Janus dumbbells near surfaces modified with tethered chains

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Abstract

Adsorption of dumbbell-shaped particles on polymer-tethered surfaces is studied using molecular dynamics simulations. The bonded layers are built of chains containing “active groups”, while the particles consist of two “chemically” different monomers. We analyze the structure of the surface layers, the excess adsorption isotherms of the dumbbells and their retention in a chromatographic process. We discuss how selected parameters affect the behavior of Janus dumbbells near the polymer layers. We show that the structure of the surface layer mainly depends on the position of the active groups in the chains and the assumed particle-chain interactions. The particles penetrate the polymer layer and accumulate close to the active groups.

Keywords Computer simulations · Adsorption · Janus dumbbells · Chromatography

1 Introduction

Over the past two decades polymer-tethered surfaces have drawn widespread attention in different fields of science and technology. The surfaces modified with grafted polymers have found numerous applications in such areas as, for example, chromatographic separations, lubrication, production of protective coatings and biocompatible materials (Advincula et al. 2009; Klein et al. 2013; Mittal 2012)

Different theoretical approaches have been used to describe the properties of the end-grafted polymer layers. These studies have been the subject of several reviews (Currie et al. 2003; Netz and Andelman 2003; Descas et al. 2008). The behavior of the polymer coating depends on its morphology. At low grafting densities, the chains are isolated and they form the “mushroom” structure. For higher grafting densities, the individual chains can overlap and the interchain repulsion causes the polymers to stretch in the direction perpendicular to the surface. Then the substrate is covered by the polymer “brush”. Another factor that affects the structure of the polymer layer is the solvent quality. In the case of “a good solvent”, chain-solvent contacts are more favorable than chain-chain contacts so chains spread.

However, in “a poor solvent” regime, the effective interactions between chains are attractive and chains collapse. These phenomena are associated with adsorption of solvent molecules on the polymer layers.

In recent years a great deal of research has focused on adsorption of different molecules on solid surfaces covered by polymer films. In these studies, several theoretical treatments have been used, as for example, the self-consistent field theory, the density functional theory and computer simulations (see the review by Binder and Milchev 2012). The behavior of small molecules (Borówko et al. 2007, 2009, 2015; Patrykiewicz et al. 2008), polymers (Milchev et al. 2010; Carignano and Szleifer 2000; Fang and Szleifer 2002), peptides, proteins (Jonsson and Johansson 2004) and Janus particles (Borówko et al. 2013) near polymer-tethered surfaces has been investigated. The density functional theory has been applied to study adsorption of Lennard-Jones spheres (Borówko et al. 2007, 2009; Patrykiewicz et al. 2008) oligomers (Borówko et al. 2011a, b) binary solutions of monomers and oligomers (Borówko et al. 2012a, b), and Janus spherical molecules (Borówko et al. 2013) on the bonded polymers. These studies have shown how the adsorption on polymer-tethered surfaces depends on the grafting density, the chain length and interactions between all species. The theoretical predictions have been consistent with the experimental results and computer simulations (Borówko et al. 2009).

The adsorbents covered by chemically bonded phases are widely used as column packings in the reversed-phase

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chromatography (Dorsey and Dill 1989). Further improving the method requires the knowledge about the mechanism of separation on a molecular level. For this reason, numerous studies have been conducted using computer simulation techniques (Rafferty et al. 2008a, b, 2009) and the density functional theory (Borówko et al. 2009, 2011a, b). The polymer-tethered surfaces are also important for numerous biological systems (Carignano and Szleifer 2000). Their technological applications include, for example, the production of biocompatible implants.

In the last few years the problem of drug delivery has been the subject of intensive studies. This process can be improved by the encapsulation of drug molecules by selected particles (Haag 2004; Zhang et al. 2008). The encapsulating structures arise through self-assembly of amphiphilic molecules, Janus particles, lipids or protein-like copolymers. Among the wide range of Janus-like particles that can be used for the encapsulation, the dumbbell-shaped particles deserve a special interest (Munao et al. 2016; O'Toole et al. 2017; Prestipino et al. 2017). Now, dumbbells of various geometrical and chemical properties can be produced (Skelton et al. 2017; Wolters et al. 2008). The Janus dumbbells are usually constituted by two monomers, one of which is solvophilic and the other one is solvophobic. The molecular simulation study (Prestipino et al. 2017) has shown that Janus dumbbells form different structures near solid surfaces. Adsorption of various heterogeneous dimers on bare solid surfaces has already been the subject of our research (Borówko and Rżysko 1996; Rżysko and Borówko 2003). These investigations have given the impetus to study adsorption of dumbbells near the surfaces modified with end-grafted chains.

In this work we present the results of molecular dynamic simulations of Janus-like dumbbells near the solid surfaces modified with grafted chains. The main goal of the study is to show how adsorption and retention on chemically bonded phases depend on the assumed model of the dumbbells and the architecture of the tethered chains.

The paper is organized as follows. In the next section we describe our model and the simulation method. Then, the results are presented and discussed in Sect. 3. The work is summarized in Sect. 4.

2 Model and simulation methodology

We study Janus-like dumbbells near the substrate modified with end-grafted chains with embedded functional group. The dumbbell is a pair of tangent spheres (labeled as 1 and 2) with diameters $\sigma_2 = 2\sigma_1$ (see Fig. 1).

The surface is covered by chains built of M_A segments A and M_B segments B. We assume that diameters of all segments are the same and equal to the diameter of the small

Fig. 1 Schematic representation of the dumbbells and isomeric forms of grafted chains. Yellow spheres are monomers “1”, green spheres are monomers “2”, blue spheres denote the segments A, magenta spheres correspond to segments B and red spheres stand for the pinned segments. (Color figure online)

sphere “1” ($\sigma_A = \sigma_B = \sigma_s = \sigma_1$). The chains are modeled as freely jointed tangent spheres.

The first segment of each chain is attached to the wall at the distance $d_0 = \sigma_s/2$ at randomly chosen points on the surface. The chain connectivity is ensured by the harmonic segment–segment potentials

$$u_{ss}^{(b)} = k_{ss}(r - \sigma_s)^2, \quad (1)$$

acting between neighboring segments. The remaining chain segments and the monomers of dumbbells (spheres “1” and “2”) interact with the substrate via the hard-wall potential

$$v_k(z) = \begin{cases} 0, & \sigma_k/2 < z, \\ \infty, & \text{otherwise,} \end{cases} \quad (2)$$

where $k = 1, 2, A, B$.

The interactions between all species are modeled by Lennard-Jones potential

$$u^{(kl)} = \begin{cases} 4\epsilon_{kl}[(\sigma_{kl}/r)^{12} - (\sigma_{kl}/r)^6] & r < r_{cut}^{(kl)} \\ 0 & \text{otherwise} \end{cases}, \quad (3)$$

where r is the distance between interacting spheres, $r_{cut}^{(kl)}$ denotes the cutoff distance, $\epsilon_{kl} = \sqrt{\epsilon_{kk}\epsilon_{ll}}$ is the parameter characterizing interactions between species k and l , while $\sigma_{kl} = 0.5(\sigma_k + \sigma_l)$ for $k, l = 1, 2, A, B$. To switch on or switch off attractive interactions we use the cutoff distance: for attractive interaction $r_{cut}^{(kl)} = 3\sigma_{kl}$, while for repulsive interactions $r_{cut}^{(kl)} = \sigma_{kl}$. Determining potential energies we have assumed that the entities which are directly bonded, do not interact via the Lennard-Jones potential. Moreover, we

assume that the grafting segments do not interact with the dumbbells.

The diameter of chain segments is assumed to be the distance unit ($\sigma_s = \sigma$) and the energy segment–segment parameter ϵ_{ss} is the energy unit, $\epsilon_{ss} = \epsilon$. The mass of a single segment is the mass unit, $m_s = m$. The masses of the monomers “1” and “2” we set arbitrary to $m_1 = m$ and $m_2 = 2m$. All species are assumed to be sufficiently light, so that the gravity effect is negligible. The basic unit of time is $\tau = \sigma\sqrt{m/\epsilon}$. The energy constant of the binding potential (1) is assumed to be $1000\epsilon/\sigma^3$.

The reduced temperature is defined as usual, $T^* = k_B T/\epsilon$. We use also the reduced density, $\rho_k^* = \rho_k \sigma_k^3$, where $\rho_k = N_k/V$, is the number density of the k th spheres, N_k denotes the number of the k th spheres and V is the volume. The total reduced density of dumbbells is equal to $\rho_d^* = \rho_1^* + \rho_2^*$.

Molecular Dynamics simulations were carried out using LAMMPS package (Plimpton 1995). One can find the description of the package at <http://lammmps.sandia.gov>.

We consider an ensemble of Janus-like dumbbells in a rectangular box with sizes $L_x = L_y$ and L_z , in directions x , y , z , respectively. The wall located at $z = 0$ is covered by end-grafted chains, while the wall at $z = L_z$ is the hard wall. The distance between these walls is large enough to ensure the existence of the region of a uniform fluid in the middle part of the box. The system is periodic in x and y directions. The distance L_z ranged from 40σ to 80σ . In the majority of the runs the box dimension L_x was 100σ . The simulations were performed for the total number of “atoms” (monomers and segments) equal at least 12,400. In the case of longer tethers, the bigger boxes were used and the total number of all atoms was 22,220.

Numerical integrations have been performed using the velocity Verlet algorithm with the time step $\Delta t = 0.005\tau$. After equilibration (during at least 10^8 time steps) the production runs for at least 10^7 time steps have been performed. The jobs were run in parallel and the number of nodes was usually 70. In order to probe uncorrelated configurations, the accumulation of the desired quantities was carried out after 100 timesteps. The temperature has been controlled by Berendsen thermostat. The simulations were carried out at $T^* = 1$. For all systems we evaluated local densities of segments, and the density profiles of the monomers “1” and “2”.

We investigate the layers built of short chains ($M = 8$ and $M = 18$). The segments A correspond to methylene groups in alkane chains, while segments B mimic functional groups. The segments B are located at the consecutive positions along the chain i_{s-1} , i_s , i_{s+1} , where i_s denotes the position of the middle segment B . A given type of grafted chains is labeled as $M - Bi_s$ (see Fig. 1). The group of B -segments was connected with the grafting segment (8-B3, 18-B3) or it was located and the chain end (8-B7, 18-B17).

We have assumed the same ratio of monomer’s diameters ($\sigma_2/\sigma_1 = 2$) that used in the study of aggregation of the dumbbells (Munao et al. 2015). The simulations have been performed for different values of parameters characterizing interactions between dumbbells (D_k , $k = 1, 2$). We have assumed the values corresponding to Janus-like particles that consist of considerably different monomers “1” and “2”. We have carried out simulations for two models of the dumbbells. In the model D1 interactions between the monomers “1” are attractive and $\epsilon_{11} = 1.2\epsilon$, while remaining interactions are repulsive. However, in the model D2 the interactions between like monomers are attractive, $\epsilon_{11} = \epsilon_{22} = 1.2\epsilon$, and only 12-interactions are repulsive. The values of the energy parameters are similar to those used in the works concerning adsorption from solutions (Borówko et al. 2011a, b). In our model the solvent is involved implicitly and it is treated as a continuous medium that affects interactions between “real” particles. We have chosen parameters which correspond to the regime of a good solvent for the polymers.

We have assumed different interactions between dumbbells and the chain segments (S_l for $l = 1, 2, 3, 4$). These parameters are collected in Table 1. We use the following code to label the models: $M - Bi_s - D_k S_l$.

The considered model of the dumbbell can be viewed as a coarse-grained model of real amphiphilic molecules or small colloidal particles (Marshall et al. 2012; Mondal and Yethiraj 2011; Thompson et al. 2012). The amphiphiles contain both solvophobic and solvophilic parts. Familiar examples are lipids and alcohols. The dumbbell (heteronuclear dimer) can be the simplest model of a surfactant (Schmid 2000). The surface with tethered copolymers mimics the chemically bonded phases with embedded polar groups, commonly used in chromatography (O’Sullivan et al. 2010).

3 Results and discussion

The aim of our calculations is to determine how the behavior of Janus-like dumbbells near the chemically bonded phases depends on the selected parameters characterizing

Table 1 Parameters ϵ_{kl}/ϵ for attractive interactions between dumbbells and chains

Model	B1	B2	A1	A2
S1	1.2	–	–	–
S2	2.0	–	–	–
S3	–	2.0	–	–
S4	1.2	–	–	1.0
S5	–	1.0	1.2	–

For repulsive interactions $\epsilon_{kl}/\epsilon = 1$ ($kl = A1, A2, B1, B2$)

the systems. We focus our attention on the position of the *B*-groups in tethers and on dumbbell–chain interactions.

Different parameters of interactions between dumbbells and the segments of tethers have been assumed (see Table 1).

All simulations have been carried out for the grafting density $\rho_p = 0.1$. In the most simulations the average reduced density of dumbbells in the whole system was equal to $\rho_{av}^* = 0.05$.

First, we discuss the results obtained for adsorption of the dumbbells of the type D1. The monomers “1” are attracted by the *B*-groups ($\epsilon_{B1} = 1.2\epsilon$), while the remaining chain–dumbbell interactions are repulsive (S1). The results are shown in Fig. 2. The upper panel (a) depicts the density profiles of bonded layers built of different chains. All profiles of tethered polymers, $\rho_s^*(z)$, exhibit high peaks corresponding to the pinned segments ($z = 0.5\sigma$). These peaks are omitted in the relevant figures. For $z > 0.5\sigma$, the structure the chain layer considerably depends on the assumed model. In the considered case, we see two well pronounced peaks connected with the successive layers of polymer segments. Then, the density of chain segments gradually decreases, and vanishes at the effective brush height, $r = h$ (Borówko et al. 2011a, b). The effective heights of the polymer layers are: $h = 5.72\sigma$ for $M = 8$ and $h = 11.01\sigma$ for $M = 18$. The grafted chains are not completely stretched due to the

moderate grafting density. Moreover, the position of the functional group does not affect the structure of polymer layer.

Figure 2b presents the total reduced densities of the dumbbells adsorbed on the polymer layers shown in Fig. 2a. Notice that the dumbbells do not exhibit a strong tendency to penetrate the bonded layers. The densities ρ_d^* near the wall and in the middle part of the polymer layer are considerably lower than those in the bulk phase. Such a depletion of the fluid density within the region occupied by polymers is stronger for longer tethers. The distribution of the dumbbells in the bonded layer depends on architecture of the chains. In the case of the *B*-groups located at the chain ends the dumbbells gather near them, and we see wide maxima in ρ_d^* in the outer parts of the “polymer brushes”. As the distance from the wall decreases, the density ρ_d^* also gradually decreases. The markedly different distributions $\rho_d^*(z)$ are found for the chains 8-B3 and 18-B3. Now, the dumbbells deeper penetrate the brush and more particles are adsorbed close to the wall. For longer chains (18-B3) we see the wide minimum in the middle of the bonded layer and the low maximum at an immediate neighborhood of the wall.

In general, one can say that dumbbells are “adsorbed on the polar groups of tethers”. The same effect has already been reported for spherical molecules near the polymer bonded layers (Borówko et al. 2011a, b).

To shed more light on the role of the internal architecture of the particles in their adsorption we analyze the density profiles of dumbbell-forming monomers. In Fig. 3 the number local densities $\rho_1(z)$ and $\rho_2(z)$ are plotted for the dumbbells D1 and longer tethers ($M = 18$). Obviously, these profiles are correlated because the monomers “1” and “2” are connected. However, we can remark subtle effects associated with interactions on particular monomers with chain segments.

Figure 3a shows the results obtained for the model D1S1 (see Fig. 2). As the *B*-groups are attached at the chain ends the profiles of both monomers have slight maxima near $z = 10.1\sigma$. However, for the tethers B3 the density profile $\rho_1(z)$ has the local maximum at $z = 2.0\sigma$. The monomers “1” accumulate near the *B*-segments. The density of big monomers, $\rho_2(z)$, attains the maximum at the wall. The small monomers can easier penetrate the brush than the big ones. Moreover, they are attracted by the segments *B*. On the contrary, the big monomers are inert with respect to the chain segments. They are pulled into the brush by the active small monomers.

The analysis of the profiles of monomers “1” and “2” allows us to draw conclusions regarding the orientation of the dumbbells relative to the surface. Note that the densities of both monomers attain maxima at similar distances from the surface. This means that there is no preferred orientations of dumbbells with respect to the wall.

Fig. 2 Profiles of reduced densities of chains (**a**) and dumbbells (**b**) estimated at $\rho_{d,av}^* = 0.05$ for the systems: 18-B17-D1S1 (black solid line), 18-B3-D1S1 (red dotted line), 8-B7-D1S1, (green dashed line), 8-B2-D1S1 (blue dotted-dashed line). (Color figure online)

Fig. 3 Profiles of number densities of monomers “1” and “2” estimated at $\rho_{d,av}^* = 0.05$ for the dumbbells: D1S1 (a) and D1S2 (b). Lines: black solid—monomers “2” and chains 18-B17, green dashed—monomers “1” and chains 18-B17, red dotted—monomers “2” and chains 18-B3, blue dotted-dashed—monomers “1” and chains 18-B3. (Color figure online)

To analyze the influence of the strength of interactions between small monomers and *B*-segments on the structure of the surface layer we have estimated the individual profiles for $\varepsilon_{B1} = 2.0\varepsilon$ (model D1S2, Fig. 3b). The remaining parameters are the same as in Fig. 3a. As one can expect, an increase of ε_{B1} causes a considerable increase in adsorption of dumbbells. Now, the maxima in the density profiles, $\rho_1(z)$, are very well pronounced. The maxima are located at $z = 1.96\sigma$ (for the chains B3) and $z = 8.54\sigma$ (for the chains B17). A comparison of Fig. 3a and b clearly demonstrates that for stronger B1-interactions the impact of the architecture of tethers on the structure of the surface layer is more significant.

In Fig. 4 we present the fragments of equilibrium configurations for the interactions parameters such as in Fig. 3b. Figure 4a demonstrates the results for the tethers 18-B17. In Fig. 4b the snapshot for the chains 18-B3 is shown. It is clear that the dumbbells always accumulate near the *B*-groups.

Next, we discuss the behavior of the dumbbells D1 when the big monomers “2” are attracted by the *B*-groups (model D1S2). The relevant results are shown in Fig. 5. It should be pointed out that now the effective attraction between dumbbells and *B*-segments are stronger than in the model D1S1 due to longer range of interactions ($r_{cut} = 3\sigma_{B2}$). As a consequence, the density of dumbbells in the surface region is higher (compare Fig. 2b and Fig. 5b). The big monomers “2” stick to the *B*-segments. For the chains B3 the dumbbells are accumulated near the wall (maximum at $z = 1.59\sigma$), while for the tethers B17 they are mainly located on the edge of the bonded layer (the maximum at $z = 8.22\sigma$). This, in turn, affects the distribution of chain segments (Fig. 5a). The density profiles of chain segments and the density profiles of dumbbells are correlated according to the rule: more dumbbells—less segments. Therefore, near the wall the density of chains B3 is considerably lower than density of the chains B17. However, for $z > 3.8\sigma$ the opposite effect

Fig. 4 The fragments of equilibrium configurations at $\rho_{d,av}^* = 0.05$ for the system 18-B17-D1S2 (a) and for the system 18-B3-D1S2 (b)

is observed. Also the effective brush heights are different for these isomers: $h = 11.5\sigma$ (B17) and $h = 11\sigma$ (B3). In this case, the structure of the bonded layer considerably depends on the location of the *B*-groups in the grafted chains. Figure 6 shows fragments of snapshots corresponding to density profiles plotted in Fig. 5. The dumbbells are similarly distributed inside the bonded phase as in the previous case (compare with Fig. 4).

Fig. 5 Profiles of reduced densities of chains (**a**) and dumbbells (**b**) estimated at $\rho_{d,av}^* = 0.05$ for the system 18-B17-D1S3 (black solid line) and for the system 18-B3-D1S3 (red dotted line). (Color figure online)

Fig. 6 The fragments of equilibrium configurations at $\rho_{d,av}^* = 0.05$ for the system 18-B17-D1S3 (**a**) and for the system 18-B3-D1S3 (**b**)

In Fig. 7 we show selected results obtained for the particles D2 which in a completely different way interact with the grafted chains (D2S3). Now, interactions of the both monomers and all segments (either A or B) are attractive. This causes that the dumbbells strongly penetrate the polymer layers. At first glance the profiles of the total reduced densities of dumbbells plotted in Fig. 7a seem to be rather surprising. The dumbbells are located mainly in the interior of the brush. One can see that close to the wall the densities ρ_d^* are greater for the tethers with “active” groups B located at their ends than those for the chains with the B-groups linked to the grafted segments. Inversely, the densities ρ_d^* for the chains 8-B7 and 18-B17 are smaller in the outer region of the bonded layer than those for the tethers 8-B3 and 18-B3. We can explain it as follows. In this case, the dumbbells are more strongly attracted by the parts of chains built of segments A than by the B-groups. Although $\epsilon_{B1} < \epsilon_{A2} = 1.2\epsilon$, the values of the energy parameters are comparable. However, as it has been already mentioned, the interactions with big monomers “2” have a longer range. Moreover, there are more segments A than B in the tethers. The stronger attractive interactions between like monomers ($\epsilon_{11} = \epsilon_{22} = 1.2\epsilon$) additionally intensify the tendency for accumulation of the dumbbells near preferred parts of tethers.

In Fig 7b we show the density profiles of monomers for the both types of longer tethers. In the case of chains 18-B17 the density of big monomers, ρ_2 , are greater than the density of small spheres in the middle part of the bonded layer. On the contrary, $\rho_2 < \rho_1$ at immediate proximity of the wall and in the outer part of the brush. This means that the dumbbells are adsorbed near the surface with monomers “1” directed to the wall, but these located farther on ($z > 2.01\sigma$) are oriented inversely. The profiles of the individual monomers plotted for 18-B3 are considerably different. Now, the profile of small monomers exhibits two well-pronounced maxima: the first at $z = 2.29\sigma$ that correspond to “adsorption on the B-groups” and the second one close to the chain ends (at $z = 6.21\sigma$). In the middle of the brush the density ρ_2 is high, while the density ρ_1 attains minimum.

In the neighborhood of the wall $\rho_1 > \rho_2$. Thus, close to the wall many dumbbells have the monomers “1” directed toward the wall. This effect is even more visible than in the case of the chains 18-B17.

The fragments of configurations for the systems in which all segments attract dumbbells are shown in Fig. 8. In this case, the dumbbells are present in the whole bonded phase. Moreover, adsorption of dumbbells is high. This is reflected by a very low concentration of dumbbells in the bulk phase (compare Fig. 4 and Fig. 8).

The analysis of the density profiles of the monomers “1” and the monomers “2” gives only preliminary information on the orientation of the Janus dumbbells with respect to

Fig. 7 Profiles of reduced densities of dumbbells (a) and profiles of number densities of monomers “1” and “2” (b) estimated at $\rho_{d,av}^* = 0.05$ for the dumbbells D2S4. Lines: (a) black solid—chains 18-B17, red dotted—chains 18-B3, green dashed—chains 8-B7, blue dotted-dashed—chains 8-B3, and (b) black solid—monomers “2” and chains 18-B17, green dashed—monomers “1” and chains 18-B17, red dotted—monomers “2” and chains 18-B3, blue dotted-dashed—monomers “1” and chains 18-B3. (Color figure online)

Fig. 8 The fragments of equilibrium configurations at $\rho_{d,av}^* = 0.05$ for the system 18-B17-D2S4 (a) and for the system 18-B3-D2S4 (b)

the surface. In the considered case, this orientation mainly depends on interactions with the polar groups in the bonded chains. A deeper discussion of these effects is beyond a scope of this study.

In the earlier works the behavior of Janus particles near solid surfaces has been considered. Mixtures of Janus dumbbells with spherical particles at a bare substrate have been studied using computer simulations (Prestipino et al. 2017). In this

Table 2 The excess adsorption, Γ^* , and the average distribution ratio, K^* , calculated at the average reduced density of the dumbbells in the whole system equal to $\rho_{d,av}^* = 0.05$

No.	System code	$\Gamma^* \times 10^{-5}$	K^*
1	8-B7-D1S1	− 1.63	0.68
2	8-B3-D1S1	− 2.32	0.53
3	18-B17-D1S1	− 4.16	0.48
4	18-B3-D1S1	− 5.14	0.39
5	18-B17-D1S2	− 2.26	0.71
6	18-B3-D1S2	− 4.11	0.50
7	18-B17-D1S3	6.52	2.70
8	18-B3-D1S3	2.42	1.49
9	8-B7-D2S4	6.64	3.29
10	8-B3-D2S4	8.80	4.56
11	18-B17-D2S4	17.80	58.02
12	18-B3-D2S4	17.90	66.05
13	8-B7-D2S5	6.78	2.7

case the complex membrane-like structures have been found. However, the density functional theory has been used to study the behavior of spherical Janus molecules near the chemically bonded phases built of homogeneous polymers (Borówko et al. 2013). The competition between interactions of the particles with the wall, with the grafted chains, and inter-particle interactions leads to various structures of the surface layer. The orientation of the Janus particles relative to the wall has been described by the suitably defined order parameter (Borówko et al. 2013).

We focus here on the quantities that characterize the adsorption on the dumbbells on the chemically bonded phases. In particular, we discuss the excess adsorption of dumbbells and their distribution ratios for the systems listed in Table 2.

Fig. 9 Excess adsorption isotherms estimated for the tethers 8-B7 and dumbbells: D1S1 (black solid line), D2S4 (green dashed line), D2S5 (red dotted line). (Color figure online)

The excess adsorption of dumbbells is defined as (Borówko et al. 2009)

$$\Gamma = \frac{1}{S} \int (\rho_d^*(z) - \rho_{db}^*) dz \quad (4)$$

where ρ_{db}^* is the total reduced density of dumbbells in the bulk phase, S is the surface area.

In Fig. 9 we have plotted the adsorption isotherms for the bonded phases 8-B7 and different interactions in the systems. We have carried simulations at the following values of the $\rho_{d,av}^*$: 0.01, 0.025, 0.05, 0.075, 0.1. For the model D1S1 the excess adsorption is negative. However, when dumbbell–chain interactions are attractive (models D2S4 and D2S5) $\Gamma > 0$.

To illustrate how excess adsorption of dumbbells depends on the assumed parameters we have calculated the values of the excess adsorption, Γ^* , at $\rho_{d,av}^* = 0.05$ for all considered models (Table 2). From the analysis of these results, it follows that: (i) for repulsive segments A the excess adsorption, Γ^* , is negative (positive) when small (big) monomers are attracted by the B -groups (systems 1–8), (ii) if all segments are attractive, Γ^* is positive (systems 9–13), (iii) the excess adsorption is greater for shorter (longer) chains with the repulsive (attractive) segments, (iv) in the case of repulsive segments A , adsorption is smaller when the B -groups are located near the surface. The impact of the position of the B -group in the attractive chains on the adsorption depends on the details of the model. For short chains, adsorption is higher on the bonded phases B3 (systems 9 and 10), but for longer chains, the values of Γ^* are almost the same (systems 11 and 12).

Fig. 10 Profiles of local distribution ratios estimated for the system 8-B7-D1S1 (black solid line) and the system 8-B7-D2S5 (green dashed line). (Color figure online)

Another quantity that can be used to characterize adsorption is the local distribution ratio (Rafferty et al. 2009; Borówko et al. 2011a, b)

$$K(z) = \rho_d(z) / \rho_{db} \quad (5)$$

Figure 10 shows the local distribution ratios for the model 8-B7-D2S3 and the model 8-B7-D1S1. In the both cases, the solute (dumbbells) penetrate the bonded phases. However, much more solute particles are located in the middle part of the bush for the strongly attractive segments A .

Moreover, we have estimated the average distribution ratio given by

$$K = \bar{\rho}_d / \rho_{db} \quad (6)$$

where

$$\bar{\rho}_d = (1/z_0) \int_0^{z_0} \rho_d(z) dz \quad (7)$$

and z_0 denotes a position of the dividing surface between the surface and bulk “phases”. As z_0 we have used the value at which the local number density ρ_d^* differs from its bulk value no more than by 1 %. The distribution coefficient K is directly associated with the retention coefficient used in chromatography: $k = KV_s/V_b$, where V_s and V_b are volumes of the surface (stationary) and the bulk (mobile) phase, respectively.

In Table 2 we have collected the average distribution ratios K calculated for $\rho_{d,av}^* = 0.05$. The analysis of these data leads to the following conclusions: (i) for the systems with repulsive segments A (systems 1–8), the retention of dumbbells on/in the tethers with the active groups located at their ends is higher than that on the brushes with the active

groups linked to the grafted segments, (ii) for the systems with attractive segments *A* (systems 9–12), the retention is higher when the functional groups *B* are located near the surface, (iii) an increase of attractive interactions with the chains always causes an increase of retention, (iv) the retention is higher for shorter (longer) chains when interactions with segments *A* are repulsive (attractive). The finding that the retention can be stronger for active groups connected with the grafted segments is rather surprising but this result is consistent with experimental observations (O’Sullivan et al. 2010).

4 Conclusions

We have studied the behavior of Janus-like dumbbells on solid surfaces modified with tethered chains using molecular dynamics simulations. The considered dumbbells consist of spheres with different diameters. Simulations have been conducted for selected sets of parameters characterizing interactions between dumbbells and dumbbell–chain interactions. We have studied chemically bonded phases with embedded functional groups located at the ends of tethers or linked to the segment pinned to the surface. The active groups are the built of three segments *B*. The remaining parts of chain consist of segments *A*. The tethers containing 8 and 18 segments have been considered.

We have focused on the structure of surface layer. For this purpose, we have evaluated local densities of dumbbells and chain segments. We have shown that the dumbbells penetrate the bonded layer. However, the distribution of the dumbbells in the bonded phase depends on the dumbbell–chain interactions and on the position of the active group in the grafted chains. Obviously, the dumbbells deeper penetrate the brushes when they are attracted by all chain segments. In this case, the density of dumbbells is high in the middle part of the surface layer. However, if the dumbbells are attracted only by the segments *B* then they accumulated near the *B*-groups, i.e. near the surface or in the outer part of the brush.

It is noteworthy that in certain cases (e.g. for systems D2S3) the orientation of particles relative to the surface changes with the distance from the wall. The dumbbells adsorbed near the surface have the small monomers “1” directed to the wall but these located in the outer part of the bonded phase are oriented inversely.

We have discussed the impact of selected parameters on excess adsorption of dumbbells and the distribution ratio that characterizes their retention in chromatographic process. Our simulations clearly demonstrate that one can considerably enhance adsorption and retention changing interactions between all species (monomers and segments) and the type of tethered chains. The detailed conclusions are presented

in Sect. 3. It is interesting that for attractive segments *A* the bonded phases with the active *B*-groups located near the surface have stronger adsorptive properties than those with the functional groups linked at the chain ends.

The properties of layers formed by tethering of polymers to surfaces depend on numerous parameters. Our model does not involve electrostatic interactions. However, when the bonded layer is immersed in an aqueous solution, these interactions can dominate. These effects are very important in biological systems. Therefore, the behavior of electrolytes near the polymer-tethered surfaces could be the subject of future research.

In summary, we have shown that the type of grafted chains affects strongly the behavior of Janus-like dumbbells near the modified substrates. Adsorption mechanism and the structure of the surface layers depend on the nature of particles and the bonded phases.

We hope that our results would provide useful information on engineering of chemically bonded phases and their applications.

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References

- Advincula, R.C., Brittain, W.J., Caster, K.C., Ruhe, J. (eds.): *Polymer Brushes: Synthesis, Characterization, Applications*. Wiley, Weinheim (2009)
- Binder, K., Milchev, A.: Polymer brushes on flat and curved surfaces: how computer simulations can help to test theories and to interpret experiments. *J. Polym. Sci. B* **50**, 1515–1555 (2012)
- Borówko, M., Rżysko, W.: Theory of adsorption from a dimer-monomer solution on a patchwise heterogeneous surface. *J. Colloid Interface Sci.* **182**, 268–274 (1996)
- Borówko, M., Rżysko, W., Sokołowski, S., Staszewski, T.: Density functional approach to the adsorption of spherical molecules on a surface modified with attached short chains. *J. Chem. Phys.* **126**, 214703 (2007)
- Borówko, M., Rżysko, W., Sokołowski, S., Staszewski, T.: Density functional approach to adsorption and retention of spherical molecules on surfaces modified with end-grafted polymers. *J. Phys. Chem. B* **113**, 4763–4770 (2009)
- Borówko, M., Sokołowski, S., Staszewski, T.: Adsorption of oligomers on the polymer-tethered surfaces. *J. Colloid Interface* **356**, 267–276 (2011a)
- Borówko, M., Sokołowski, S., Staszewski, T.: A density functional approach to retention in chromatography with chemically bonded phases. *J. Chromatogr. A* **1218**, 711–720 (2011b)

- Borówko, M., Sokołowski, S., Staszewski, T.: Adsorption from binary solutions on the polymer-tethered surfaces. *J. Phys. Chem. B* **116**, 3115–3124 (2012a)
- Borówko, M., Sokołowski, S., Staszewski, T.: Adsorption from oligomer-monomer solutions on the surfaces modified with end-grafted chains. *J. Phys. Chem. B* **116**, 12842–12849 (2012b)
- Borówko, M., Poeschel, T., Sokołowski, S., Staszewski, T.: Janus particles at walls modified with tethered chains. *J. Phys. Chem. B* **117**, 1166–1175 (2013)
- Borówko, M., Sokołowski, S., Staszewski, T.: Adsorption on chemically bonded chain layers with embedded active groups. *Mol. Phys.* **113**, 1014–1021 (2015)
- Carignano, M.A., Szeleifer, I.: Prevention of protein adsorption by flexible and rigid chain molecules. *Colloids Surf. B* **18**, 169–182 (2000)
- Currie, E.P.K., Norde, W., Cohen Stuart, M.A.: Tethered polymer chains: surface chemistry and their impact on colloidal and surface properties. *Adv. Colloid Interface Sci.* **100**, 205–265 (2003)
- Dorsey, J.G., Dill, K.A.: The molecular mechanism of retention in reversed-phase liquid chromatography. *Chem. Rev.* **89**, 331–346 (1989)
- Descas, R., Sommer, J.U., Blumen, A.: Grafted polymer chains interacting with substrates: computer simulations and scaling. *Macromol. Theory Simul.* **17**, 429–453 (2008)
- Fang, F., Szeleifer, I.: Effect of molecular structure on the adsorption of protein on surfaces with grafted polymers. *Langmuir* **18**, 5497–5510 (2002)
- Haag, R.: Supramolecular drug-delivery systems based on polymeric core-shell architectures. *Angew. Chem. Int. Ed.* **43**, 278–282 (2004)
- Jonsson, M., Johansson, H.O.: Effect of surface grafted polymers on the adsorption of different model proteins. *Colloids Surf. B* **37**, 71–81 (2004)
- Klein, J., Briscoe, W.H., Chen, M., Kampf, N., Raviv, U., Tadmor, R., Tsarkova, L.: Polymer brushes and surface forces, Chap. 4. In: Zeng, H. (ed.) *Polymer, Adhesion, Friction and Lubrication*. Wiley, Hoboken (2013)
- Marshall, B.D., Emborsky, C., Cox, K., Chapman, W.G.: Effect of bond rigidity and molecular structure on the self-assembly of amphiphilic molecules using second-order classical density functional theory. *J. Phys. Chem. B* **116**, 2730–2788 (2012)
- Milchev, A., Egorov, S.A., Binder, K.: Absorption/expulsion of oligomers and linear macromolecules in a polymer brush. *J. Chem. Phys.* **132**, 184905 (2010)
- Mittal, V. (ed.): *Polymer Brushes: Substrates, Technologies and Properties*, Chap. 1. CRC Press, Boca Raton (2012)
- Mondal, J., Yethiraj, A.: Driving force for the association of amphiphilic molecules. *J. Phys. Chem. Lett.* **2**, 2391–2395 (2011)
- Munao, G., O’Toole, P., Hudson, T.S., Costa, D., Caccamo, C., Sciorino, F., Giacometti, A.: Cluster formation and phase separation in heteronuclear Janus dumbbells. *J. Phys.: Condens. Matter* **27**, 234101 (2015)
- Munao, G., Costa, D., Prestipino, S., Caccamo, C.: Encapsulation of spherical nanoparticles by colloidal dimers. *Phys. Chem. Chem. Phys.* **18**, 24922–24930 (2016)
- Netz, R.R., Andelman, D.: Neutral and charged polymers at interfaces. *Phys. Rep.* **380**, 1–95 (2003)
- O’Toole, P., Munao, G., Giacometti, A., Hudson, T.S.: Self-assembly behaviour of hetero-nuclear Janus dumbbells. *Soft Matter* **13**, 7141–7153 (2017)
- O’Sullivan, G.P., Scully, N.M., Glennon, J.D.: Polar-embedded and polar-endcapped stationary phases for LC. *Anal. Lett.* **43**, 1609–1629 (2010)
- Patrykiewicz, A., Sokołowski, S., Tscheliessnig, R., Fischer, J., Pizio, O.: Density functional approach to adsorption of simple fluids on surfaces modified with a brush-like chain structure. *J. Phys. Chem. B* **112**, 4552–4560 (2008)
- Plimpton, S.: Fast parallel algorithms for short-range molecular dynamics. *J. Comput. Phys.* **117**, 1–19 (1995)
- Prestipino, S., Munao, G., Costa, D., Pellicane, G., Caccamo, C.: Two-dimensional mixture of amphiphilic dimers and spheres: self-assembly behaviour. *J. Chem. Phys.* **147**, 144902 (2017)
- Rafferty, J.L., Siepmann, J.I., Schure, M.R.: Influence of bonded-phase coverage in reversed-phase liquid chromatography via molecular simulation: I. Effects on chain conformation and interfacial properties. *J. Chromatogr. A* **1204**, 11–19 (2008)
- Rafferty, J.L., Siepmann, J.I., Schure, M.R.: Influence of bonded-phase coverage in reversed-phase liquid chromatography via molecular simulation: II. Effects on solute retention. *J. Chromatogr. A* **1204**, 20–27 (2008)
- Rafferty, J.L., Siepmann, J.I., Schure, M.R.: The effects of chain length, embedded polar groups, pressure, and pore shape on structure and retention in reversed-phase liquid chromatography: molecular-level insights from Monte Carlo simulations. *J. Chromatogr. A* **1216**, 2320–2331 (2009)
- Rzysko, W., Borówko, M.: Monte Carlo study of adsorption of heteronuclear dimers on heterogeneous surfaces. *Thin Solid Films* **425**, 304–311 (2003)
- Schmid, F.: Systems involving surfactants. In: Borówko, M. (ed.) *Computational Methods in Surface and Colloid Science*, Surfactant Science Series vol. 89. M. Dekker, Inc., New York (2000)
- Skelhon, T.S., Chen, Y., Bon, S.A.F.: Synthesis of “hard-soft” Janus particles by seeded dispersion polymerization. *Langmuir* **30**, 13525–13532 (2014)
- Thompson, R.B., Jeib, T., Wen, Y.: Benchmarking self-consistent field theory for small amphiphilic molecules. *Soft Matter* **8**, 9877–9885 (2012)
- Wolters, J.R., Verweij, J.E., Avvisati, G., Dijkstra, M., Kegel, W.K.: Depletion-induced encapsulation by dumbbell-shaped patchy colloids stabilize microspheres against aggregation. *Langmuir* **33**, 3270–3280 (2017)
- Zhang, L., Chan, J.M., Gu, F.X., Rhee, J.W., Wang, A.Z., Radovic-Moreno, A.F., Alexis, F., Langer, R., Farokhzad, O.C.: Self-assembled lipid-polymer hybrid nanoparticles: a robust drug delivery platform. *ACS Nano* **2**, 1696–1702 (2008)

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