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Modelling water adsorption on Au(210) surfaces: II. Monte Carlo simulations

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Abstract

Canonical Monte Carlo simulations for the Au(210)/H_2O interface, using a force field recently proposed by us, are reported. The results exhibit the main features normally observed in simulations of water molecules in contact with different noble metal surfaces. The calculations also assess the influence of the surface topography on the structural aspects of the adsorbed water and on the distribution of the water molecules in the direction normal to the metal surface plane. The adsorption process is preferential at sites in the first layer of the metal. The analysis of the density profiles and dipole moment distributions points to two predominant orientations. Most of the molecules are adsorbed with the molecular plane parallel to surface, while others adsorb with one of the O–H bonds parallel to the surface and the other bond pointing towards the bulk liquid phase. There is also evidence of hydrogen bond formation between the first and second solvent layers at the interface.

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1. Introduction

In the last decades, molecular simulations, namely Monte Carlo (MC) and molecular dynamics (MD), have become a powerful tool in the branch of interfacial electrochemistry. Several works on the subject have contributed with important information about the molecular behaviour at electrochemical interfaces.

Simulations of water in contact with noble metal single-crystal surfaces have probed the distribution of the water molecules in the interfacial region and its dependence on the nature and structure of the surface [1–8]. These studies have systematically demonstrated the preferential adsorption of the molecules on specific sites of the surface, showing that the structure of the adsorbed water layer strongly depends on the surface topography.

Simulations of ions [7,9–13] and of organic molecules [14–17] adsorption on electrode surfaces, have also shown a similar preferential site adsorption behaviour. Additionally, calculations of the potential of mean force (PMF) [13,15,16,18,19] have enabled the identification of the solvent contributions to the ionic and molecular adsorptions at different sites of the surface and, in the case of organic molecules, have led to a better understanding of the molecular reorientations along the adsorption process.

The first step for the realization of this kind of simulations is the construction of consistent force fields to model the water-surface interactions, which account for the influence of the structural properties of the surface on the solvent layers, and on the preferential sites for the

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adsorption. In a previous paper we have proposed an analytical potential function to describe the interaction between water molecules and the Au(210) surface [20], based on DFT calculations. In the present article, we report canonical Monte Carlo simulations of water adsorption on Au(210) surfaces, at potential of zero charge (pzc), using the referred to force field.

The interest in simulating water on Au(210) surfaces is concerned with some experimental features. This surface does not undergo the charge induced reconstruction phenomena, observed in lower index gold single-crystal surfaces [21]. It is therefore, in experimental terms, a stable surface for adsorption studies in the total range of the electrical double layer potential region. As a consequence, the Au(210) surface is a suitable choice, e.g., for the study of dissipative processes accompanying adsorption phenomena [22] and reorientations in the adsorbed solvent layer [23,24], since the reconstruction process itself is also a source of dissipation and may couple with adsorption dissipation, as in the case of halides adsorption onto Au(111) [25].

Once the scope of dissipation associated to phase transitions in the interface is still an open subject, molecular simulations of the Au(210)/water interface regarding the adsorption process can contribute to a better understanding of experimental results obtained by two of us [22–25]. The other motivation of the present paper is just to test the consistency of the results obtained by using the force field for that interface recently proposed by us [20]. Indeed, the test of interaction potentials is one of the goals of computer simulation.

Section 2 contains the methodology and models used in the Monte Carlo simulations. Section 3 discusses the simulation results. Section 4 presents the concluding remarks of the work.

2. Methodology and models

The canonical Monte Carlo simulations were performed on a system composed by 1000 molecules of water encapsulated between two Au(210) surfaces. The simulation box was rectangular in shape, with the dimensions of $22.43 \times 26.40 \times 50.47$ Å in the directions x, y and z, respectively. Standard periodic boundary conditions (PBC) were applied on the x and y directions. The dimensions of the box in the directions x and y were chosen in order to ensure the periodicity of the crystallographic surface under the PBC. The total volume of the box reproduces the density of water at temperature and pressure of 298.25 K and 1 bar, respectively.

Equilibration runs of 5000 Monte Carlo cycles were followed by production runs of 25,000 cycles. One MC cycle is composed of random translations and rotations applied to each water molecule of the sample, with an acceptance rate of ~50%. The computational program used the time saving energy-repository algorithm, recently discussed by Fartaria et al. [26].

The TIP4P [27] model for the interaction between water molecules was used, considering its success in the simulation of some water–metal interfaces [15,18,19,28,29]. It is a rigid model describing the water molecule by four interaction centres, three of them coinciding with the molecule atoms and the fourth related to the electronic density associated to the pair of electrons of the oxygen atom. This last centre is located at 0.15 Å from the oxygen, between the two hydrogen atoms. The calculations of the interactions between the water molecules were conducted with a cut-off radius of 8.0 Å and the usual long-range corrections for the dispersion terms of the potential.

The long-range corrections for the electrostatic component of the water potential were calculated by the Ewald sum method adapted to a two-dimensional periodic system [30,31] in the x and y directions.

The interactions between water molecules and the Au(210) surfaces were worked out using the force field presented in our previous work [20], with a cut-off radius of 25 Å.

3. Results and discussion

The normalised density profiles for the distribution of the water molecule atoms as a function of the distance from the surface, considering the average value over both surfaces of the model, are shown on Fig. 1.

The results clearly show the formation of two well defined water layers on the metallic surface. The first layer corresponds to the region from ~1.2 to ~3.8 Å. In this region, the location of the two most intense peaks, for the O and H atoms, at nearly the same distance of ~2.5 Å, shows that most of the water molecules are, on average, adsorbed with the molecular plane parallel to the electrode surface. The peaks are narrow, indicating that the molecules have well defined positions and orientations. However, the occurrence of the small peak **a**, at ~3.3 Å from the surface, suggests that some molecules have a different orientation with one or the two hydrogen atoms

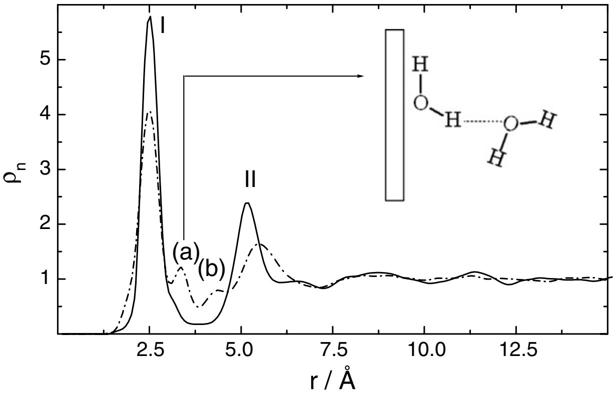

Fig. 1. Normalised density profiles for water molecules at the interface. Oxygen (——) and hydrogen (—-—). The inset shows a conformation consistent with hydrogen bond formation.

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