Molecular Dynamics Study of the Cu - Water Interface in the Presence of Chlorine

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Abstract

As part of a program to model and explain the sensitivity of electron transfer reactions at metal interfaces to trace amounts of chloride in aqueous solutions, we report preliminary results on a direct dynamics model for the adsorption of chloride ion on a copper 100 surface in water. The model predicts the charge state of the chlorine in water and vacuum correctly but gives a solvation energy which is too large. We discuss possible reasons for this.

Keywords: chlorine, copper, electro-chemistry, electron transfer, metal-water interface, molecular dynamics, simulation, solvation

1 Introduction

Electrochemical interfaces present a challenge and an opportunity for condensed matter physicists and chemists using rapidly improving computational capabilities and rigoroously established microscopic theoretical models to make macroscopic predictions in complex systems useful to engineers, geophysicists and biologists. Here we report progress on a problem of this sort. We have chosen to study the chloride ion at an electrochemical interface because it is well known[1] that adsorbed chloride greatly enhances the rates of electron transfer reactions at electrochemical interfaces. Such electron transfer rates are believed in turn to be the rate limiting step in stress corrosion cracking in sensitive environments of great interest to engineers [2] . It is widely believed[3] that the role of adsorbed chloride is to provide a 'bridge' by which the electron can pass to or from the metal electrode to the ion in solution through some sort of resonant state. However such a picture is not supported by any quantum mechanical calculations of which we are aware, and indeed some explorations of this question using quantum chemical techniques by our associates at Argonne did not provide much support for it[4] . The limitations of quantum chemical methods are first that it is impractical to use large enough metallic clusters to reduce the gap between HOMO and LUMO to the scale of thermal energies (so that the clusters are not really metallic) and second that it is difficult to study a large enough set of positions of solvent molecules to fully account for the entire ensemble of configurations which are sampled in thermal equilibrium.

For these reasons we have undertaken a study using direct dynamics methods in which a molecular dynamics simulation of the water molecule trajectories is carried out for a few hundred water molecules in the presence of the electrons of the metal and chloride ion as a first step in the development of a model for these electron transfer processes. In the preliminary study reported here, no electron acceptor is present and we only seek to describe the binding of the chloride to a metal surface in vacuum and in the presence of water using these methods. To facilitate the effort we began with a code[5] which provides an approximate description of a 100 copper surface in the presence of water and modified it to take account of a chloride ion as described below.

In this preliminary report we can relate several successes of this approach: The configuration of the ion at the surface is the same in the vacuum and in water but, as it is pulled away, and without artificial constraints, it becomes a neutral chlorine atom in vacuum and a chloride ion in the model water. The energy of the chloride ion in the water can be used to estimate a solvation energy which is negative, but unfortunately substantially larger than the experimental one. A closer look shows that the coordination of the water to the chloride ion is related to this discrepancy: There are too many water molecules around the chloride and they are too tightly bound. In the rest of this paper, we describe the methods in more detail, present preliminary results and discuss the problems and successes in the last section together with a brief outline of future plans.

2 Simulation Details

The study has been carried out using a Car-Parrinello type combination of molecular dynamics and density functional methods, which was developed earlier in a simulation of copper-water interface [5]. In that work a supercell containing a five-layer slab of copper (180 Cu atoms) and 245 H_2O molecules was constructed. The H_2O molecules were described by the TIPS model [6], and the wavefunctions and densities of Cu valence electrons were calculated using the density functional method with pseudopotential in a planewave basis. To reduce the computational effort, the local-form of pseudopotential was employed, thus only $4s$-electrons of Cu were considered explicitly.

Here we adopt the same supercell with the addition of a chlorine atom in the solvent, which is allowed to move following its molecular dynamical trajectory while Cu atoms are fixed at their bulk equilibrium lattice positions. In order to generate a realistic local pseudopotential $V^{ps}(r)$ for the 7 valence electrons from Cl $3s$ and $3p$ states, the following expression has been used:

$$V^{ps}(r) = 0.25V^{ps}_{3s}(r) + 0.75V^{ps}_{3p}(r) \tag{1}$$

where $V_{3s}^{ps}(r)$ and $V_{3p}^{ps}(r)$ are the pseudopotentials for Cl $3s$ and $3p$ orbitals derived from the Troullier and Martins scheme [7]. The resulted Cl pseudopotential has been tested extensively on molecules including NaCl, HCl and CuCl, yielding reasonable agreements with exact values for interatomic distances and vibrational frequencies. For example, the calculated H–Cl bondlength and H vibrational frequency along the bond are listed in Table 1. It should be noted that the inaccuracy in the result is comparatively larger than that from the standard density-functional method because of the lack of non-local pseudopotentials and the relatively low kinetic energy cutoff employed in this work. Similarly the derived value for the equilibrium lattice constant of bulk Cu is 4.2 Å, which is an overestimate of the experimental value of 3.6 Å. The results are expected to be improved when non-local pseudopotentials are implemented.

Table 1: *The HCl bondlength and H vibration frequency calculated using non-local pseudopotential and the local-form of the Cl pseudopotential generated with Eq.(1) A kinetic-energy cut-off of* $10Ry.$ *is used, comparable to the value used for the simulation.*

	non-local pot.	local pot. (mix)	exact
H-Cl bond-length (Å)	1.264	1.343	1.274
H frequency (1/cm)		3006	2949

To partially account for the polarization of water in various environments, the water model introduced by Toukan and Rahman [18] has been incorporated in our simulation, replacing the TIPS model for rigid water molecules used in the earlier study.

In the previous study without Cl [5], two supercells were employed: the larger one ($29 \times 29 \times 80a.u.$) contains all atoms in the system, whereas the smaller one ($29 \times 29 \times 40a.u.$) centered at the Cu slab includes only the volume where the valence electron density is not zero. It is for this smaller supercell that the density functional method is applied to obtain the electron wavefunctions. In the current study, however, the region with non-zero electron density expands significantly beyond the Cu slab because of the valence electrons carried by the Cl atom in the solvent. Therefore the dimension of the smaller supercell is chosen as $29 \times 29 \times 60a.u.$, resulting an increasing computational effort.

The study becomes more computationally demanding with the inclusion of Cl in other aspects as well. Comparing with a more uniformly distributed electron density within the Cu slab, there is a large concentration of valence electrons surrounding Cl. which requires a more dense real-space grid for a detailed description. After much experimenting, it is found a basis set containing 54,000 planewaves is sufficient. In addition, because Cl is allowed to move, it is more difficult to obtain the equilibrium electronic structure of the system after each MD step. To reach rapid self-consistent convergence in the electron wavefunction for a fixed atomic configuration, it is found that the steepest descent algorithm works efficiently. Assuming a wavefunction after i-th iteration is $|\psi^i\rangle$, then it is constructed in the next iteration following

$$|\psi^{i+1}\rangle = |\psi^i\rangle - \alpha(H - \lambda)|\psi^i\rangle \tag{2}$$

where α is an adjustable mixing parameter, and

$$\lambda \equiv \langle\psi^i|H|\psi^i\rangle. \tag{3}$$

Typically after two such self-consistent iterations, convergence similar to that without Cl is reached. One MD step requires approximately 29 CPU seconds on a Cray C90. Except for those described above, all other physical parameters used in the simulation are the same as those in reference [5].

3 Results

We first examine the Cl adsorption on Cu in the absence of solvent. Two symmetry positions for Cl are seen to be stable: it can either occupy a site above the center of a square formed by 4 neighboring Cu (4-fold site), or a site directly above a surface Cu atom (on-top site). Figure 1 shows the total energy as a function of the distance from Cl to the Cu surface (top layer of Cu) for both cases. The equilibrium configuration can be reached when Cl is located at a 4-fold site,

in agreement with previous studies.

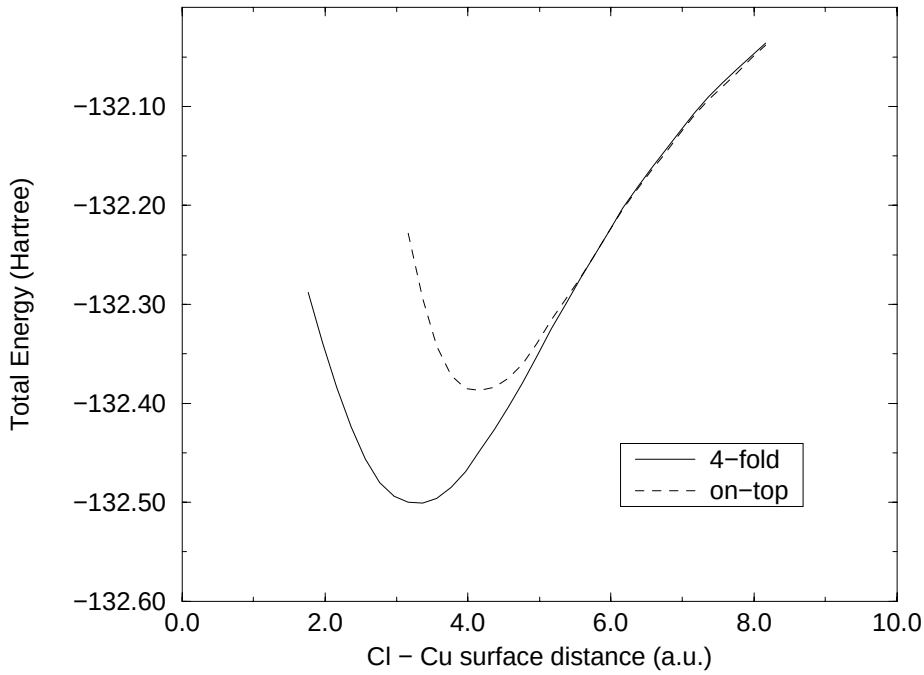

Figure 1: *Total energy as a function of Cl to Cu surface distance for both 4-fold and on-top configurations. The system contains no water.*

Derived stable positions for both 4-fold site and on-top site are listed in Table 2. For the 4-fold configuration, the current calculation yields a Cl to Cu distance in better agreement with experimental measurements than that from a small cluster approach [8]. This is not surprising as the number of Cu atoms used here (180) is much larger, thus better simulates a Cu surface. In the case of Cl on-top configuration, the estimated stable Cl–Cu surface distance is close to that in a CuCl diatomic molecule.

In all following discussions we shall focus on the 4-fold configuration for Cl since it corresponds to the structure with a lower energy.

The electron density distribution in a (100) plane with Cl and perpendicular to the Cu surface is shown in Fig.2. In order to evaluate the ionic charge attributed to Cl, we have also plotted in Fig.3 the transverse charge density distribution for various Cl positions, the integral over z

Table 2: *Geometric parameters for stable positions of Cl at 4-fold and on-top adsorption sites on Cu. The system contains no water.*

	4-fold hollow site				**on-top site**	
	cluster[8]	present	LEED[10]	SEXAFS[11]	present	CuCl[12]
Cl–surface (Å)	2.20	1.76	1.55			
Cl–Cu (Å)	2.84	2.52		2.37	2.21	2.05

(perpendicular to the surface) yields the total valence charge, and the area under the peak centered at Cl offers an estimate of the valence charge on Cl. For example, the resulted Cl valence charge is 7.87 for Cl at (z=13 a.u.), in qualitative agreement with reference [8] where the Cl ionicity in its equilibrium configuration is found to be essentially -1. However, with increasing Cl–Cu surface distance, Cl becomes more and more neutral. At (z=22 a.u.), the valence charge on Cl is reduced to 7.07. Later in the section this will be compared with the result obtained in the presence of water.

To study the Cu-water interface, we allow the supercell filled with water outside the Cu slab. While the Cu lattice is fixed, water molecules move around following molecular dynamics trajectories. Figure 4 shows a 'snap shot' of the electron density distribution for a Cl position identical to that in Fig.2(a). The disturbing effect of water molecules to the valence electrons of Cl as well as those in the metal is significant, which has been omitted in studies that employ fixed effective metal-water potentials. The largest deviation from the symmetric electron density observed in the absence of water occurs in the vicinity of Cl, where the H_2O molecules forming the solvation shell tend to have H pointing towards Cl because of the Coulomb attraction, resulting oxygens sticking out with negative charges which repel the valence electrons on the Cu surface There are also deviations away from Cl due to some on-top oxygen-in H_2O orientations [5].

The effect of Cl solvation is seen when Cl is slowly moved away from the metal surface. Figure 5 shows the drastic difference in the valence charge associated with Cl in systems with and without water. While similar for both systems when Cl is bonded to the surface, it is rapidly ionized going into the solvent by absorbing an electron from the metal surface, a favorable electronic

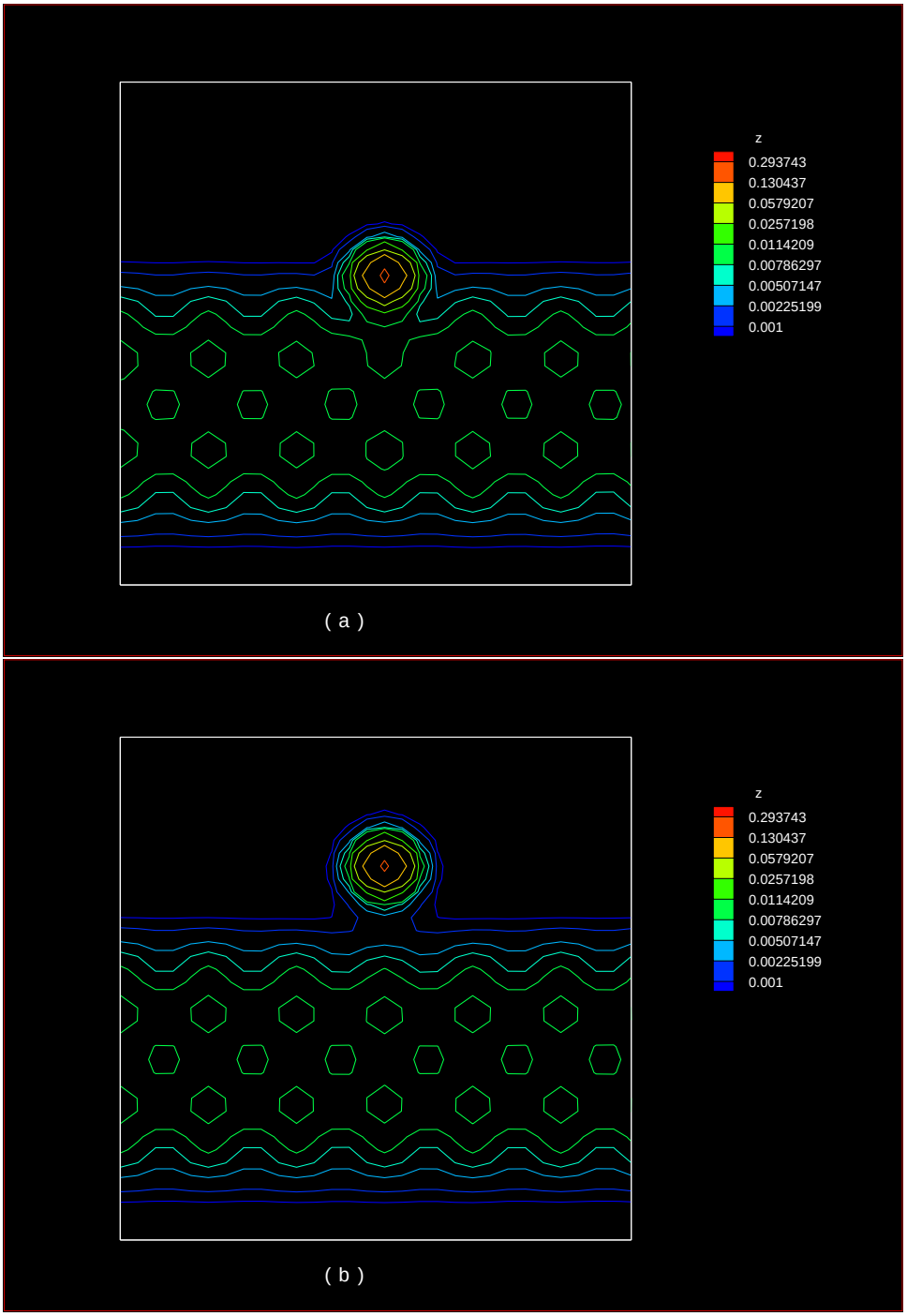

Figure 2: *The logrithmic contour plot of the valence electron density for Cl adsorption on Cu in the absence of water. The plot is in the (100) plane of the Cu fcc structure, with Cl located at a 4-fold hollow site within this plane. The distance of Cl to the top layer of Cu is (a) 1.67 Åand (b) 4.32 Å, respectively.*

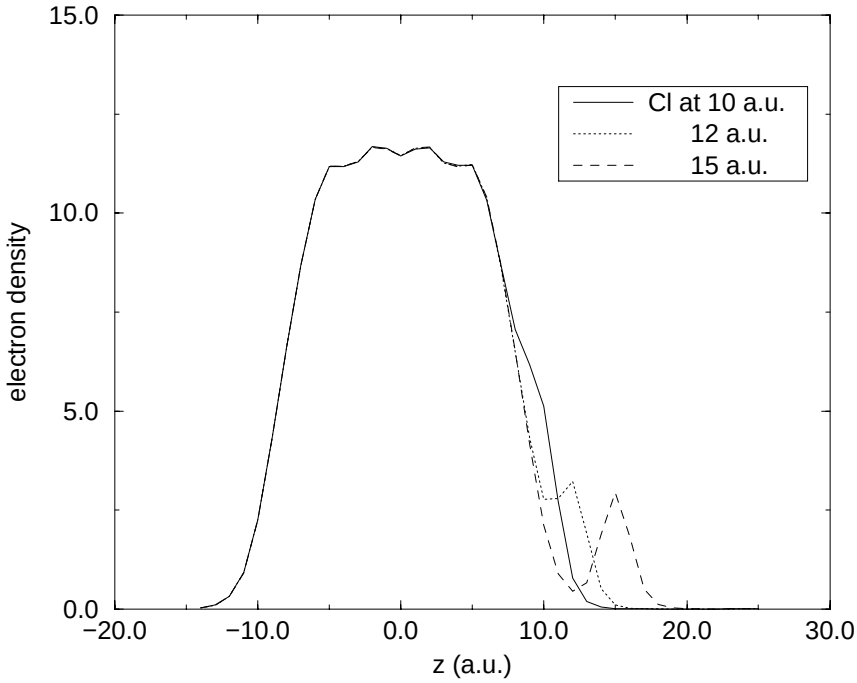

Figure 3: *The transverse electron density distribution. The broad feature centered at z=0 corresponds to the relatively uniformly distributed valence electrons of Cu, where as the peak at the end indicates the concentrated Cl valence charge.*

structure because of the accomodations by surrounding water molecules. On the contrary, in the absence of solvent, it is energetically preferable for the Cl to be charge neutral when removed from the metal surface.

Comparing with the electronically rigid vacuum, formation of the solvation shell lowers the total energy of the system because of the re-orientations of surrounding water molecules in reaction to the negatively charged Cl. This is readily shown in figure 6 where the total energy as a function of Cl to Cu surface distance is plotted for both systems with and without solvent. For direct comparison the latter is shifted vertically so that the two energy curves coincide at their lowest states (equilibrium positions). Similar curvatures at the ground state indicate that solvent has minimal effect when Cl is bonded to the Cu surface. However, as Cl separates from the surface, the difference in energy increases becomes apparent.

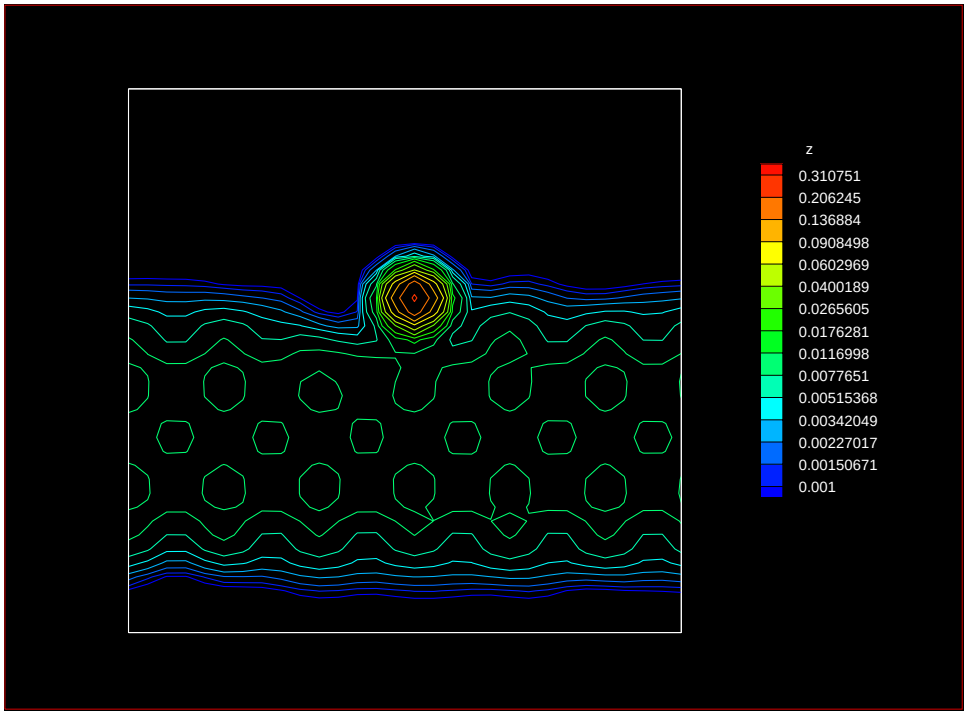

Figure 4: *The logrithmic contour plot of the valence electron density for Cl adsorption on Cu in the presence of water. The distance of Cl to the top layer of Cu is 1.67 Å, identical to that in Fig. 2(a).*

To estimate the Cl^- solvation energy, we compare the two potential energy surfaces at large z (i.e., Cl is far from the metal surface) using

$$\Delta E = (E - E_{Cu,water}) - (E_{Cu,Cl} - E_{Cu}) \tag{4}$$

where E is the total energy of the complete system of a Cl in the Cu-water interface, and $E_{Cu,water}$ denotes the total energy of equilibrated Cu-water system only. Similarly, E_{Cu} and $E_{Cu,Cl}$ represent the total energy of the Cu slab and the Cu slab plus a Cl atom, respectively. Finally, the solvation energy can be evaluated by taking into account the two difference Cl charge states:

$$S_{Cl^-} = \Delta E - A_{Cl} + W_{Cu} \tag{5}$$

where $A_{Cl} = 3.61$eV and $W_{Cu} = 4.59$eV are Cl electron affinity and Cu work function, re-

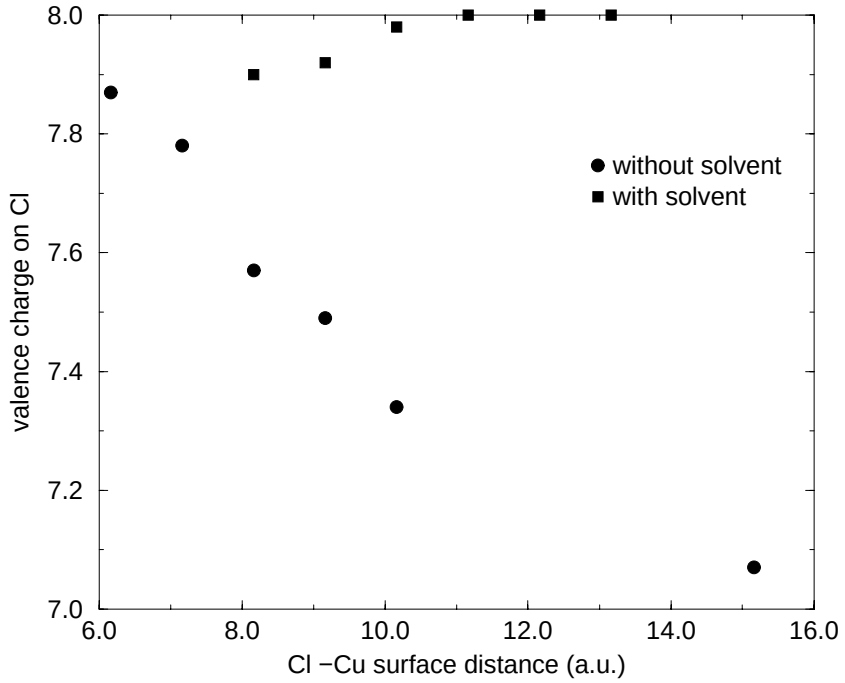

Figure 5: *The valence charge associated with Cl in systems with and without water, shown as functions of Cl distance to Cu surface. The neutral Cl atom has 7 valence electrons in the current pseudo-potential approach.*

spectively. Derived Cl^- solvation energy is 11.1 eV, significantly larger than the experimental measurement of 3.63 eV [9].

The overestimate of the Cl^- solvation energy can be attributed to the large solvation shell obtained in the simulation. Fig. 7 and Fig. 8 shows the radial distribution functions of Cl-O and Cl-H, and the corresponding running integration of association numbers surrounding the Cl. In contrast to previous classical MD simulations and Monte Carlo studies [13, 14] where the number of water molecules in the first solvation shell is averaged around 7.4, the estimated association number obtained here is 10.6. Detailed comparison is presented in Table 3. An examination of the radial distribution function in Fig. 7 shows that the water molecules within the first solvation shell exhibit an 'oxygen out' structure, with two H in each water molecule pointing toward the Cl. This results in an exceedingly strong solvation effect, thus yields a high solvation energy

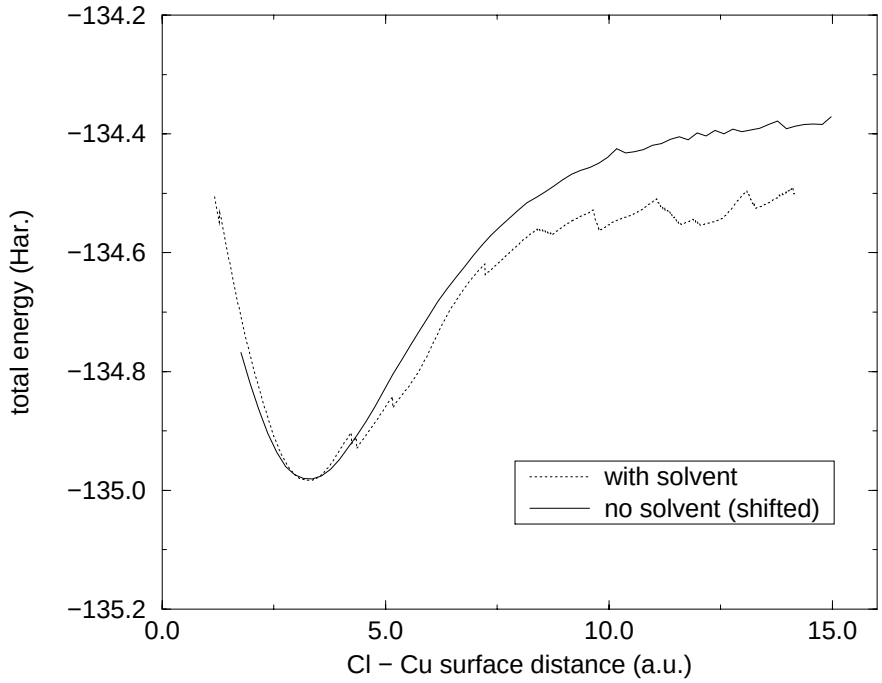

Figure 6: *Total energy as a function of Cl to Cu surface distance with and without water. For comparison, the curve corresponding to a system without water has been shifted vertically to compensate the bulk-water energy.*

value. The origin for the large solvation shell is currently under investigation. One of the sources maybe the simple center-form for Cl pseudopotential, which overestimates the Cl electron affinity by 1.31 eV in the single-atom calculation. In addition, the polarization of the water molecule due to the partial charge transfer between H and O has not been taken into acocunt. In a study of Cl^- – H_2O cluster using Gaussian 94 program, it is seen that approximately $0.1e$ of additional charge has been transferred to O from the H bonded to Cl. We are in the progress of implementing a dissociable water model [17] which approximates this polarization by introducing a dipole at every oxygen site.

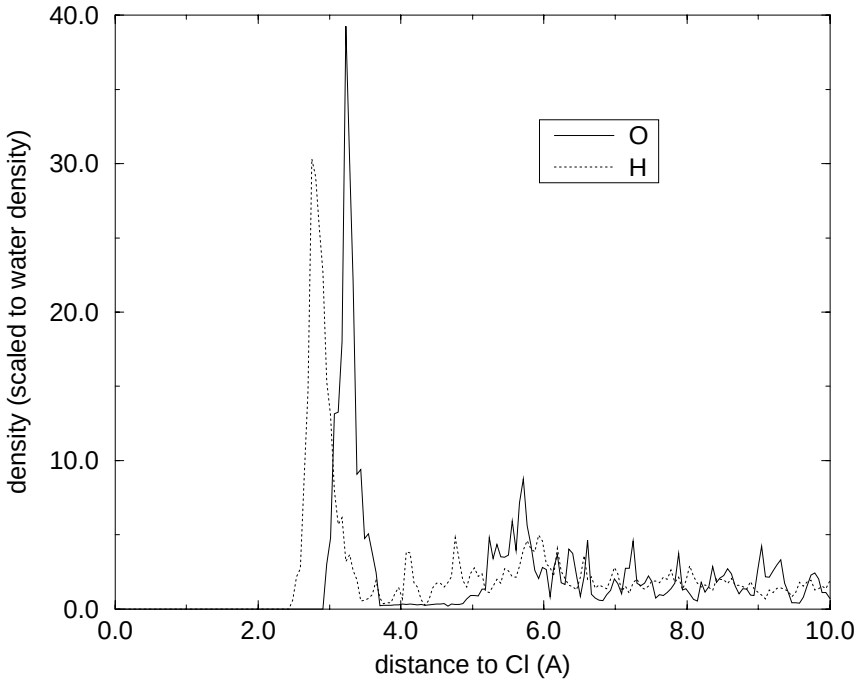

Figure 7: *Radial distribution functions for Cl–O and Cl–H.*

4 Discussion

This calculation shows that some qualitative aspects of halide adsorption on metallic surfaces in aqueous solvents can be reproduced by our methods. The main problem is that the solvation behavior of the chloride ion is not correctly described by the model. We are exploring the following possible origins of this difficulty : 1) the local pseudopotential on the chloride ion should more properly be replaced by a nonlocal one 2) the polarizability of the water molecule

Table 3: *The geometry of Cl solvation shell.*

	MD[13]	MC[14]	present	X-ray[15]	neutron diffraction[16]
Cl–O (Å)	2.7	3.21	3.23	3.10-3.35	3.20-3.34
Cl–H (Å)	1.7	2.25	2.75		2.22-2.26
coordination number	7.4	7.4	10.6	5-11	5.3-6.2

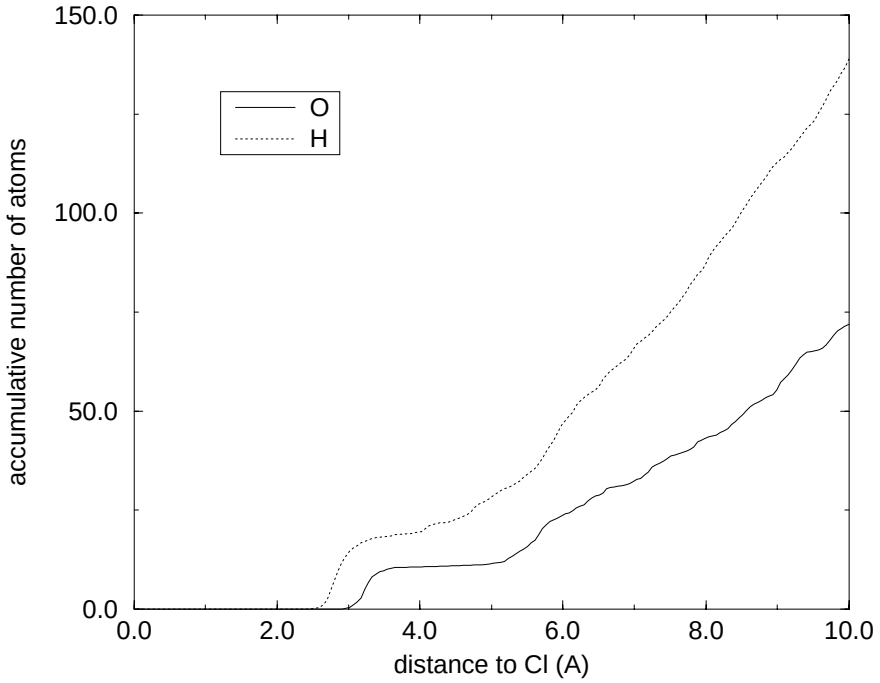

Figure 8: *Running integration of association numbers for O and H surrounding Cl.*

should be taken into account or 3) despite the reasonable properties of our model for the copper-solvent interface, the hydrogen or oxygen pseudopotentials may not be adequately representing the water molecules. Possiblities 2 and 3 are not entirely logically independent. To improve on these features of the model we plan to introduce non-local pseudopotentials and a dissociable and polarizable model of water[17] into this model in the near future.

Acknowledgments

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