

Note

Computer simulations of surfactant monolayers at solid walls

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Abstract

A series of molecular dynamics simulations to study the structure of a surfactant monolayer near real surfaces was carried out. A comparison of two different surfaces, TiO₂ and SiO₂, with the same monolayer was performed. Moreover, each surface was modeled by two different approaches, the first model considers the complete structure of a TiO₂ (or SiO₂) wall, whereas the second model is a continuous solid wall with an effective potential. Both wall models give essentially the same monolayer configuration suggesting that the explicit form of the wall does not play a relevant role to study the structure of surfactant monolayers close to planar surfaces.

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1. Introduction

Studies of surfactant molecules at liquid/vapor and liquid/liquid interfaces have been the subject of several investigations for long time, not only for their scientific interest but also for their industrial applicability. Therefore, several experimental techniques have been used to study those systems [1–5].

However, the effect of surfactants close to solid surfaces has not been extensively researched, although they show several noteworthy features. For instance, some experiments show that amphiphilic molecules present spherical, cylindrical or lamellar structures depending on the solid–molecule interactions [6,7].

Over the last several years, research has been conducted on the structure and composition of surfactant monolayers, e.g., the arrangement of the surfactants at the interface, the extension of the chains, the thickness of the monolayer, etc. Particularly, in the case of monolayers at solid surfaces, the structure and location of surfactant molecules strongly depend on the interactions between the molecules and the substrate [7].

On the other hand, due to the considerable increase in computational power, computer simulations became an important

tool to study such complex interfacial systems [8–11]. From these studies it is possible to obtain information about dynamical and structural properties of interfacial problems from a molecular level, which is not easy to get from real experiments.

From the theoretical point of view, one question that arises from the simulation of monolayers close to walls is whether the explicit form of the surface has to be considered in order to analyze the structure of the surfactants. Therefore, in the present communication we investigate the role of solid surfaces in the structure formation of surfactant molecules. Particularly, we investigate whether the morphology of structured and structureless surfaces affect the arrangement and position of the molecules close to walls.

2. Computational method and results

For the present study, molecular dynamics simulations, of two different systems were carried out on a surfactant monolayer close to a solid wall. The initial configuration was prepared with 1364 water molecules (SPC/E model [12]) to form an air/water/air interface in a simulation box of dimensions $x = y = 31.918 \text{ \AA}$ and z -dimension of 144.3 \AA . Then, a monolayer of 13 molecules in all-*trans* configuration was placed at one end of the water/air interface corresponding to an area per

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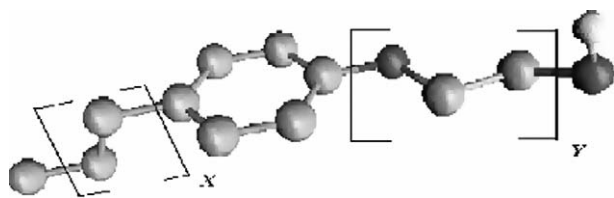


Fig. 1. The chemical structure of the molecule used in the simulations $\text{CH}_3-(\text{CH}_2-\text{CH}_2)_x-\text{benzene}-(\text{O}-\text{CH}_2-\text{CH}_2)_y\text{OH}$.

head group of $78.4 \text{ \AA}^2/\text{molec}$. This value is in the range of those found in typical industrial applications of surfactants diluted in solvents. The surfactant molecule has the chemical structure shown in Fig. 1.

This molecule has the common components of the surfactants used in several industrial products such as shampoo, washing powder, etc. It consists of a weakly polar head and a nonpolar hydrocarbon chain joined by a benzene group. The length of the molecule is given by the parameters X (non-polar) and Y (polar) which indicate the number of times that each group is repeated. We use the following chemical formula $\text{CH}_3-(\text{CH}_2-\text{CH}_2)_x-\text{benzene}-(\text{O}-\text{CH}_2-\text{CH}_2)_y\text{OH}$ to denote the general molecular structure. All simulations were conducted for a monolayer with $X = 1$ and $Y = 6$ ($X1Y6$) and were carried out in the NVT ensemble with a time step of 0.0015 ps using the velocity-Verlet algorithm. The temperature was fixed at $T = 298 \text{ K}$, controlled by rescaling the velocities at each time to the desired value. For the long-range electrostatic potential we used the Ewald method. Moreover, for the appropriate calculations of these forces we included the surface term in the case of the simulations with a continuous wall [13]. Periodic boundary conditions were imposed in all directions and the van der Waals interactions were cutoff at 10 \AA . For the surfactant molecule we used angular (harmonic) and torsional (Ryckaert–Belleman) potentials described elsewhere [14] whereas the distances were kept constant using the shake method.

Once the system was equilibrated a wall was placed close to the surfactant molecules next to the nonpolar groups. In the case of SiO_2 , because the LJ interactions are less attractive, the non-polar groups were located 5 \AA apart from the wall. Therefore, the system not only considers the interactions between the different molecules but also the interaction of the molecules with the wall. Furthermore the array of the surfactants on the wall is determined by all these interactions. The Ewald parameters α and κ_{max} were chosen such the error in the potential energy was less than 10^{-3} .

In a first set of simulations, the TiO_2 wall was modeled in two different forms. In the first model the complete structure of a TiO_2 wall in the form of rutile [15] was used. Lennard Jones and Coulombic potentials were used for the site–site interaction between the atoms of the wall and the atoms of the surfactant/water system. Table 1 shows the parameters used in the simulations where some of them were taken from Refs. [16–18]. For the CH_n groups a united atom model was used. The unlike interactions were calculated with the Lorentz–Berthelot rules. Then the system wall/surfactant/water/air, was run for a total 2.0 ns after 500 ps of equilibration. The struc-

Table 1
Intermolecular potential parameters

Site	q (e)	σ (\AA)	ϵ (K)
$\text{CH}_3-(\text{CH}_2-\text{CH}_2)_x-\text{benzene}-(\text{O}-\text{CH}_2-\text{CH}_2)_y\text{OH}$			
O (water)	-0.8476	3.166	78.2
H (water)	0.4238	0	0
H (attached to O)	0.435	0	0
O (attached to CH_2)	-0.7	3.07	85.5
C (attached to O)	0.265	3.78	104.2
Benzene	0	3.71	73.97
CH_2	0	3.93	45.7
CH_3	0	3.85	102.6
TiO_2			
Ti	1.15	3.788	205.39
O	-0.575	3.627	93.99
TiO_2^a		3.734	1150.89
SiO_2			
Si	2.0	4.29	52.8
O	-1.0	3.3	40.25
SiO_2^a		3.934	287.72

^a σ and ϵ parameters used for the continuous wall model. The potential parameters for the surfactants were taken from [16–18]. The unlike interactions were calculated using the Lorentz–Berthelot mixture rules.

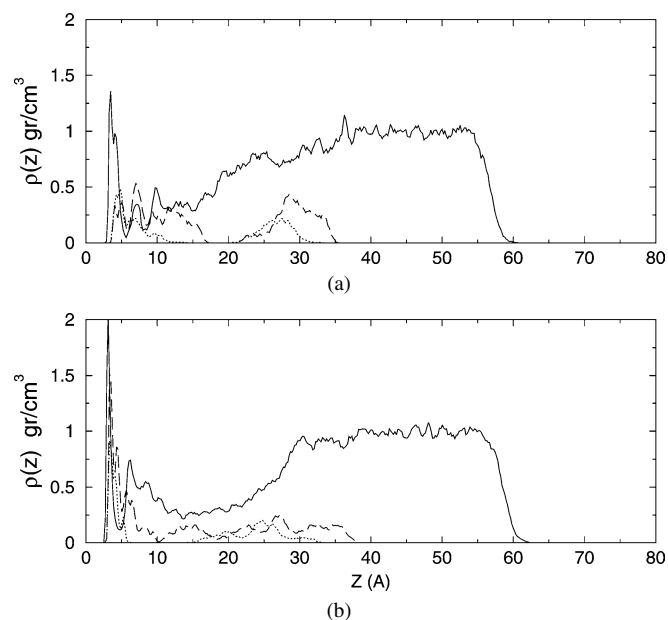


Fig. 2. Density profiles of the $X1Y6$ monolayer at the TiO_2 wall: (a) structured wall and (b) structureless wall. Water is depicted by the solid line, the polar headgroup by the dashed line and the tail group by the dotted line.

tured rutile(110) wall was constructed using the modules of the Materials Studio modeling software package of Accelrys [19], with dimension $30 \times 30 \times 9 \text{ \AA}^3$, and containing 294 molecules of TiO_2 .

The structure of the monolayer was analyzed in terms of the density profiles calculated from the position of each atom of the surfactant molecule. In the case of water molecules the density profile was calculated from the position of the oxygens only. In Fig. 2a the z -dependent density profiles for water, headgroups and tails of the surfactant molecules are plotted separately.

One salient feature is the low water density region observed in a region of the density profile (Fig. 2a). It seems that the water bin splits in two parts, one adsorbed at the wall and the other remained in a bulk phase. It is also observed that there are surfactants molecules in each side of the two water regions. Next to the bulk water region there are surfactant molecules placed with their polar head groups deep into the bulk phase, whereas the nonpolar part is located in the low-density water region. On the other hand, there are also surfactant molecules close to the wall.

In order to determine if the explicit structure of the wall is necessary to study the form of the monolayer near the wall/liquid interface, a second model was analyzed. The model consisted of the construction of an effective interaction given by the wall on the water/surfactant system. Then, the total interactions are due to short- and long-range interactions in the simulations. If we consider the wall as a continuum of molecules of uniform number density in a parallel layer structure with Lennard Jones forces between the wall and the surfactant/water atoms, then one can use the well-known Steele potential [20] for the short-range interactions.

$$\phi(z) = 2\rho\pi\sigma^2\epsilon\Delta l \times \left[\frac{2}{5} \left(\frac{\sigma}{z} \right)^{10} - \left(\frac{\sigma}{z} \right)^4 - \frac{\sigma^4}{3\Delta l(z + 0.61\Delta l)^3} \right], \quad (1)$$

where ρ is the density of the solid and Δl is the separation between the planes which form the solid wall. For the TiO_2 surface $\rho = 4 \text{ g/cm}^3$ and $\Delta l = 3.8 \text{ \AA}$. The parameters which define the strength of the wall interaction with the molecules of the system are ϵ and σ . In this model we used a set of ϵ and σ parameters for the complete TiO_2 molecule which were calculated by fitting a curve to the superposition of all the potentials produced by each site in the molecule (see Table 1).

The electrostatic interactions were calculated using a continuous potential obtained from the Coulombic forces between the wall and the water–surfactant atoms. For a planar surface of TiO_2 molecules with uniform density (oxygens pointing to the surfactant/water interface) the interaction of a small charge element dq of the wall with a charged particle is given by

$$d\vec{F} = \frac{1}{4\pi\epsilon_0} \left(\frac{dq_{\text{ox}}q'_i}{r_1^2} \hat{r}_1 + \frac{dq_{\text{ox}}q'_i}{r_2^2} \hat{r}_2 + \frac{dq_{\text{Ti}}q'_i}{r^2} \hat{r} \right), \quad (2)$$

where q_{ox} and q_{Ti} are charges of the oxygen and titanium in the TiO_2 molecule, respectively, and q'_i is the charge of any particle of the water/surfactant system.

Using $\vec{r}_1 = \vec{r} - \vec{a}$, $\vec{r}_2 = \vec{r} - \vec{l}$ (\vec{a} and \vec{l} are the bond vectors from the Ti to each O in the molecule with $\|\vec{a}\| = \|\vec{l}\|$, absolute values) and considering that $r \gg (a, l)$ we obtained for a symmetric wall in the x – y plane

$$dF_z = \frac{q_i}{4\pi\epsilon_0} \left[\frac{2a_z}{r^3} + \frac{6za_z^2}{r^5} - \frac{6z^2a_z}{r^5} \right] dq_{\text{ox}}. \quad (3)$$

Then by integration in cylindrical coordinates we get an effective force acting only perpendicular to the wall,

$$F_z = \frac{q'_i}{\epsilon_0} \frac{\rho_{\text{ox}}a_z^2}{z}, \quad (4)$$

where ρ_{ox} (0.042 e/\AA^3) is the charge density of oxygens in the wall and a_z (1.27 \AA) is z -component of the \vec{a} vector.

The density profiles of the X1Y6 monolayer with the continuous wall are shown in Fig. 2b. As in Fig. 2a, for clarity of the pictures the polar and the nonpolar part of the surfactant molecule were plotted separately. The same behavior is depicted on the profiles obtained with the corrugated wall. Basically, water splits again in two regions with some water and surfactant molecules adsorbed at the surface whereas few surfactant molecules remained in the bulk water phase. However, in this case water presents a larger low-density region (around 15–20 \AA) than that of the previous simulation with a structured wall. The surfactant molecules also spread more in this region and there are more few molecules close to wall. The peaks of the profiles next to the wall are also higher compared with those in a structured wall. In spite of these seeming differences, it should be noted that the profiles of water and the surfactant groups show the same tendencies (they look alike) regardless of the model used to simulate the wall.

Finally, a second set of simulations with the same surfactant/water system were carried out but using in this case a SiO_2 wall. The corrugated wall was modeled from an amorphous distribution of 200 molecules and the z -density profiles for this system are shown in Fig. 3a.

The SiO_2 wall is amorphous and the atoms can approach more to the surface than if it were planar. However, the adsorption of molecules is less than in TiO_2 surface due to a weaker short ranged interactions. It is not shown but if the molecules of the fluid were initially located at a distance more than 10 \AA apart from the wall there would not had adsorption of molecules on the surface even if the system evolves for more than 2 ns. We recalled that the results shown in Fig. 3a are for molecules initially located at 5 \AA from the wall. It is seen that once the wall is

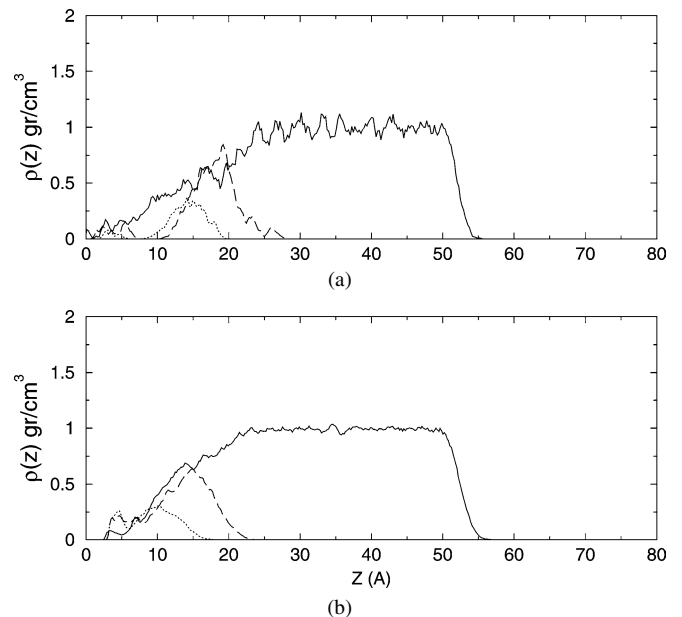


Fig. 3. Density profiles of the X1Y6 monolayer at the SiO_2 wall: (a) structured wall and (b) structureless wall. The same notation as in Fig. 2.

saturated the polar and nonpolar groups leave the surface, this trend was also observed in the TiO₂ (see Fig. 2a).

The continuous wall was also constructed using the same idea used for the TiO₂ wall (the TiO₂ and the SiO₂ molecules have similar geometry, although our structured silica wall is amorphous). The parameters used for the SiO₂ surface are $\rho = 1.45 \text{ g/cm}^3$, $\Delta l = 3.8 \text{ \AA}$, $\rho_{\text{ox}} = 0.029 \text{ e/\AA}^3$ and $a_z = 0.8997 \text{ \AA}$. The density profiles of the different molecules are shown in Fig. 3b. The results obtained for this planar wall are quite similar to those of the amorphous silica. It is seen a slightly more structured fluid close to the wall because the surface is flat. Moreover the profiles in these both simulations show a clear contrast with the profiles obtained with the TiO₂ wall and they are more alike each other.

It is worth to mention that in both systems (TiO₂ and SiO₂) the structure of the monolayer is the result of a balance between the wall–headgroup, the wall–water and headgroup–water interactions. Whereas the LJ forces indicate that the TiO₂ wall is much more strongly attractive than the SiO₂ (although the diameters of the TiO₂ and SiO₂ are similar the TiO₂ “ ϵ ’s” are much higher than those of the SiO₂) the electrostatic forces help the wall to be more or less attractive. A simple analysis of the forces (not shown here) shows that in some cases some of the interactions (e.g., electrostatic) help wetting and in other cases produce less attractive forces which compete with the other forces to obtain the final configuration of the water–surfactant system.

3. Conclusions

We performed molecular dynamics simulations of a surfactant/water system close to a solid surface. Even though the surface was constructed with two different models (corrugated and continuous wall) the results show the same trend with respect to the structure and location of the surfactant and water molecules given by the density profiles. It seems that at this level of information the structure of the wall does not play an important role in the formation of the monolayer at the surface. Therefore, the results suggest that a continuous wall model can give us good insights into the absorption and array of molecules next to surfaces. This treatment is convenient and cheaper particularly when simulations are performed to study these computationally expensive systems. The final configuration of the monolayer is

a subtle competition of the LJ and electrostatic forces which determine the wetting at the interface. However, it was found that the adsorption of water molecules on TiO₂ wall is higher than in the SiO₂. This is in agreement with experiments where TiO₂ is hydrophilic whereas the SiO₂ wall is hydrophobic.

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