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Molecular Dynamics Study of the Cu–Water Interface in the Presence of Chlorine[1]

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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, preliminary results on a direct dynamics model for the adsorption of chloride ion on a copper 100 surface in water are reported. The model predicts the charge state of the chlorine in water and vacuum correctly, but gives a solvation energy which is too large. Possible reasons for this are discussed.

KEY WORDS: chloride; electrochemistry; simulation.

1. INTRODUCTION

Electrochemical interfaces present a challenge and an opportunity for condensed matter physicists and chemists using rapidly improving computational capabilities and rigorously 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 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, which are of great interest to engineers [2]. It is believed [3] that the role of adsorbed chloride is to provide a "bridge" by which the electron can pass to or from

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the metal electrode to the ion in solution through some sort of resonant state, though quantum chemical calculations on small clusters do not provide much support for it [4].

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 the 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 molecular dynamics (MD) model [6], and the wave functions and densities of the copper valence electrons were calculated using the density functional method with a pseudo-potential in a plane-wave basis. To reduce the computational effort, local pseudo-potentials were employed and only $4s$-electrons of Cu were considered explicitly.

Here we adopt the same supercell, with the addition of a chlorine atom in the solvent. The molecules of the solvent are allowed to move following a molecular dynamics trajectory, while the copper atoms are fixed at their bulk equilibrium lattice positions. We used the following local pseudopotential $V^{\mathrm{ps}}(r)$ for the seven valence electrons from Cl $3s$ and $3p$ states:

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

where $V^{\mathrm{ps}}_{3s}(r)$ and $V^{\mathrm{ps}}_{3p}(r)$ are the pseudopotentials for Cl $3s$ and $3p$ orbitals derived from the Troullier and Martins scheme [7]. This chlorine pseudopotential yields values of the interatomic distances and vibrational frequencies of the NaCl, HCl, and CuCl molecules which are in reasonable agreement with exact values from full Hartree Fock CI calculations. (See Table I for results for HCl, for example.) The results for these molecules could be improved by use of nonlocal pseudo-potentials and a larger kinetic energy cutoff but the cost of running the resulting code to describe the full system of water, electrode, and chlorine would be prohibitive. To account partially for the polarization of water in various environments, a flexible classical central potential molecular dynamics model for water was used [8], replacing the TIPS model of rigid water molecules used in the earlier study.

In the previous study without chlorine [5], two supercells were employed: the larger one ($29 \times 29 \times 80$ a.u.) contained all the atoms in the system, whereas the smaller one ($29 \times 29 \times 40$ a.u.), centered at the copper slab, included only the volume where the valence electron density was not zero. In the present study, the region with nonzero electron density expands significantly beyond the electrode because of the presence of valence electrons carried by the chlorine atom and it was necessary to use the larger dimension of $29 \times 29 \times 60$ a.u. for the smaller supercell. The presence of chlorine results in a less uniform electron distribution than in the case of a pure copper water interface, and, as a result, we needed a more dense real-space grid and a larger basis set containing 54,000 plane waves. Because the chlorine is allowed to move, it is more difficult to obtain the equilibrium electronic structure of the system after each MD

Table I. The H–Cl Bond Length and H Vibration Frequency[a]

	Nonlocal pot.	Local pot. (mix)	Exact
H–Cl bond length (A)	1.264	1.343	1.274
H frequency (cm^{-1})		3006	2949

[a] The nonlocal pseudo-potential and the local form of the Cl pseudo-potential generated with Eq. (1) were used. A kinetic energy cutoff of 10 ry was used, comparable to the value used for the simulation.

step and we found it useful to modify the algorithm used in the solution of the Schroedinger equation to have the form

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

where $|\psi^{i}\rangle$ and $|\psi^{i+1}\rangle$ are the one-electron wave functions at successive iterations of the algorithm. This differs from the algorithm used in the work reported in Ref. 5 by the subtraction of $\lambda = \langle\psi^{i}|\,H\,|\psi^{i}\rangle$ from the Hamiltonian on the right-hand side and is a version of the well-known steepest descent algorithm. Typically after two self-consistent iterations, convergence similar to that without Cl was reached. One MD step requires approximately 29 CPU s on a Cray C90. Except as described above, all physical parameters used in the simulation were the same as those reported in Ref. 5.

3. RESULTS

We first examine chlorine adsorption on copper in the absence of solvent. Two symmetry positions for Cl are found to be stable: a site above the center of a square formed by four neighboring Cu atoms (4-fold site) and a site directly above a surface Cu atom (on-top site). Figure 1 shows the calculated total energy as a function of the distance from chlorine to the first layer of copper atoms in vacuum for both cases. We find the lowest energy for the chlorine in the 4-fold site, in agreement with previous studies (Table II). For the 4-fold configuration, the current calculation yields a

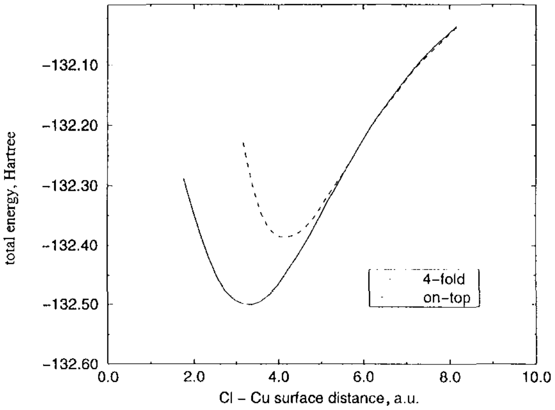

Fig. 1. Total energy as a function of Cl-to-Cu surface distance for both the 4-fold and the on-top configurations. The system contains no water.

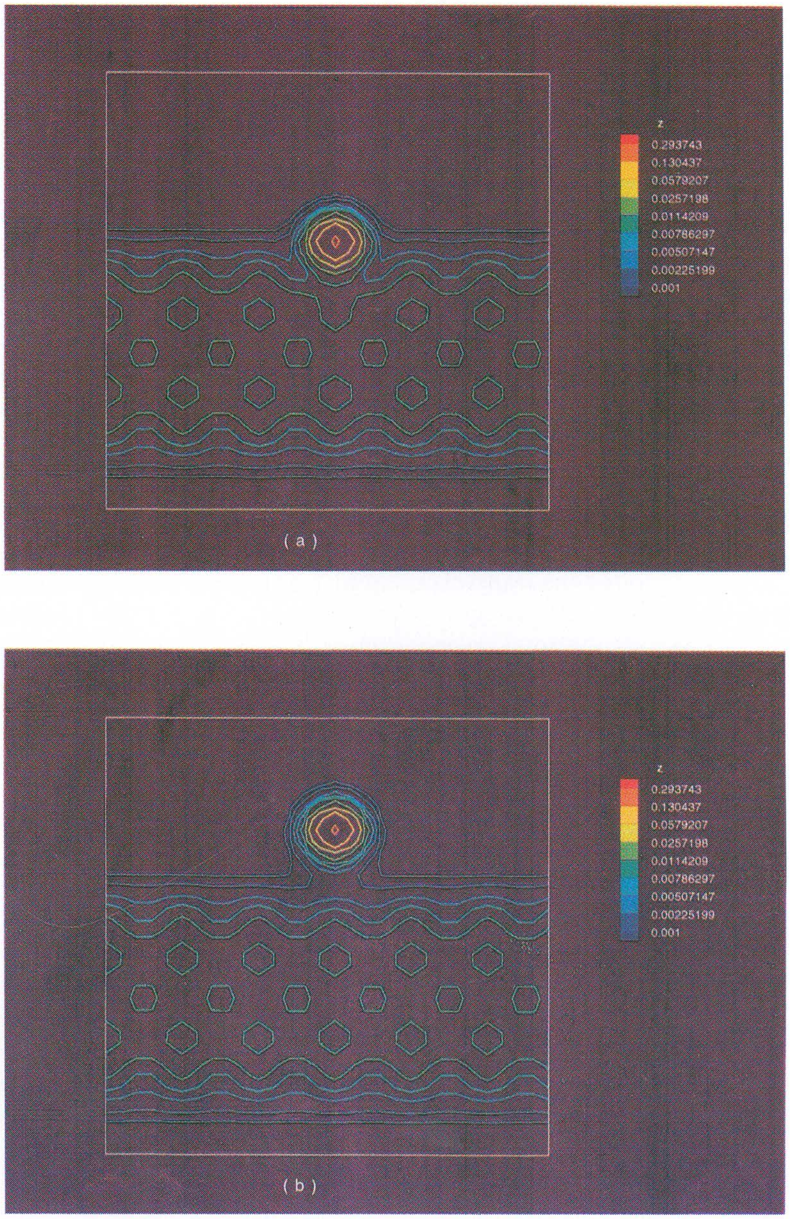

Fig. 2. *The logarithmic contour plot of the valence electron density for Cl adsorption* on Cu in the absence of water. The plot is in the (100) plane of the Cu fcc structure, with Cl located at a 4-fold hollow site within this plane. The distance of Cl to the top layer of Cu is (a) 1.67 Å and (b) 4.32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

Table II. Geometric Parameters for Stable Positions of Cl at the 4-Fold and On-Top Adsorption Sites on Cu: The System Contains No Water

	4-Fold hollow site				On-top site	
	Cluster [12]	Present	LEED [9]	SEXAFS [10]	Present	CuCl diatomic [11]
Cl–surface (Å)	2.20	1.76	1.55			
Cl–Cu (Å)	2.84	2.52		2.37	2.21	2.05

nearest neighbor chlorine-to-copper distance in better agreement with experimental measurements than that from a small cluster approach [12]. In the case of the on-top configuration, the calculated stable Cl–Cu surface distance is close to that in a CuCl diatomic molecule. In the following discussion we focus on the lowest-energy 4-fold configuration for chlorine. The calculated electron density distribution in a (100) plane containing the chlorine atom and perpendicular to the metal surface is shown in Fig. 2. We have also plotted the transverse charge density distribution in Fig. 3 for various Cl positions. The integral of this quantity over z (perpendicular to the surface) yields the total valence charge, and the area under the peak centered at the chlorine nucleus offers an estimate of the valence charge on the chlorine (see discussion of Fig. 5 below).

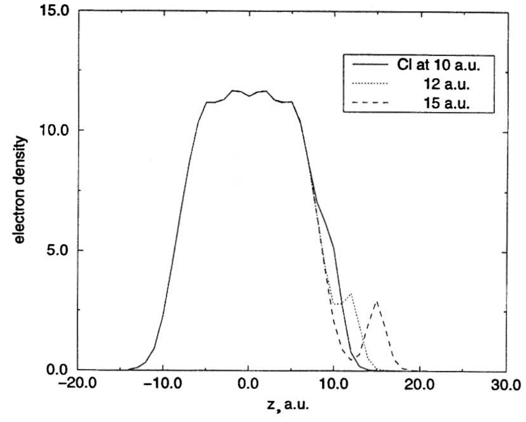

Fig. 3. The transverse electron density distribution. The broad feature centered a $z = 0$ corresponds to the relatively uniformly distributed valence electrons of Cu, whereas the peak at the end indicates the concentrated Cl valence charge.

To study chlorine at the copper–water interface, we allow the supercell to be filled with water outside the metal slab. As in Ref. 5 metal atoms do not move during the molecular dynamics simulation but the water molecules follow molecular dynamics trajectories. Figure 4 shows a "snap shot" of the electron density distribution for a chlorine position identical to that in Fig. 3a. The disturbing effect of water molecules on the valence electrons of the chlorine and the electrons in the metal is evident. The largest deviation from the symmetric electron density observed in the absence of water occurs in the vicinity of the chlorine, where the H_2O molecules forming the solvation shell tend to have a hydrogen atom pointing towards the chlorine because of the Coulomb attraction. The negatively charged oxygen atoms which stick out as a result repel the valence electrons on the copper surface. We also see effects in the water distribution of some on-top oxygen-in-water orientations as found earlier in this model [5].

In Fig. 5 we show the valence charge on the chlorine (obtained by integration of the small charge density peak in Fig. 3) as a function of the distance of the chlorine from the metal surface in the two cases in which

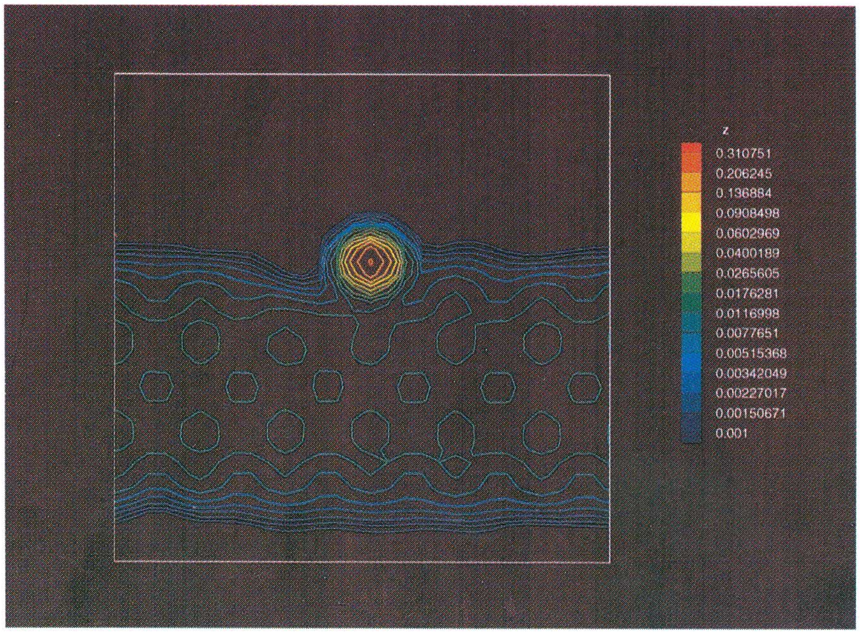

Fig. 4. The logarithmic contour plot of the valence electron density for Cl adsorption on Cu in the presence of water. The distance of Cl to the top layer of Cu is 1.67 Å, identical to that in Fig. 2a.

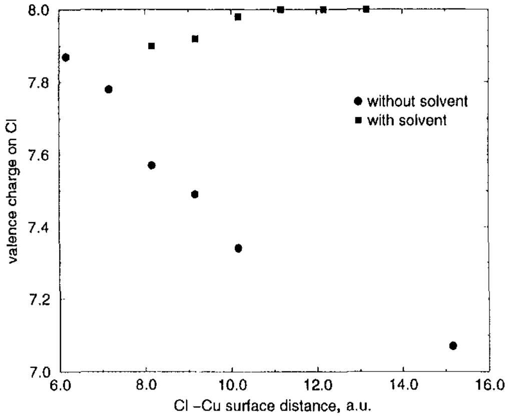

Fig. 5. The valence charge associated with Cl in systems with and without water, shown as function of Cl distance to Cu surface. The neutral Cl atom has seven valence electrons in the current pseudo-potential approach.

water is present and in which it is not. The results are similar in the two cases when the chlorine is near the surface, but in water, the chloride ion is seen to be the stable entity at larger z, whereas in vacuum the chlorine atom is the stable ground state entity at large distances. Thus, the ionic configuration is stabilized by the solvation by the surrounding water molecules as expected. We show the calculated total energies as a function of z for the cases with and without water in Fig. 6. The vacuum curve has been shifted to facilitate comparison of the shapes of the curves at small z. One sees that the binding forces are very similar near the copper surface whether water is present or not, but differences appear at larger z.

To estimate the Cl^- solvation energy when the ion is deep in the fluid, we compared the energies in the presence and absence of water at large z:

$$\Delta E = (E - E_{\mathrm{Cu,water}}) - (E_{\mathrm{Cu,Cl}} - E_{\mathrm{Cu}}) \tag{3}$$

Here E is the total energy of the complete system of a chlorine atom in the Cu–water interface, and $E_{\mathrm{Cu,water}}$ denotes the total energy of the equilibrated Cu–water system only. Similarly, E_{Cu} and $E_{\mathrm{Cu,Cl}}$ represent the total energy of the Cu slab in vacuum and the Cu slab plus a Cl atom in vacuum, respectively. The solvation energy S_{Cl^-} is defined not as this difference but as the energy difference between the energy of the chloride ion in water and the energy $E_{\mathrm{Cu,Cl}^-} - E_{\mathrm{Cu}}$ of the chloride ion in vacuum far from bulk water:

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

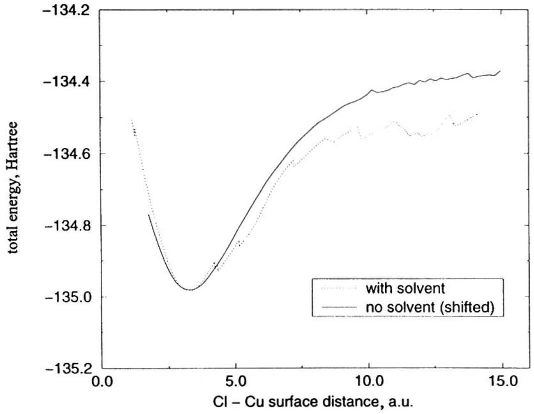

Fig. 6. Total energy as a function of Cl-to-Cu surface distance with and without water. For comparison, the curve corresponding to a system without water has been shifted vertically to compensate the bulk-water energy.

The difference between S and ΔE is the cost of moving an electron from the copper electrode to a neutral chlorine ion in vacuum or the work function W_{Cu} of copper minus the electron affinity A_{Cl} of the chlorine atom:

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

We take $A_{\mathrm{Cl}} = 3.61$ eV [13] and $W_{\mathrm{Cu}} = 4.59$ eV [14] for the chlorine electron affinity and copper work function, respectively. The resulting Cl^- solvation energy is 11.1 eV, which is significantly larger than the experimental value of 3.63 eV [15].

To understand the origin of the error in the calculated Cl^- solvation energy, we calculated the radial distribution functions Cl–O and Cl–H (equivalent to the normalized densities of oxygen and hydrogen around the chloride ion) and the corresponding running coordination numbers surrounding the Cl large solvation shell for large z in the simulation, with the results shown in Figs. 7 and 8. In contrast to previous classical molecular dynamics and Monte Carlo studies [17] and experiments [18, 19] in which coordination numbers of 7.4 and 6, respectively, are reported, we find a value of 10.6 (Table III). Furthermore, in contrast to previous models, we find (Fig. 8) that both hydrogen atoms of each water molecule are at the same close distance to the chloride ion. To establish that this is the origin of the wrong solvation energy, we calculated the binding energy of one water molecule to the chloride ion using the same pseudopotentials and obtained 0.0455 hartree. Multiplying this by the coordination number

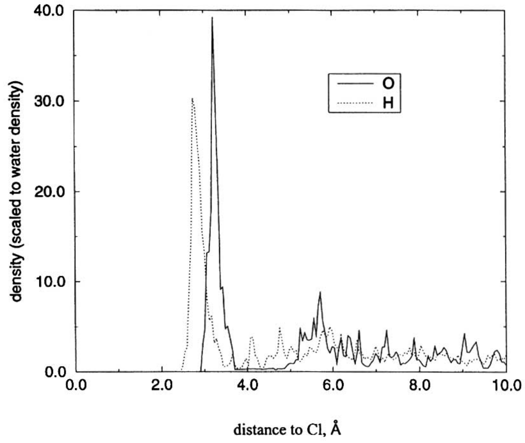

Fig. 7. Radial distribution functions for Cl–O and Cl–H.

10.6 which we obtain from the full simulation, we obtain an estimate of the solvation energy of 13 eV, which is 2 V higher than the solvation energy obtained in the full calculation. The difference is probably due mainly to repulsion between the water molecules. On the other hand, if we use a water chloride interaction energy obtained from the standard Gaussian 94 Hartree Fock code, we obtain a binding energy of -0.0197 hartree. Multiplying this by a coordination number of 6 (close to the experimental number) gives an estimate for the solvation energy of 3.2 eV, quite close to the

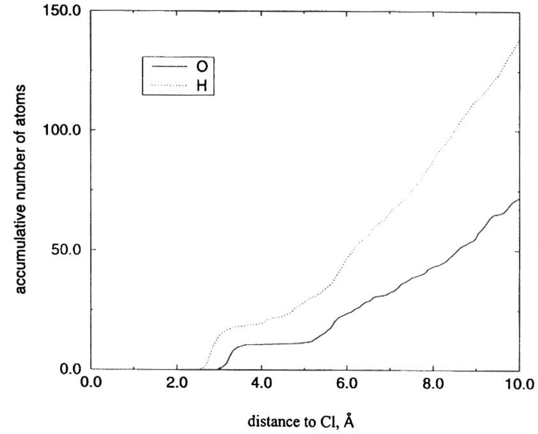

Fig. 8. Running integration of association numbers for O and H surrounding Cl.

Table III. The Geometry of the Cl Solvation Shell

	MD [16]	MC [17]	Present	X-ray [18]	Neutron diffraction [19]
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

experimental value. Thus, the error in the solvation energy arises as a result of the related facts that there are too many nearest-neighbor water molecules and each is too strongly bound in the model.

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 have explored the following possible origins of this difficulty: (1) the local pseudo-potential on the chloride ion should more properly be replaced by a nonlocal one, (2) the polarizability of the water molecule should be taken into account, and (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. Recently we have established that (3) is the origin of the incorrect solvation behavior and have developed an improved pseudo-potential for the hydrogen–electron interaction in the model which gives a greatly improved description of the solvation structure and energy. Details will appear elsewhere.

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