative for $\varepsilon^{(12)} = 1.5$. If $\varepsilon^{(12)} = 0.8$, the dimer−monomer (1−2) contacts are unfavorable. Thus, for a dilute solution the presence of dimers in the surface region is energetically profitable. This means that the concentration of dimers in the surface layer will be enhanced. However, at high concentrations of dimers in the bulk solution monomer (a dilute component) is preferentially adsorbed. For $\varepsilon^{(12)} = 1.5$ the dimer−monomer contacts are favored. Therefore, in a dilute solution dimers are "sucked" into the bulk phase.

The relative excess adsorption of octamers is negative in all investigated cases. In this case the entropic effects prevail those connected with attractive molecular interactions, even for the $\varepsilon^{(12)} = 1.5$. The presented results confirm the conclusion that interactions in the bulk solution play a very important role in adsorption processes in liquid.

Finally, we discuss the influence of the grafting density on the relative adsorption of dimers and tetramers. For selected systems we compare the values of the relative excess adsorption at the volume fraction $x_b^{(1)} = 0.2$. In Figure 6 we show the relative adsorption amounts, N_1^e, as functions of grafting density for two values of the energy parameter, $\varepsilon^{(P1)} = 1.25$ and $\varepsilon^{(P1)} = 1.5$. The attractive interactions between grafted chains and free molecules are stronger than the remaining interactions in the system. This leads to binding of free molecules to tethered chains. On the other hand, the grafted chains act as a barrier toward penetration of small molecules, so the binding is constrained. As a result, the adsorption of short chains can vary
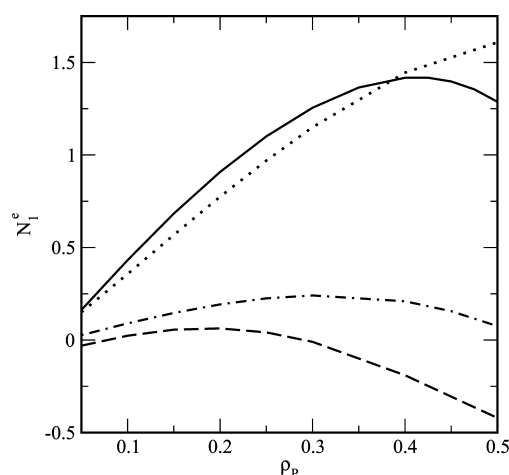

Figure 6. Influence of the grafted density on the relative excess adsorption of dimers and tetramers, N_1^e, calculated at $x_b^{(1)} = 0.2$. Dotted-dashed line ($\varepsilon^{(P1)} = 1.25$) and dotted line ($\varepsilon^{(P1)} = 1.5$) are for dimers, and dashed line ($\varepsilon^{(P1)} = 1.25$) and solid line ($\varepsilon^{(P1)} = 1.5$) are for longer free chains, $M_1 = 4$. The remaining parameters are the same as in Figure 1.

with the grafting density in a nonmonotonic way. At low grafting densities the relative adsorption, N_1^e, increases when the grafting density increases. The relative adsorption of small dimer molecules that strongly interact with the brush is an increasing function in the region of grafting densities under study. In the other cases the relative adsorption, N_1^e, exhibits a maximum. This maximum shifts in the direction of higher grafting densities when interactions with the grafting chains are stronger or when the length of free chains decreases. At higher grafting densities the relative adsorption gradually decreases.

Figure 7 illustrates the distribution of tetramers in the surface layer at the volume fraction $x_b^{(1)} = 0.2$, for two values of the
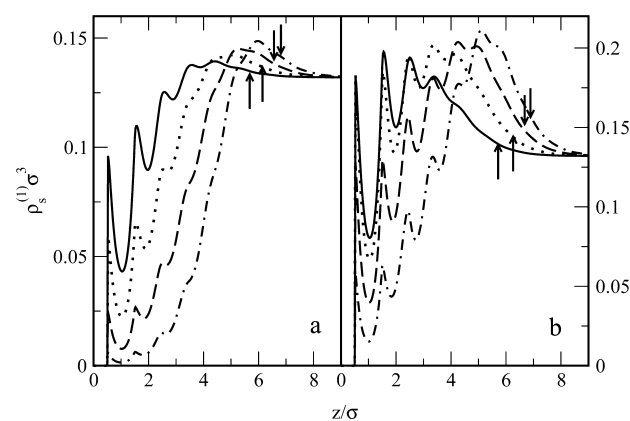

Figure 7. Density profiles of tetramers ($M_1 = 4$) for two values of parameter $\varepsilon^{(P1)}$ characterizing oligomer−brush interactions, 1.25 (part a) and 1.5 (part b), and different grafting densities, ρ_P, 0.1 (solid lines), 0.2 (dotted lines), 0.3 (dashed lines), and 0.4 (dotted-dashed lines). The volume fraction of tetramers in the bulk solution is fixed at $x_b^{(1)} = 0.2$. The remaining parameters are the same as in Figure 1.

parameter $\varepsilon^{(P1)}$ and for varying grafting density. The remaining parameters are the same as in Figure 6. We see that tetramers are present in the whole brush interior, but their distribution depends strongly on the grafting density. The density profiles of tetramers plotted for different grafting densities cross together. One can expect that the penetration of tetramers

into the brush interior rapidly decreases when the grafting density increases. In the case of weakly attracting grafted chains (part a) the tetramer density in the vicinity of the substrate is lower than in the bulk solution. For a sufficiently dense brush, the density of tetramers is close to zero in this region. When the bonded chains strongly attract tetramers (part b), the primary adsorption on the wall is also found. However, if the grafting density is high enough, the local density of tetramers in the middle part of the brush decreases below the bulk density. For both values of the parameter $\varepsilon^{(P1)}$ local densities of tetramers in the outer part of the brushes are higher than in the bulk solution. In other words, there occurs a secondary adsorption of tetramers.

The adsorption is stronger for denser bonded phases. This can be envisaged as follows. The excluded volume effects intensify in dense brushes. This leads to stronger entropic repulsion of free chains from the interior of the brush. On the other hand, attractive interactions with the brush cause the retention of the free chains on top of the brush where they have enough void space. The attraction by a denser bonded phase is stronger. Therefore, adsorption at the brush edge (secondary adsorption) increases with increasing grafting density.

The behavior of free chains near a hairy surface is very complex. The interplay between the size of molecules and the interactions between all species present in the system, along with the effects of the grafting density, leads to different scenarios of adsorption. The knowledge of the adsorption mechanism can be used for controlling of numerous technological processes.

IV. SUMMARY

In this work the density functional theory has been employed to study adsorption from oligomer−monomer solutions on the surfaces modified with grafted chains. We have considered the tethered chains that are not attracted by the substrate. However, the fluid molecules are attracted by the solid surface via Lennard-Jones (9-3) potential. The free chains, monomers, as well as segments of the grafted chains interact via Lennard-Jones (12-6) potential.

We have analyzed the influence of different parameters on the relative excess adsorption of short chains from solutions. The shape of the relative excess isotherm strongly depends on the relations between parameters characterizing attractive interaction in the system. When all of these parameters are the same, the relative excess isotherms are negative. In this case monomers are preferentially adsorbed on the modified surface. On the other hand, when the free chains have a high affinity to the brush, the relative excess is positive in the whole concentration region. For moderated oligomer−brush interactions, the S-shaped isotherms are observed. The position of the adsorption azeotropic point in such isotherm varies with the length of free chains. In all cases the length of oligomers considerably affect the relative excess adsorption. This effect weakens for sufficiently long free chains. It has been shown that interactions of free chains with the substrate and interactions in the bulk solution cause significant changes in the relative excess adsorption isotherms.

Finally, we have discussed the impact of the grafting density on the relative excess adsorption for selected model systems. The obtained relationships between the relative excess adsorption and the grafting density are consistent with the experimental results.[44]

The structure of the surface layer has also been explored. We have found that the interface was highly inhomogeneous. The density profiles of the mixture components are very sensitive on the system parameters. Free chains can be adsorbed in the interior of the brush and on its edge, depending on conditions.

We have shown that adsorption of oligomers from solutions on surfaces modified with end-grafted chains is to a considerable degree similar to their behavior on bare solid surfaces. However, the mechanism of the process and the structure of the surface region is much more complicated. Our predictions are in broad agreement with other theoretical works and experimental observations of the systems to which underlying assumption of the model are expected to apply.[10,36,63−68] The density functional theory is an effective tool to study adsorption of short chains from solutions. The presented here results can be used for the modeling of separation processes.

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Notes
The authors declare no competing financial interest.

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