Structuring of water molecules near a copper surface

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Abstract. Using the molecular dynamics method, the structuring of water molecules near copper surfaces at various temperatures is studied. Samples with crystallographic orientations of 100 and 111 are considered at temperatures from 300 K to 350 K. It is found that the planes of water molecules in the near-surface region with the size is about six angstroms are oriented mainly parallel to the copper surface. However, the character of the structuring of water molecules near the copper surface weakly depends on the considered crystallographic orientations and temperatures.

1. Introduction

Currently, the processes occurring at micro- and nanoscale in the near-surface regions attract significant attention. This is largely due to the miniaturization of catalysts [1], heat exchangers, etc. Structuring of water molecules in the near-surface regions can affect the heat transfer and kinetics of the processes occurring there. Structuring of water, for example, using the molecular dynamics method, has been studied for a long time [2]. Subsequently, similar studies were carried out in nanochannels, for example, in [3] it was shown that the orientation of water dipoles along the surface changes the mobility of water molecules near the surface, which in some cases can be considered as local cooling of the system. Similar structuring is also observed in porous media, moreover, on the same scales as near solid surfaces. The characteristic examples of such structuring include the structuring of water molecules near the surface of silicon [4], talc [5], various metals [6], including precious ones [7] and others. Unfortunately, the temperature dependence of water structuring near the surface has not been well studied up to date despite the established presence and significance of such a dependence in free volume [2]. In addition, despite the availability of information on the dependence of catalytic processes on the crystallographic orientation of copper atoms [1], the role of water structuring in this has not yet been studied. In this work, the structuring of water near the surface of a copper plate is studied. Copper material is chosen because of its wide use both in many catalysts [1], and as a substrate for applying various materials, including MEMS devices.

2. System and methods

The system was studied by the molecular dynamics method using the CHARMM (Chemistry at Harvard Macromolecular Mechanics) software package [8] and charmm36m force fields [9]. The width and length of the copper plate was forty angstroms, and the thickness of the plate was approximately ten angstroms. During the simulation, the crystallographic properties (Miller indices) of the copper samples were changed. Samples with Miller indices 100 and 111 were considered, as shown in Figure 1.
Figure 1. An example of the copper samples used in the simulation: (a) the Miller index 100, (b) the Miller index 111. The thickness of the substrates is approximately ten angstroms.

The water medium was considered explicitly. One of the most reliable models was chosen as a water model, namely the three-point model TIP3, which is schematically presented in Figure 2. A similar model also allows you to track the formation of hydrogen bonds. A possible hydrogen bond is defined by the following criteria: given an atom D with a hydrogen H bonded to it and an atom A with no hydrogen bonded to it, a hydrogen bond exists between A and H if the distance |D-A| < 4 angstroms and the angle D-H-A < 30 degrees.

Figure 2. Schematic representation of the TIP3 water model and the hydrogen bond formed. The hydrogen bond is depicted as vertical dashed lines.

At the initial moment, the plate was flooded by water molecules on both sides, as shown in Figure 3. The thickness of the flooding layer was twenty angstroms on each side of the plate. The distance was counted from the centers of copper atoms of the surface layer.
Figure 3. Illustration of the initial state of the system under study, namely a copper sample in water. The copper sample has a crystallographic orientation of 100.

The system was simulated in the approximation of an isothermal – isobaric ensemble. In the directions along the plate plane, periodic boundary conditions were realized. In the simulation, the temperature of the system varied in the range from 300 K to 350 K.

When studying the structuring of water molecules near a copper surface, the following were calculated: water density profiles, sum concentration profiles of oxygen and hydrogen atoms, and also possible hydrogen bonds were determined.

3. Results and discussion

Let us consider the distribution of water near a copper surface. Figure 4 shows the dependences of water density on the distance to the copper surface at various temperatures and Miller's crystallographic indices. Significant differences in the density of water in the surface layers from the that in the free volume are observed only at distances of up to six to seven angstroms from the surface of copper. These differences are due to intense interactions between water and copper molecules. Moreover, these differences are resistant to changes in temperature and crystallographic Miller indices. This fact is illustrated by the extremely weak dependence of the positions and values of the maxima and minima of the density in the near-surface layers, which is illustrated in Figure 4.
Figure 4. Dependence of water density on the distance to the copper surface for various temperatures and Miller's crystallographic indices. The distance is calculated from centers of the copper atoms of the surface layer. The density is normalized to the average density of water in the free volume.

To analyze the orientation of water molecules in the surface layers, we compare water density profiles, total concentration profiles of oxygen and hydrogen atoms. The density profiles of water, due to the difference in masses of oxygen atoms and hydrogen atoms, mainly depend on the position of the oxygen atoms. On the other hand, the profile of the sum concentration of oxygen and hydrogen atoms is, greatly, determined by the position of the hydrogen atoms. Figure 5 shows the corresponding profiles. The correspondence of positions and characters of the first maximum in density and concentration can be associated with the distribution of the planes of molecules mainly in the plane parallel to that of the copper surface. Visual analysis of the investigated system also confirms this statement. The discrepancy in the positions of further extremums of profiles is associated with the violation of such orientations.

Figure 5. Dependences of the density of water and the total concentration of oxygen and hydrogen atoms on the distance to the surface of copper. Density and concentration are normalized to the corresponding values in free volume.
Let us consider in more detail the distribution of molecules in the first near-surface layer, i.e. at a distance not exceeding four angstroms from the surface of the copper plate. Figure 6 shows the corresponding illustrations for various crystallographic orientations. The orientation of the planes of molecules mainly in the plane parallel to that of the copper surface leads to an increase in the number of arising hydrogen bonds in comparison with the free volume. This fact is associated with a purely geometric effect. Hydrogen bonds are determined according to the criteria given in the previous section. In Figure 6 they are shown as dashed lines.

![Figure 6](image)

**Figure 6.** The illustration of the structuring of the nearest water layer near a copper surface (a) Miller index 100, (b) Miller index 111. Dashed lines indicate hydrogen bonds. The temperature is equal to 300 K.

The intense formation of hydrogen bonds leads to the local occurrence of short-lived correlated states of water molecules in the layer under consideration. Moreover, many of the resulting hydrogen bonds are oriented along the crystallographic directions of the copper samples, which leads to the dependence of the arising states on the properties of the copper samples. It is also worth noting that with increasing temperature, the probability of formation and lifetime of hydrogen bonds decreases, which also applies to the near-surface layer. Thus, it has been found that in the first near-surface layer there are local correlations in the distribution of water molecules, depending both on temperature and on the crystallographic properties of copper.

**Conclusions**

Summarizing the results, we can conclude that the distribution of the density of water near the copper surface is stable and weakly depends on the temperature and type of crystallographic properties of copper. At least, this conclusion is valid for the considered temperatures and crystallographic orientations of copper samples. In addition, the density distribution is also time independent. The manifestation of correlations between the directions of formation of hydrogen bonds and the crystallographic directions of copper samples can lead to the occurrence of local voltage drops. Such voltage drops, associated with the specific distribution of molecules in the near-surface layers, can affect current flows in thin plates. The distribution of hydrogen bonds and related correlations, in contrast to the density, depends on the temperature and crystallographic orientations of copper. However, the determination of the role of these correlations and their quantitative contribution to the distribution of electric fields in the surface layers of copper requires further detailed investigation.

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