

Simulations of liquid water in contact with a Cu(100) surface

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Abstract

An analytical potential for the description of the Cu(100)–H₂O interaction derived from quantum calculations is proposed. As a test of its quality, a simulation of liquid water between two parallel copper electrodes was performed using Monte Carlo method. Several properties as obtained with this new potential, such as the oxygen and hydrogen density profiles, charge distribution profile, and the surface potential of water in contact with the hydrophobic metal surface, are presented. The perturbation caused in the structure of liquid water by the formation of the water–copper interface was found to be of a relatively short range. The relatively minor importance of the water–metal specific interaction and the decisive role of hydrogen bonding on the structure of water near the electrode are confirmed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Water adsorption; Metal surface; Simulation

1. Introduction

The properties of water in contact with metal surfaces were widely investigated in the past using simulation methods [1–13]. As in most theoretical studies of the interfacial phenomena, the initially used crudely approximated descriptions of the interactions in the interfacial region are being replaced by more realistic models. These potentials, based in most cases on cluster model calculations, take into account specific characteristics of the interactions of this type, like their dependence on the corrugation of the surface, on the adsorption site, and, for molecules, also on their orientation relative to the surface. A major reason for the application of such a model for the water–metal potential in simulations is to gain insight at the microscopic level into the region

where many important electrochemical processes occur.

Most work in this area was done for the platinum (100) surface [4–9], but other metals and surface orientations were also considered [7,10–13]. To our knowledge not much work is done for copper surfaces. In the MC simulations of Parsonage et al. [1,2] the copper–water interaction was approximated by Lennard-Jones and electrostatic image forces. In more recent Md studies of Siepmann et al. [7] an empirical model was developed that is a compromise between the image charge formalism and the microscopic site-specific interaction. These authors performed comparative studies of water adsorption of several metals, among them the Cu(110) surface.

Very recently, the present authors reported on B3LYP calculations for the Cu₁₂–H₂O system, testing 10 different orientations of water molecule towards the Cu(100) surface [14]. The same DFT method used for these calculations was also tested for adsorption of other species on copper clusters [15,16]. For the adsorption of single water on a copper surface, the picture arising from this study is different from that

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Table 1

The parameters used in the V_{W-M} potential for the interaction of water molecule with copper

Parameter	Value	Units
C_1	1965.230320	a.u.
C_2	3.695870	-1
C_3	-1819.638230	a.u.
C_4	3.647810	-1
C_5	2.979500	-2
C_6	16.978450	a.u.
C_7	3.275780	-1
C_8	53.803870	a.u.
C_9	1.810800	-1
C_{10}	-52.525770	a.u.
C_{11}	1.801320	-1
β	2.0	-1
λ	4.0	

most commonly quoted. In our calculations the bridge site was found to be slightly preferred with respect to the top position, the adsorption on both sites having a competitive character. In the present work a water–copper interaction potential is proposed for the description of the potential energy surface found from those DFT calculations. The new potential appears to describe well the most preferred conformations and, in a qualitative way, also other less favoured orientations. It is then used in Monte Carlo (MC) simulations of the water lamina between two parallel Cu(100) neutral surfaces. The properties of the interfacial region obtained with this new potential were studied and results are presented and compared with those reported from simulations for other metals as well as with experimental investigations.

2. A new analytical potential

A new water–copper interaction potential was constructed using results of B3LYP calculations [14], where different orientations and several distances of the water monomer with respect to the Cu(100) surface represented by a Cu_{12} cluster (two layers each consisting of 6 atoms) were studied. It should be noticed (see Fig. 6 in Ref. [14]) that in this twelve-atom structure the bridge site is closer to an edge of the cluster than are the top and hollow sites. Nevertheless, this model allows for the continuous study of the three main adsorption sites on the (100)

surface and avoids the need of changing of the size and shape of the cluster used in calculations. The use of a single cluster is especially important for the comparative studies of the adsorption of molecules and ions on several positions of the metal surface. It has been shown [34] that by using different clusters one introduces an additional source of error in the energy values that may change the relative preference of the sites for adsorption. In the paper just referred to, the authors had to apply a special correction to the adsorption energies to obtain the right relative values.

The strategy for the construction of the water–metal potential used in the present work is similar to that proposed by Spohr [5], where the $H_2O-Pt(100)$ analytical potential was derived from semiempirical cluster calculations. In this latter work, the interaction energy obtained with a fine cluster modelling the metal surface was decomposed into two body atom–atom interaction terms.

The new water–copper potential was assumed to have an additive form where each water–metal atom interaction is described by the following function:

$$V_{W-M} = V_{O-M} + V_{H1-M} + V_{H2-M}, \quad (1)$$

where

$$\begin{aligned} V_{O-M} &= [C_1 \exp(-C_2 r_{O-M}) + C_3 \exp(-C_4 r_{O-M})] \\ &\quad \times [1 - f(\rho)] + C_6 \exp(C_7 r_{O-M}), \quad f(\rho) \\ &= \exp\left(-C_5 \left(\rho - \frac{a}{2}\right)^2\right), \end{aligned}$$

$$V_{H1-M} = C_8 \exp(-C_9 r_{H1-M}) + C_{10} \exp(-C_{11} r_{H1-M}),$$

$$V_{H2-M} = C_8 \exp(-C_9 r_{H2-M}) + C_{10} \exp(C_{11} r_{H2-M}). \quad (2)$$

The variables r_{O-M} , r_{H1-M} and r_{H2-M} are the distances of the Cu atom to, respectively, the oxygen and hydrogen atoms of the water molecule; the ρ variable is a projection of the oxygen to metal atom vector onto the surface; a is the metal lattice constant for copper, equal to 3.6077 Å. Function $f(\rho)$ is introduced to make the hollow site relatively repulsive and thus force bridge and top positions on the surface to be preferred for the water adsorption, as predicted by the results of DFT calculations. Additionally, each two-body term is multiplied by the function $f_s = 1/$

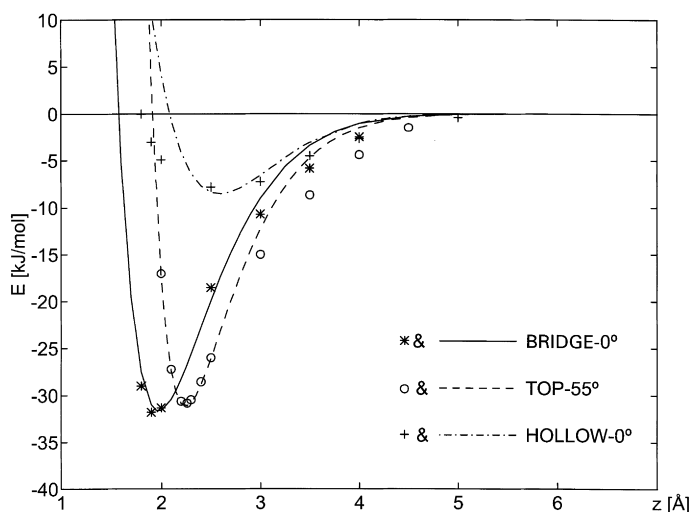


Fig. 1. The water–copper interaction potential versus z , the distance from the surface (lines) calculated for Cu_{12} – H_2O system for three different positions of water on the $\text{Cu}(1\ 0\ 0)$ surface, together with quantum points (*, o, +) used for the fitting. In all cases the water molecule interacts with the surface through its oxygen end. For each site the value of the angle between the dipole moment and the normal to the surface is inserted together with the notations used.

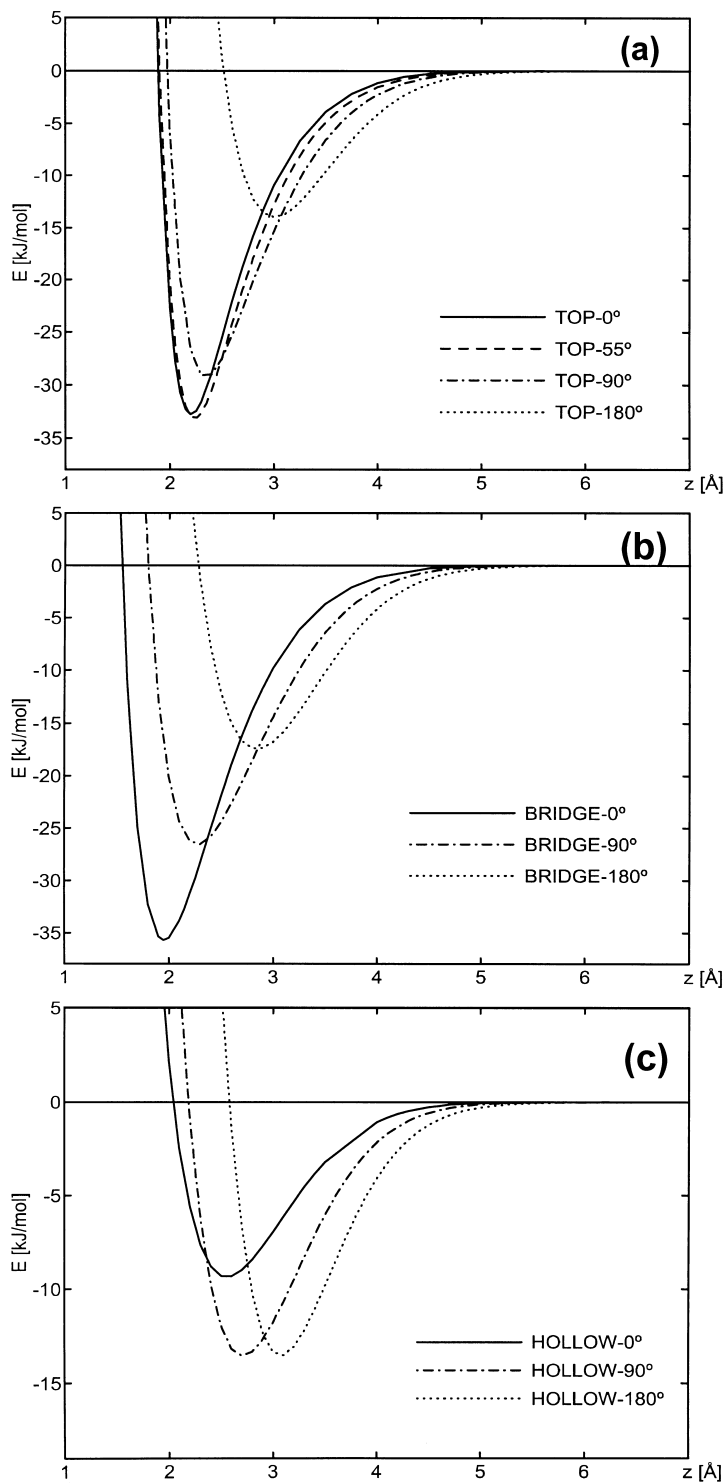
$(1 + \exp(\beta(r_{\text{O-M}} - \lambda)))$ to switch it smoothly to zero for longer atom–molecule distances. This function was introduced to avoid an artificial increase in the water–copper interaction when the twelve-atom cluster is substituted by a much larger structure to represent the infinite wall.

The parameters for the water–copper potential obtained by fitting the potential to quantum points are presented in Table 1. In the parametrization of the potential energy surface $V_{\text{W-M1}}$ special attention was given to the orientation of the water molecule with its oxygen pointing towards copper that are typical of the most stable conformations, but other orientations [14] have also been taken into account.

In Fig. 1, the behaviour of copper–water potential described by Eq. (1) when summed over twelve Cu atoms, is plotted for orientations of the H_2O molecule with the oxygen end towards the surface on the three sites—bridge, top and hollow—of the Cu_{12} cluster. For the adsorption of water on metals, this orientation was found to be the one preferred on the bridge and top sites and these conformations were given an extra weight in the fittings. For comparison, the results of B3LYP quantum calculations used for the parametrization of the analytical potential are also shown. In all cases the H–H axis is parallel to the surface. At the bridge and hollow site the molecular plane of the

water monomer is perpendicular to the metal surface, while at the top site the most stable conformation is that with a tilt angle, θ , of 55° between the dipole moment of the water and the normal to the surface.

It should be stressed that the total number of orientations/sites considered here is larger than that in similar studies by other authors and that some of the new orientations/sites used, show a peculiar behaviour (see below for a discussion of the difficulties arising from these new points for the construction of the potential). Several different functions were tested to describe the water–copper interaction and the one presented here appears to be the best compromise. A major difficulty of this potential arises from the ordering of the top and hollow site interaction energies, which depend on the orientation of the water molecule with respect to the surface. For top and bridge sites, the most stable orientation of water is that with its oxygen pointing towards the surface. However, for the hollow site the most preferred orientation is the one where oxygen points away from the surface. An additional problem comes from the different behaviour of this interaction at longer distances for various orientations of water. In DFT calculations, the interaction in the range of about 4–6 Å is much weaker when the water molecule approaches the surface by its oxygen end (Fig. 1) than for the two other orientations, parallel to the surface



and perpendicular with the hydrogen pointing to the surface. The former orientation is favoured only for the shorter range, where the interaction with the metal may occur through chemical bonding. For the two other orientations, the interaction has a mainly physical character what the almost zero charge transfer between the particle and the metal confirmed. However, as it was shown in the work of Romanowski [32,33], the neutral metal that is usually assumed in simulations to have no charge, in fact has an internal charge distribution that makes the superficial layers more negative than the bulk of the metal. The long-range interaction as found from the quantum calculations should then be treated with caution, as the cluster is characterised by its own inner charge distribution. The non-uniform charge distribution reported for the metal slab by Romanowski [32,33] was also a reason why the interaction of the water monomer with images of other waters has not been considered. In the simple model, the metal wall is treated as a neutral mirror producing images of approaching charges; a real metal is, according to Romanowski [32,33], a set of metal layers, each of them with its own particular distribution of charges. The polarisation of such a structure by a water molecule approaching it is certainly much more complicated than that predicted by the simple image charge model. Another factor, important for the liquid phase, is the representation of the interaction of the water with the metal when it interacts only indirectly with the wall, i.e. beyond the first hydration layer, for distances of 4 Å and more. At these longer distances it may be considered that the water molecule is screened from the wall by its aqueous environment and so its interaction with metal is overestimated by quantum calculations. The analytical potential V_{W-M} was made to tend to zero in this region.

Given all the difficulties pointed above, the authors concentrated rather on the proper description of the conformations most preferred for adsorption, assuming that the analytical potential chosen should give a global description of the interaction, especially in the regions thermodynamically more relevant. As can be seen in Fig. 1, the proposed form of the potential does this to a large extent. The description of the

orientations preferred for the adsorption is indeed in good agreement with quantum points.

In Fig. 2 the behaviour of the new potential is shown for the interaction of the water molecule with an infinite wall of Cu(100). The interaction with a wall is slightly stronger than with a cluster and has the minimum of energy at the bridge site of 35.5 kJ/mol, in good agreement with experimental predictions for the strength of water–copper interaction [17,18]. Notice, that the strength of adsorption described by this potential in relation of the angle between the dipole moment of water and the normal to the surface follow the ordering $55^\circ > 0^\circ > 90^\circ > 180^\circ$ at the top site and the reversed tendency at the hollow site, as found in quantum results [14].

3. Simulations of water near the copper wall

The potential presented above was used in the MC simulation of a system containing 256 water molecules between two Cu(100) surfaces. In all simulations the well-known TIP4P rigid model of water [19] was used. This has been applied in many studies on aqueous solutions as well as interfacial phenomena, and it has been shown to describe sufficiently well the properties of liquid water. Its simple form makes it suitable for the simulation of more complex systems.

The standard Metropolis Monte Carlo simulation of aqueous solution Cu(100) was carried out at a temperature of 298.15 K on the NVT ensemble. The separation between the metal electrodes was chosen so that the density of the water at the center of the box is about 1 g/cm³. The simulation box containing the aqueous solution is of about $18 \times 18 \times 24.4 \text{ \AA}^3$. The electrodes are modelled by two slabs, each consisting of 300 Cu atoms (6, layers, 50 atoms each) arranged in accordance with a fcc crystallographic structure. Periodic boundary conditions along the x and y directions parallel to the electrode surfaces were applied, both for the liquid and solids. More than 6×10^6 configurations were used for statistical equilibration and the same number again for sampling.

The structure of liquid water in contact with the

Fig. 2. The behaviour of the water–copper potential when computed for the infinite Cu(100) wall for different orientations of the water molecule when it is adsorbed (a) at the top site (b) at the bridge site (c) at the hollow site.

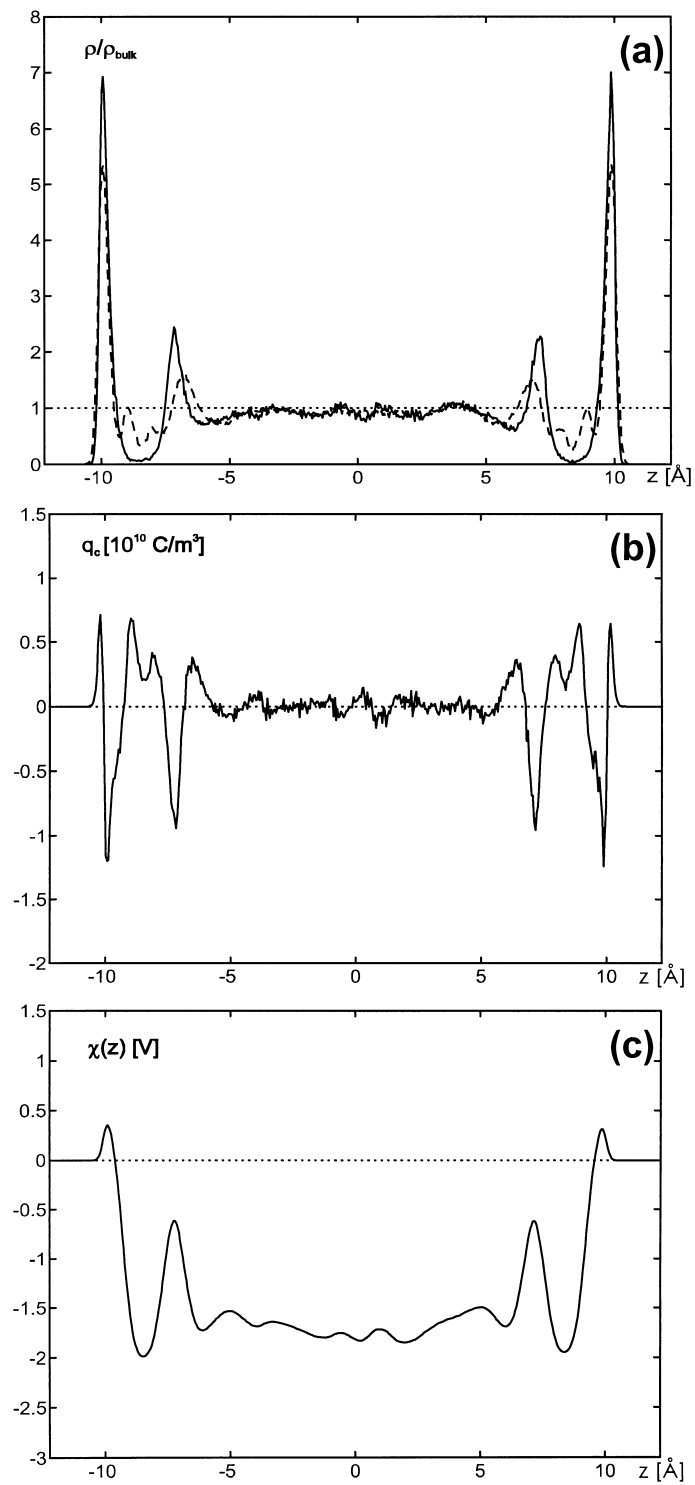


Table 2

Positions of the peaks defining the first (I) and the second (II) hydration layers found for oxygen (ρ_{O}) and for hydrogen (ρ_{H}) density profiles. The values are calculated as z distances from the closest metal surface. The “left” and “right” sides are related to the left (negative z coordinates) and right (positive z coordinates) halves of the density profiles shown in Fig. 3a. Positions Z_1 and Z_2 refer to the additional peaks found on ρ_{H} in the region between hydration layers as defined by maxima on ρ_{O}

	Left side		Right side		Left side		Z(I)
	Z(1)	Z ₁	Z(II)	Z ₂	Z ₁	Z(1)	
ρ_{O}	2.275	–	5.125	5.125	–	–	2.325
ρ_{H}	2.275	3.225	4.275	5.475	5.375	4.325	3.225

neutral copper wall was studied by means of normalized oxygen (ρ_{O}) and hydrogen (ρ_{H}) density profiles that are shown in Fig. 3a. Some more detailed data about properties of oxygen and hydrogen density profiles of our system are given in Table 2. From the density profiles we have also calculated the charge density profile ρ_{c} (Fig. 3b) and the surface potential (Fig. 3c) computed from the charge density using one-dimensional Poisson equation:

$$\chi(z) = \frac{1}{\varepsilon_0} \int_{-\infty}^z \rho_{\text{c}}(z_i)(z - z_i) dz_i. \quad (3)$$

The oxygen and hydrogen density profiles shown in Fig. 3a are approximately symmetric with respect to the center of mass of the system. Their shape in the middle part of the water lamina is relatively flat, with small fluctuations (because of statistical uncertainties) as expected for bulk water. Therefore the system can be considered as being large enough to model properties of the water between two non-interacting copper surfaces. The isotropy of bulk water appears to be perturbed in the interfacial region. This is shown by the existence of well-defined peaks on the density profiles near the edges where electrodes are located. The range of this perturbation is relatively short and corresponds to the formation of only two hydration layers on each metal surface. The first hydration layer of the metal is clearly much better defined when compared with the second layer, what is clearly seen from the different size and shape of peaks in Fig.

3a. Integration of the oxygen density function up to its first minimum gives an estimation of the surface coverage and, in this case, a value of about 0.77 water molecule per metal atom is obtained.

The first (the closest to the metal surface) maximum of ρ_{O} coincides exactly with the first maximum of ρ_{H} , showing that water is adsorbed mostly parallel to the surface. This orientation is different from that of the most stable conformation found from DFT calculations. The position of the coinciding maxima on the density profiles was found at a distance of 2.275 Å from the Cu(100) surface. Comparison of this value with results of DFT calculations is an additional confirmation that a water molecule in solution does not occupy the bridge position that was found to be the most stable for the H₂O monomer (at the optimal distance of 1.9 Å). Thus, for the adsorption of water on a metal as weakly interacting as copper, the hydrogen bonds between water molecules must play a very important, perhaps decisive role. Perhaps, more detailed analysis of ρ_{O} and ρ_{H} suggests that the orientation of water parallel to the Cu(100) surface is not the only one possible. In fact, while the oxygen distribution defines very clearly the first hydration shell, the hydrogen distribution shows a secondary peak (Z_1 , in Table 2) at about 1 Å away from the oxygen location. Considering the values of the running coordination number that are obtained by integration of the ρ_{O} and ρ_{H} between successive minima, this allows one to conclude that 65% of the water molecules in the first solvation shell are parallel to the metal surface and 35% are oriented with O–H bond perpendicular to the surface and pointing away from it. The existence of a smaller hydrogen peak, Z_2 , within the second hydration shell as defined by the oxygen distribution suggests that a similar situation may occur here; however, the broader peaks show that the second solvation layer is less well structured than the first one.

The charge density profile, ρ_{c} in Fig. 3b, shows strong fluctuations in the interfacial regions while only small oscillations around zero are seen in the center of the lamina. Similar charge density profiles were obtained from simulations of the water adsorbed

Fig. 3. Some properties of the solution obtained from the simulation (a) The oxygen ρ_{O} (solid line) and hydrogen ρ_{H} (dashed line) density profiles obtained from the simulation of the water lamina between two Cu(100) surfaces (b) The charge distribution ρ_{c} obtained from the density profiles (c) The surface potential $\chi(z)$ obtained from the ρ_{c} distribution.

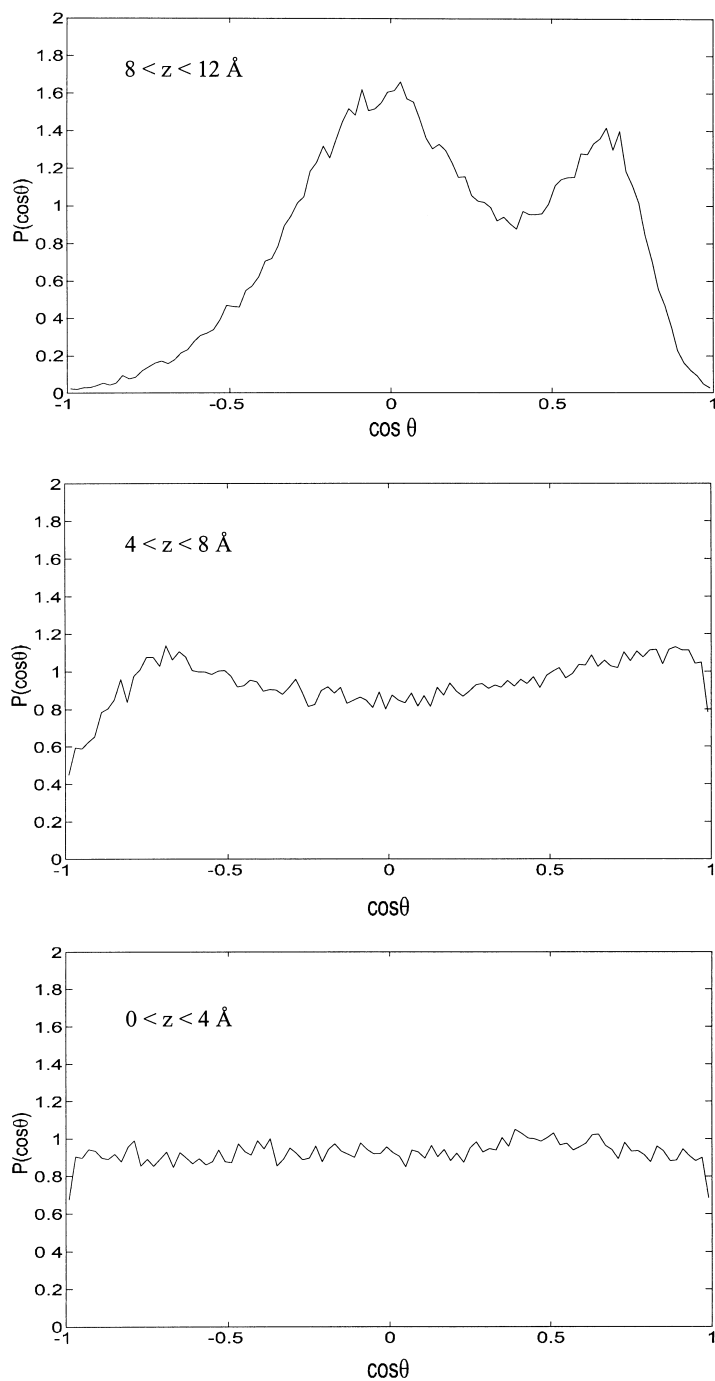


Fig. 4. The distribution of the cosine of the tilt angle (between the dipole moment of water molecule and the normal to the surface) for three water slabs parallel to the surface, each of about 4 Å thickness (a) the region of the first hydration layer (b) the slab containing the second hydration layer (c) the water lamina in the center of the simulation box.

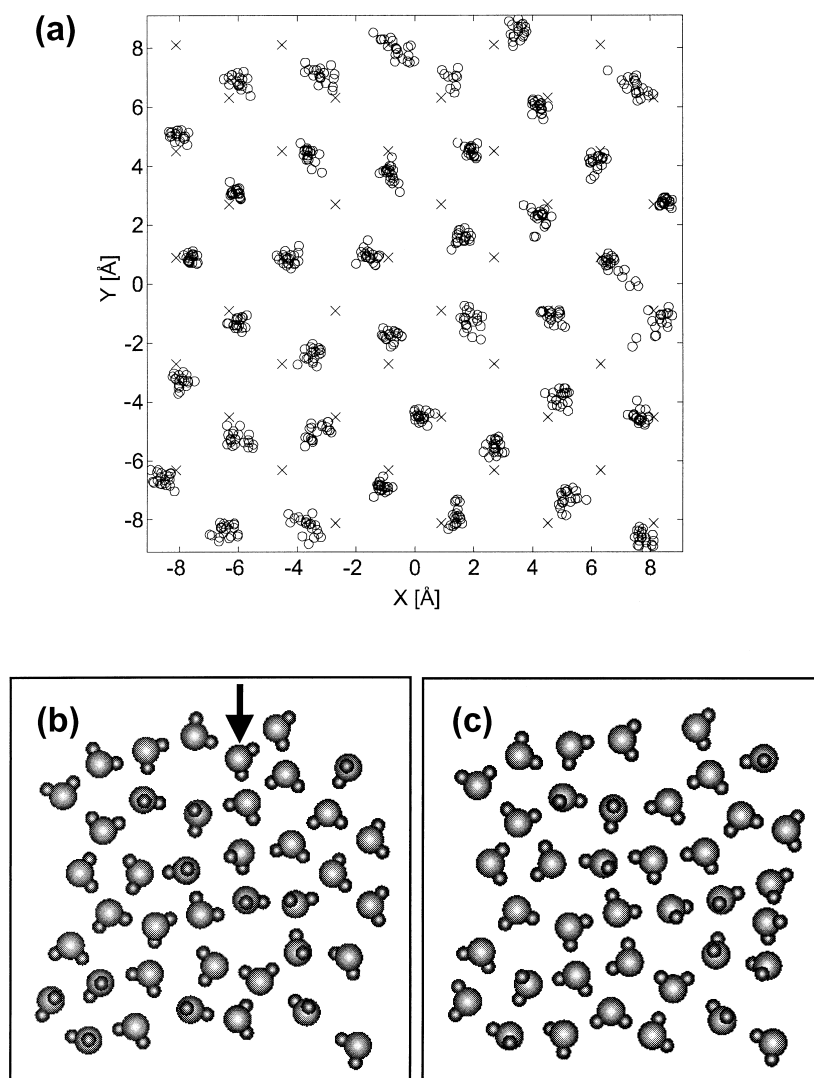


Fig. 5. The projection of positions of oxygens (O) belonging to the first hydration layer on the surface, collected sequentially from the last 20 macrosteps of the simulation. The (x) signs correspond to the positions of copper atoms forming the Cu(100) surface. The figures (b) and (c) are examples of the distribution of waters on the surface taken from the first (b) and the last (c) configuration of the total 20 used in figure (a). The arrow on figure (b) points towards the molecule that during simulation migrates from the first to the second hydration layer and hence is not seen in (c) (see text).

on other metals. The charge fluctuations in the interfacial region found in our studies for copper are not as big as those reported for Hg(111) [12] but larger than those found for Pt(100) [5]. This is reflected in the surface potential $\chi(z)$ that was obtained from the charge density ρ_c and is shown in Fig. 3c. The surface potential curve for water–copper interface is rather smooth, giving a potential drop across the first layer

of about 1.95 V while in the center of the box it reaches a level of about 1.75 V. Apparently most theoretical models do overestimate this property comparing to the value of c.a. 0.3 V usually proposed by experimentalists [20–22]. However, it should be remembered that both methods—theoretical and experimental—are not free from assumptions in the evaluation of the potential drop, thus the comparison

of theoretical quantities with experimental ones should be done with caution. However, one must be aware of the fact that this result of theoretical studies may depend strongly on several assumptions, such as the model of water used, the rigid surface lattice, etc. The high sensitivity of $\chi(Z)$ values on conditions of this type can be seen from comparison of the two MD studies performed for Hg(111) surface, where very different values of the potential drop cross the first layer are reported [11,12].

The structure of the water lamina in the interfacial region was additionally studied by plotting the distribution of the cosine of the angle θ between the dipole moment of H₂O molecules and the Z-axis perpendicular to the metal surface. This is shown in Fig. 4 for three water laminas of about 4 Å thickness each. Given the symmetry of the system, these plots were made by averaging the results obtained for the two sides (to the right and to the left with respect to the origin at $z = 0$) of the system. As can be seen in Fig. 4a–c, the influence of the wall on the water structure is very weak beyond the first layer, showing still some preferred orientation of water in the second layer, while for the central layers the cosine distribution is flat. This agrees with results of most theoretical works for similar systems. However, it can be seen in Fig. 4a that, unlike most earlier results for neutral Pt(100) [5–9], the distribution of the cosine shows not only one, but two preferred orientations. One of them is indeed approximately parallel to the surface corresponding to the maximum at $\theta \approx 90^\circ$. The second peak is found for a tilt angle, θ , of about 47° . This value is in close agreement with the conclusions taken above from the discussion of the density profiles, i.e. with one O–H bond parallel to the surface and the molecular plane perpendicular to it. This also agrees with findings from recently reported MD simulations performed for smooth (111) surfaces [10,11,13]. For the second layer favoured orientations are only weakly marked, but a clear preference of non-parallel conformations can be observed in Fig. 4b. The back-bonding of waters towards the first layer as well as the orientation with the dipole moment pointing away from the surface, noted already on the hydrogen profiles, are confirmed here. As mentioned above, no preferred orientation is observed in the central lamina (Fig. 4c).

Fig. 5a–c gives a picture of the first hydration layer.

Fig. 5a was made by collecting periodically coordinates of oxygen at a distance of less than c.a. 4 Å from the surface. This distribution of oxygen does not exhibit the highly regular geometry that was found for other surfaces from MD simulations. The oxygen tends to be placed above the metal atoms, as was found for other metals and also for the Cu (110) surface [13]. However, unlike other metals, the geometrical properties of the Cu (100) surface do not allow it to cooperate in forming a two-dimensional water layer with long-range order. The nearest-neighbours distances for other metals are closer to the length of hydrogen bonds (2.77 Å) between waters, while the Cu–Cu distance of 2.55 Å is definitely too small. The detailed analysis of the structures formed on the surface allows one to find some 4-sided, 5-sided and also the 6-sided rings, typical for ice-like structures, but no regular distribution of them is found. In fact, it should be noted that migration of waters along the surface might be observed, as for example near middle of the right edge of Fig. 5a. This relatively high mobility of water molecules is an effect of the particular balance between the water–water and water–metal interactions together with the steric limitations caused by the geometrical parameters of the Cu(100) surface. The structure of the first layer is determined by the tendency of the liquid to preserve hydrogen bonds but the metal–water interaction has some influence on it. Experimentally, it was suggested that on the clean Cu(100) no ordered patterns were observed [23].

Fig. 5b and c show examples of water structures of the first layer on the surface. The former is the first of all conformations plotted in Fig. 5a, while the latter figure is the last one. The positions of the hydrogen are also shown in these two pictures. As can be seen, most water molecules take a parallel orientation (both hydrogens belonging to each oxygen can be easily located) and preserve this conformation even after changing their site on the (100) surface. However, as was concluded already from density profiles and from the additional peak in probability distribution for the tilt angle, the orientation with one O–H bond pointing away from the surface, can be also found in Fig. 5b and c. This, sometimes called ‘flip-up’ orientation was reported to be found in several recent experimental investigations as the one involved in the formation of three-dimensional ice-like structures

at low temperatures [24,25]. Most experimental data shows the existence of tilted conformations when multilayers on the surface are formed [26–30]. The reorganization of the first hydration layer under addition of a second layer was seen in those studies manifested by a stronger inclination of the dipole moment of water relatively to the normal to the surface. However, according to a recent study of the Cu(100) surface [31], experimental reports for well oriented surfaces should be treated with caution, as the results can be strongly modified by the existence of defects on the surface. Nevertheless, the formation of hydrogen bonds between the first and second layers at the interfacial region was also found in the present study. Another interesting feature of the water forming an interface with the Cu(100) surface is its mobility not only along the surface but also the exchange of waters between the first and the second layer. The detailed comparison of Fig. 5b and c shows that the number of waters on the surface differs by 1. Thus one water molecule during simulation changed its location from the first to the second hydration layer allowing better adjustment of waters on the surface. Exchanges of this type must be relatively frequent as the average number of waters in the first layer was found to be 38.5 while 40 and 39 water molecules are shown in Fig. 5b and c. Migration of water molecules to and from the first solvation layer as found here is likely to be a common feature on hydrophobic surfaces like copper.

4. Conclusions

In this article a new potential for the interaction of water molecule with the Cu(100) surface was proposed. It was parametrized by fitting to the results of recently performed B3LYP DFT calculations, where the interaction of H₂O monomer and Cu₁₂ was calculated for ten different orientations of water molecule at several distances. The new potential describes properly the most stable orientations of a water molecule as found from DFT calculations; for an infinite copper surface, it gives an optimal energy value of 35.5 kJ/mol, in agreement with experimental measurements. This potential, is then used for the simulation of water near a copper wall. To our knowledge, this is the first report of a simulation of water in

contact with Cu(100) surface where a realistic potential based on quantum calculations is used.

The results of the simulation of liquid water in contact with copper surface described by this new potential agree quite well with experimental reports about properties of aqueous solutions in contact with metal surfaces. On the Cu(100) electrode no rigid two-dimensional superstructure was found for the first hydration layer, unlike that proposed for Cu(110) Hg (111) or Ag(111) surfaces. However, the properties of the aqueous solution in contact with copper do differ significantly from those of bulk water, and are similar in a qualitative way to those found for other metals. Two orientations of water on Cu(100) were found to dominate, one which is parallel to the surface, and a second conformation where the molecular plane of water is perpendicular to the electrode surface and the dipole moment of water forms with the normal to the surface a tilt angle of about 47°. The structure of the first hydration layer is found to consist of 4-, 5- and 6- sided rings of hydrogen-bonded waters but they appear to be organized in a disordered way. Migration of waters along the surface as well as between the surface and bulk water was observed in the simulation, showing their relatively high mobility.

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