

Footprint organization of chiral molecules on metallic surfaces

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Abstract

We study the behavior of chiral molecules adsorbed on clean metallic surfaces using a lattice-gas model and Monte Carlo simulation. The aim is to model and simulate the structure (footprints and organization) formed by molecules on the surface as they adsorb. The model, which is applicable to chiral species like *S*- and *R*-alanine, or similar, discloses the conditions to generate different ordered phases that have been observed in experiments by other authors.

In our model, each enantiomer may adsorb in two different configurations (species) and several effects are taken into account: inhibition, blockage of neighboring adsorptive sites (steric effects) and promotion of sites representing, in some sense, modifications in the surface properties due to molecule-surface interactions. These adsorption rules are inspired by the enantiomeric character of adsorbed species. We perform a systematic study of the different phases formed in order to qualitatively understand the mechanism for the formation of adsorbate structures experimentally found by other authors.

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1. Introduction

Chiral organic molecular arrangements of species adsorbed onto metallic surfaces have captured the attention of researchers over the last decade because of their important applications mainly in the pharmaceutical and technological fields [1–3]. This interest is assisted and encouraged by the great improvement in experimental microscopic and spectroscopic techniques, combined with advances in simulation and *ab initio* techniques, which can be used to determine the supramolecular adsorption structures in the above systems.

Under appropriate conditions, the adsorption of an enantiomerically pure chiral species may lead to the formation of patterns that are chiral themselves, thus generating an “extended chirality” [2]. The scale of these chiral patterns ranges from nano-structures of few molecules to macroscopic dimensions [1,4]. It is known that the nature of these bi-dimensional patterns

depends on the balance among adsorbate–substrate (*A–S*) and adsorbate–adsorbate (*A–A*) interactions [5,6]. However, some general characteristics seem to emerge for many of these structures [4]: (a) chiral molecules adsorb in different configurations (or “adsorbed species”), like, for example, flat, tilted, dimmer-like or monomer-like, depending on the coverage; (b) the structure changes with the surface coverage and may preserve or not the extended chirality feature; (c) interactions leading to extended chirality must be strongly non-isotropic.

A system which has been intensively studied from the experimental point of view is that of *R*- and *S*-alanine on Cu(1 1 0) [7,8], where local and supramolecular adsorption structures created by the enantiomeric forms of alanine molecules have been determined and different hypotheses have been advanced in order to explain the observed polymorphism. The organization and chirality of the observed structures are discussed on the basis of the two aspects of the problem: inherent molecular chirality and footprint chirality of the alaninate.

Inspired by the results obtained for that system, we study here under what conditions the molecule-surface geometric and energetic characteristics could give rise to a bi-dimensional

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organization of adsorbed chiral species, with properties that change with coverage. In this sense, we propose a simple model to simulate the adsorption of simple enantiomerically pure chiral molecules and to characterize the different patterns developed when molecular chirality is transferred to the metallic surface of the substrate through the molecular footprint. This model can be also easily applied to the adsorption of racemic mixtures, as it will be shown below.

2. Simulation model

We use a lattice-gas model and a Monte Carlo technique to simulate the adsorption of simple chiral molecules, like the *S*- and *R*-alanine, on a metallic surface, like Cu(1 1 0). Each enantiomer has a biased orientation (left or right handed, *S* and *R* enantiomers) and may adsorb as two different species named α_3 and α_2 and their corresponding rotated versions around a given preferential direction on the surface, as suggested in Ref. [7,8]. To mimic the (unknown) *A*–*S* and *A*–*A* interactions, we use a promotion mechanism during the adsorption of new molecules from the gas phase. In addition, the steric effect of exclusion due to the chiral structure of the molecule is taken into account by the inhibition of particular nearest neighbor sites for the adsorption of molecules in the neighborhood of an already adsorbed one.

2.1. Lattice-gas model

The substrate is simulated through an “effective” square lattice of sites. An adsorbed chiral molecule is represented by an array of chemical groups occupying a central site (chiral center *C*) and neighboring sites (*N*). Irreversible adsorption is considered and diffusive effects are not taken into account.

2.2. Interactions

When a molecule is adsorbed on the surface two interactions can occur: inhibitions due to steric effects and promotion of neighboring sites. This last effect simulates *A*–*S* interactions that change the energy topography of the surface, favoring the adsorption of new molecules. The new molecules can only adsorb on promoted sites and this requires that seeds or defects have to be set initially. We have also tried the case of no promotion of sites.

2.3. Species of adsorbed chiral molecules

For a given enantiomer (*R* or *S*) two possibilities are considered, named α_3 and α_2 , as shown in Fig. 1(a) and (c). The chiral center is indicated with an arrow. The molecule can be thought of as adsorbed on a four (three) sites structure on the surface: its center (*C*) and three (two) neighboring sites (*N*) for α_3 (α_2), defining the “footprint” of the molecule. The site of the metallic surface taken as the center is completely occupied by the molecule and cannot be shared with any other. The other three (two) *N*-sites of the surface can be shared by another molecule only as *N* sites. In the case where no enough empty space is

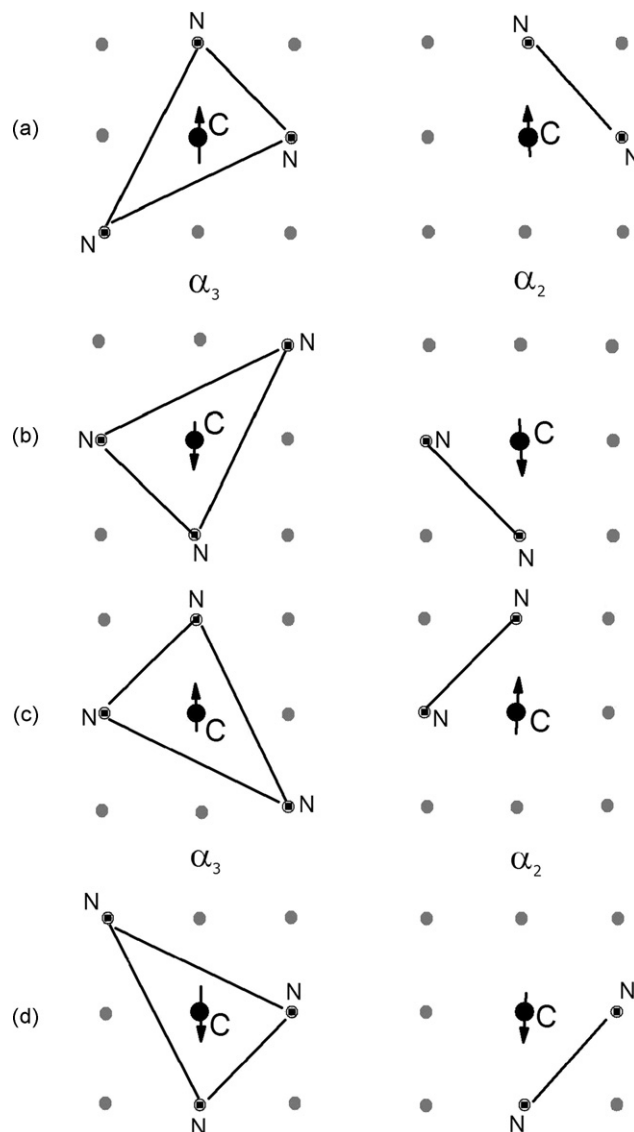


Fig. 1. Schematic representation of the footprints of adsorbed molecules on the square lattice indicating different kind of sites: *C*, chiral center site; *N*, neighboring sites; gray solid circles represent promoted sites. (a) Corresponds to non-rotated species of *S*-molecules. (b) Corresponds to rotated species of *S*-molecules. (c) Corresponds to non-rotated species of *R*-molecules. (d) Corresponds to rotated species of *R*-molecules.

available on the surface, the molecule is allowed to adsorb with a different footprint, the one indicated on the right of Fig. 1(a) and (c). The way this occurs will be explained below.

2.4. Molecular rotations

We define two possible rotations for α_3 footprint: “simple” rotations (SR), as shown in Fig. 1(b) and (d) on the left, and “complex” rotations (CR), as shown in Fig. 1(b) and (d) on the right.

2.5. Adsorption mechanisms

Two different kinds of mechanisms were used for both enantiomers. A sequential process, in which, once a site on

the surface has been randomly selected, we always try to adsorb a α_3 footprint. If this is not possible, we try to adsorb it with another footprint, trying again until a particular sequence is completed. The other mechanism is a random process, in which we choose randomly, with the same probability, among the up (\uparrow) or down (\downarrow) α_3 species. If this is not possible, we try to adsorb α_2 (\uparrow or \downarrow) species. In both mechanisms, once a molecule is adsorbed, sites C and N are labeled.

If promotion of sites is implemented in the model, the rest of the empty neighboring sites are set as promoted (gray sites on Fig. 1) and the center of new molecules from the gas phase can only adsorb on these sites. Otherwise, the center of new molecules can adsorb anywhere on empty sites. The order of the species in the sequences above and the promotion of sites represent qualitatively the different relative intensity of the A–S and A–A interactions for each species.

3. Results and discussion

Our results indicate that the features and direction of the patterns formed on the surface depend not only on the molecular structure of enantiomers, but also on A–S and A–A interactions. We classify the obtained patterns into two groups, depending on the extent of chiral chain assemblies. In all cases studied a biased chiral orientation on the surface appears, being the same as the one of the chiral structural axis of the molecule.

3.1. Short range order

In this group we observe the development of short double and single chains of molecules, randomly distributed on the substrate. The adsorption mechanism employed here does not involve promotion. Nevertheless, we observe simple and double short chains due to steric effects related to the accommodation of adsorbed molecules, building up a dispersed phase.

Fig. 2(a)–(c) presents snapshots of surfaces belonging to this group for the case of S-molecules. Fig. 2(d) and (f) shows the corresponding behavior of the coverage for each species as a function of the total coverage of the surface up to saturation.

In (a) and (b) the adsorption of molecules was randomly performed, while in (c) it was sequential. Fig. 2(a) shows the case when no rotations are allowed, favoring the growth of double short ordered chains, $\alpha_3\uparrow\alpha_3\downarrow$, in a disperse phase, with almost no adsorption of α_2 . Practically no simple chains are found. The coverage grows linearly (Fig. 2(d)). Fig. 2(b) depicts the case where CR are present. Short double and simple chains develop. They are heterogeneous and disperse. The variation of coverage is non-linear (Fig. 2(e)). Fig. 2(c) shows a sequential adsorption where CR and SR are performed in the sequence: $\alpha_3\uparrow\alpha_2\downarrow\alpha_3\downarrow\alpha_2\uparrow$. A non-linear behavior with coverage is obtained here again (Fig. 2(f)). This non-linear behavior is directly related to the fact that the volume excluded by α_3 is greater than that for α_2 , i.e., it is easier to adsorb the second than the first one. Besides, the better assembling (both steric and

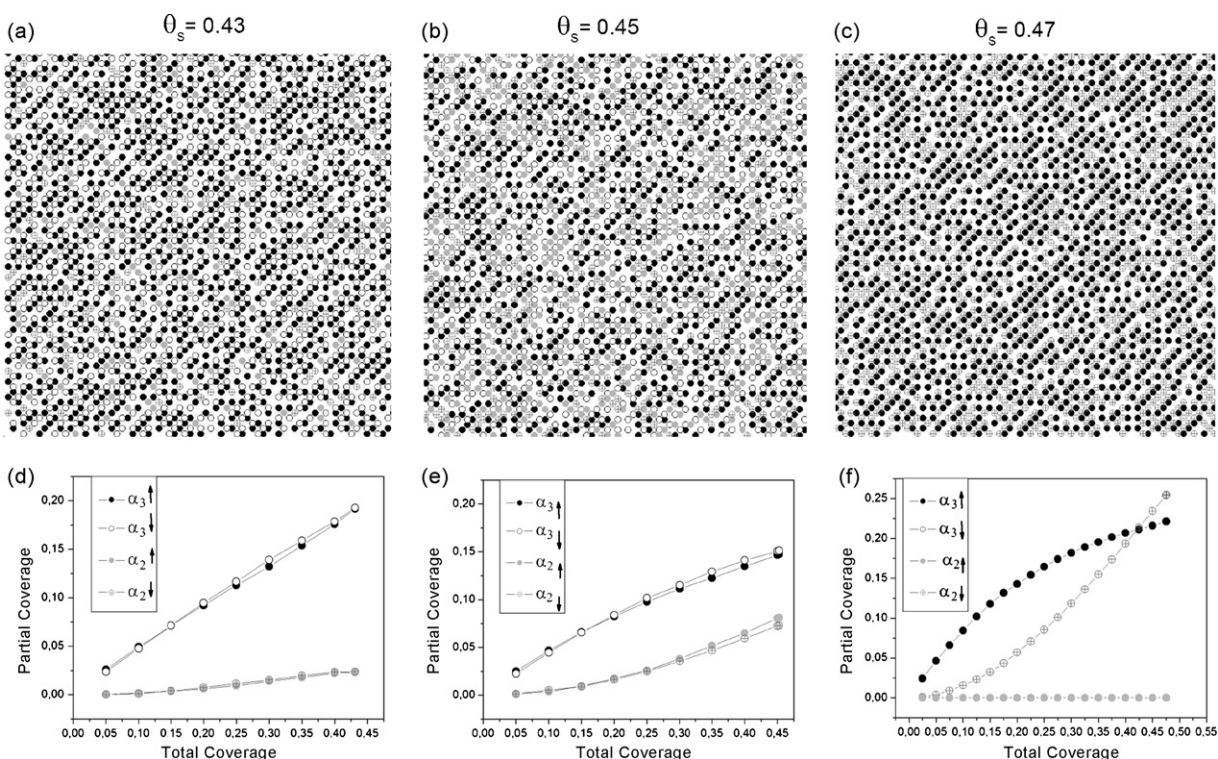


Fig. 2. Snapshots of surfaces belonging to the first group. (a) No rotations are allowed with a random adsorption mechanism without promotion. (b) Rotations are allowed with a random adsorption mechanism without promotion. (c) Rotations are allowed with a sequential adsorption mechanism ($\alpha_3\uparrow\alpha_2\downarrow\alpha_3\downarrow\alpha_2\uparrow$) without promotion. The symbols here are the same as those indicated in parts (d)–(f). These last parts show the coverage for each species against the total coverage of the surface until saturation for parts (a)–(c), respectively.

energetically) is the one joining $\alpha_3\uparrow\alpha_3\downarrow$ or $\alpha_3\uparrow\alpha_2\downarrow$ (conversely, $\alpha_3\downarrow\alpha_3\uparrow$ or $\alpha_3\downarrow\alpha_2\uparrow$). When rotations are allowed, pairs $\alpha_3\uparrow\alpha_3\downarrow$ or $\alpha_3\uparrow\alpha_2\downarrow$ are the most favorable. But, as we will see below, if promotion is also present, those pairs form long organized chains that efficiently fill the surface without steric effects. The absence of strong $A-S$ interactions (non-promoting mechanism) causes random adsorption to be less efficient and steric effects show up.

In Fig. 2(a), there is no promotion, but rotations are excluded in the random adsorption, and the net effect is a random distribution of $\alpha_3\uparrow$ and $\alpha_3\downarrow$. Steric effects, $\alpha_3-\alpha_2$, do not have the opportunity to develop before saturation is achieved. The main difference between Fig. 2(b) and (c) is that adsorption is random in the first, giving the same likelihood to $\alpha_3\uparrow$ and $\alpha_3\downarrow$, thus both species $\alpha_2\uparrow$ and $\alpha_2\downarrow$ can compete for occupation of the non-inhibited surface sites. The mechanism employed in Fig. 2(c) is sequential, favoring first the adsorption of $\alpha_3\uparrow$ and then of $\alpha_2\downarrow$; the other species being in the last steps of the sequence and, thus, their likelihood of being adsorbed is almost null.

3.2. Long range order

We find the development of long double and single chains of molecules with different topological features. There are

condensed phases related to the promotion of neighboring sites (N) when a molecule adsorbs, favoring the adsorption of new ones. We start the simulation using an initial coverage of random adsorbed molecules with footprint α_3 , representing defects on the substrate. The richness of the patterns is due to the different adsorption mechanisms employed and to the fact that molecules can rotate before adsorption (SR or CR).

Figs. 3 and 4 show examples belonging to this group for the case of S -molecules. They were generated with an adsorption mechanism with promotion, i.e., molecules can only adsorb on promoted sites and, each time a new molecule is added to the surface, its neighboring sites (gray sites) are promoted for new molecules. This strong $A-S$ interaction causes the formation of clusters of different sizes with chains along the chiral preferential direction.

We present examples for a random mechanism (Fig. 3) and for a sequential one (Fig. 4). In the latter we distinguish different sequences in the order of adsorption footprints. In Fig. 3(a) we show the results of simulations for a random adsorption without rotations, like in Fig. 2(a), but here with promotion of sites. We observe ordered double $\alpha_3\uparrow\alpha_3\downarrow$ chains with medium size clustered in medium domains. Dispersed α_2 simple chains are also developed. Comparing Fig. 2(a) and Fig. 3(a), we find that the promotion causes more adsorption of α_2 species, see Fig. 3(c). The mechanism of promotion,

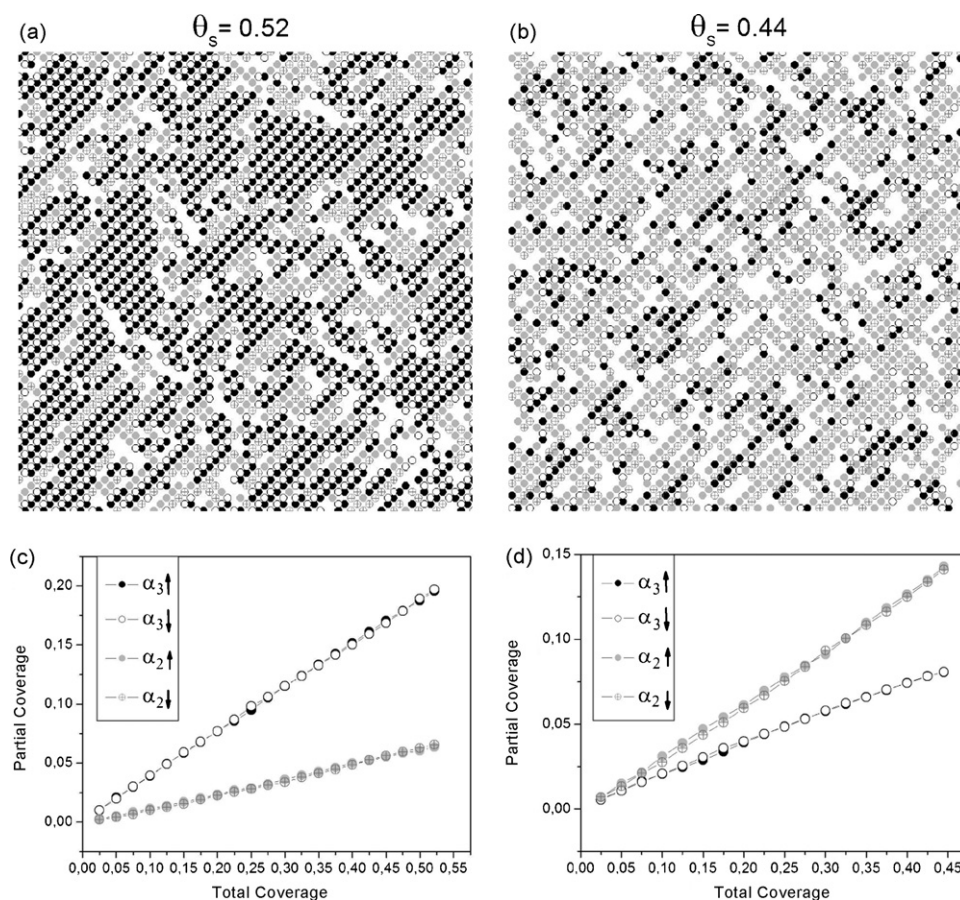


Fig. 3. Snapshots of surfaces belonging to the second group with their respective coverage for each species against the total coverage of the surface until saturation. (a) No rotations are allowed with a random adsorption mechanism with promotion. (b) Rotations are allowed with a random adsorption mechanism with promotion. Symbols are the same like as before.

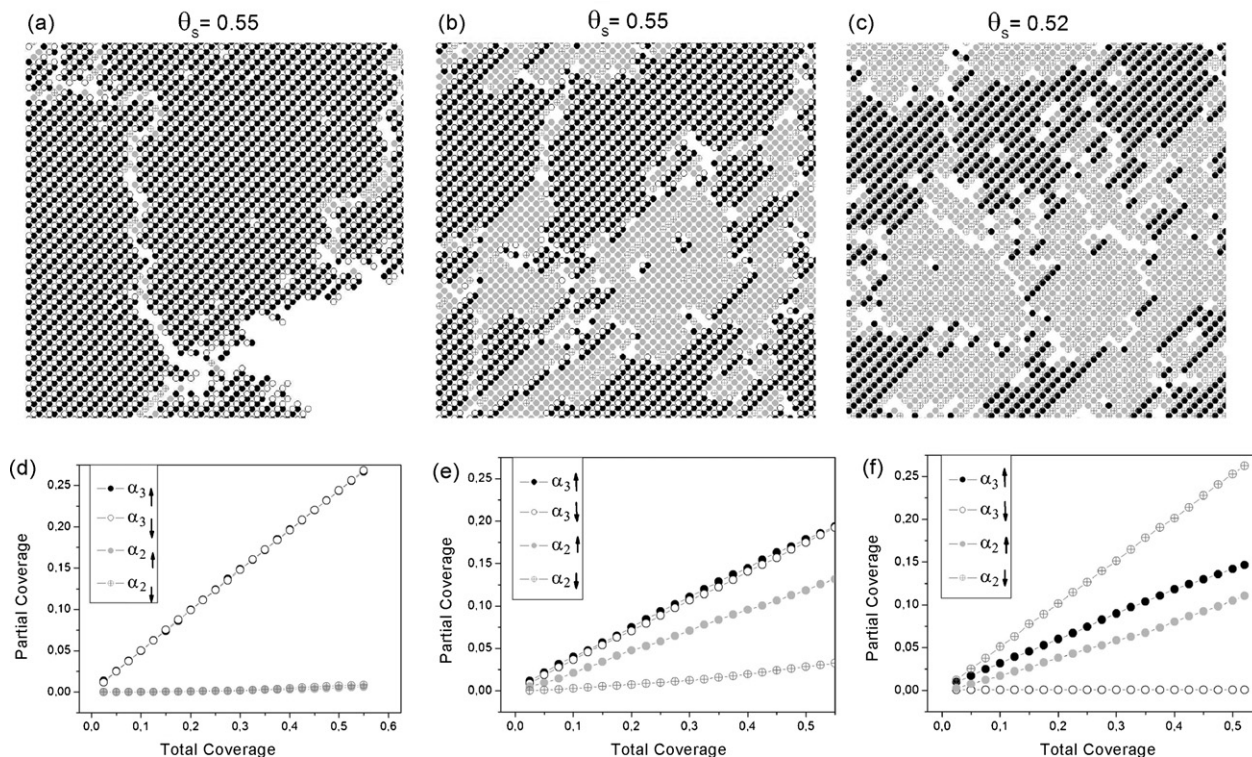


Fig. 4. Snapshots of surfaces belonging to the second group and using sequential adsorption with promotion with their respective coverage for each species against the total coverage of the surface until saturation. (a) Sequence: $\alpha_3 \uparrow \alpha_3 \downarrow \alpha_2 \uparrow \alpha_2 \downarrow$. (b) Sequence: $\alpha_3 \uparrow \alpha_2 \uparrow \alpha_3 \downarrow \alpha_2 \downarrow$. (c) Sequence: $\alpha_3 \uparrow \alpha_2 \downarrow \alpha_3 \downarrow \alpha_2 \uparrow$. Symbols are the same like as before.

which orders the double chains, also favors the formation and growth of simple chains of α_2 at the interface of the α_3 clusters. This results in a more efficiently filled surface, and a higher θ_s .

In Fig. 3(b) we show a surface for random adsorption with rotations, like in Fig. 2(b), but here with promotion of sites. We can see two main features. First, α_2 adsorption is favored in respect to the former case of Fig. 3(a), and second, simple alternated $\alpha_2 \uparrow \alpha_2 \downarrow$ chains show up forming more irregular shaped clusters. Due to the fact that the molecule can have CR, it occupies sites that do not favor the later adsorption of α_3 species, thus no pairs $\alpha_3 \uparrow \alpha_3 \downarrow$ are formed. This fact makes the topography of Fig. 3(b) less efficiently filled compared to the case of Fig. 3(a) (see the values for θ_s indicated). Comparing Figs. 2(b) and 3(b), we also find a greater adsorption of α_2 due to promotion effects (see Fig. 3(d)).

Fig. 4(a) corresponds to the following sequence: $\alpha_3 \uparrow \alpha_3 \downarrow \alpha_2 \uparrow \alpha_2 \downarrow$. As observed, the strong trend of species $\alpha_3 \uparrow \alpha_3 \downarrow$ to form a compact pair (steric effect) that occupies most efficiently the surface, gives place to the growth of large chains condensed in big clusters.

In Fig. 4(b) we present the case $\alpha_3 \uparrow \alpha_2 \uparrow \alpha_3 \downarrow \alpha_2 \downarrow$. It is evident that when the adsorption of $\alpha_3 \uparrow$ is not possible, the adsorption of $\alpha_2 \uparrow$, as a second chance, has a low likelihood, then the adsorption of $\alpha_3 \downarrow$ species occurs. When adsorption of $\alpha_2 \uparrow$ takes place, a single chain of this species begins to grow. As a final result we have two well-defined domains: single chains of $\alpha_2 \uparrow$

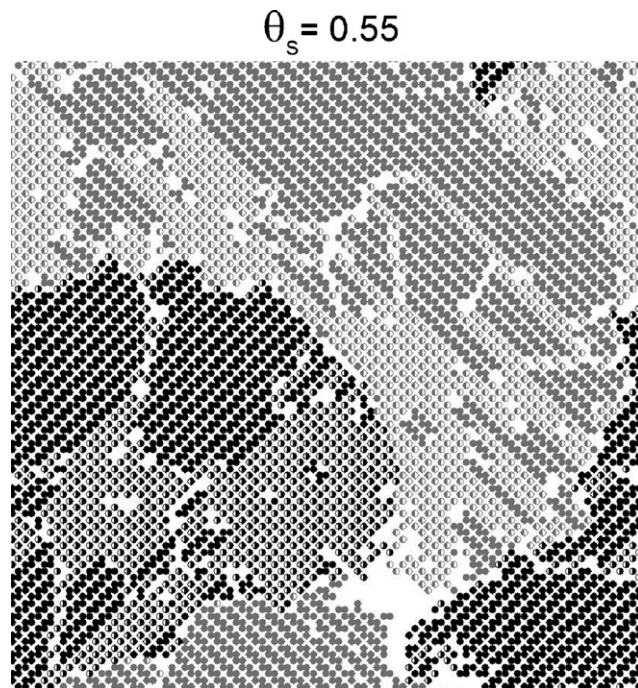


Fig. 5. Snapshot of a surface obtained for a racemic adlayer, i.e., R and S enantiomers are adsorbed with the same probability. Here we use a sequential adsorption process like the one in Fig. 4(b). Symbols represent: solid black circle ($S\text{-}\alpha_3 \uparrow, S\text{-}\alpha_3 \downarrow$); semi-solid black circle ($S\text{-}\alpha_2 \uparrow, S\text{-}\alpha_2 \downarrow$); solid gray circle ($R\text{-}\alpha_3 \uparrow, R\text{-}\alpha_3 \downarrow$); semi-solid gray circle ($R\text{-}\alpha_2 \uparrow, R\text{-}\alpha_2 \downarrow$).

and double chains of $\alpha_3\uparrow\alpha_3\downarrow$. There is almost no possibility that $\alpha_2\downarrow$ species can be adsorbed (Fig. 4(e)).

Finally, in Fig. 4(c), where the sequence $\alpha_3\uparrow\alpha_2\downarrow\alpha_3\downarrow\alpha_2\uparrow$ is used, the formation of pairs $\uparrow\downarrow$ is the more efficient way of filling the surface, and, again in this case, the formation of two well defined domains is present.

In all the above cases the biased direction of the chains on the surface is unique and it is definitely associated with the chiral character of *S*-molecules, independently of any adsorption feature.

The same cases developed above were repeated for pure *R*-molecules adsorption. All the features found reproduced the same results like those for *S*-molecules but here the patterns resulted to be the mirror image of the previous ones, i.e., the only difference noted was the change in the direction of the chains on the surface. This fact proves again the statement expressed above: the chiral character of molecules is directly transferred to the metallic surface. For this reason and for the sake of brevity, we do not show here results for *R* enantiomers. We do show, however, the case of a racemic mixture of *S* and *R* enantiomers (Fig. 5), where clearly different domains of *S* and *R* clusters with their pertinent directions are shown with quite good agreement with experiments [8–10].

4. Conclusions

The different behaviors found here resemble qualitatively some of the features shown and discussed in experiments by many authors, mainly in what regards the chiral organization of the surface and the formation of ordered domains of double and single chains of molecules [2,4,8–12]. In particular, the steric effect observed in the first group resembles the behavior of systems such as alaninate on Cu(1 1 0) [7,8]. Besides, this model can generate many patterns using very simple rules and can be compared with those used in Ref. [13].

In our results, it is evident that the chiral character of the adsorbate is transferred to the substrate. The two main behaviors: long and short range chains assemblies, are related, respectively, to the promotion and non-promotion of sites and the steric effects present in the model.

From the results of the racemic mixture, the development of chiral domains on the surface is clear and explains the patterns obtained experimentally [8–10].

Finally, this simple model provides a basis for the understanding of the behavior of complex adsorption systems in which chiral molecules interact with a metallic surface.

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