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Supporting Information

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## **Why Silver Deposition is so Fast: Solving the Enigma of Metal Deposition\*\***

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## Supporting Information

### Molecular dynamics simulations

Purely classical molecular dynamics were performed using the LAMMPS code [1]. The system consisted of a Ag(100) slab modeled by three layers (4.09 Å thickness), an ensemble of 470 water molecules, and the Ag<sup>+</sup> ion initially located in the bulk of the water. Periodic boundary conditions were used only in the  $xy$ -directions. The dimensions of the box were  $23.14 \times 23.14 \times 32.09$  Å<sup>3</sup>. The correction for the electrostatic long-range interactions was done by using a pppm/cg solver. The temperature was set to 300 K using the NVT canonical ensemble.

The following interactions were used: the parameters for the interaction between the water molecules with the silver surface have been taken from a previous work [2]; the interactions between the water molecules in the bulk and between the silver ion with the water were specified by well-established Lennard-Jones potentials. For the water, we used the SPC/E model and the corresponding parameters for the oxygen and hydrogen have been taken from Yoshida et al. [3]. The parameters for Ag<sup>+</sup>/O interaction have been taken from Spezia et al. [4]. The Weighted Histogram Analysis Method (WHAM) code developed by Grossfield [5] was used to obtain the potential of mean force from a series of umbrella sampling simulations. A total of 40 umbrella samplings were performed. First we carried out an equilibration run of 500 ps and then each sample ran for 200 ps, with a time step of 2.0 fs.

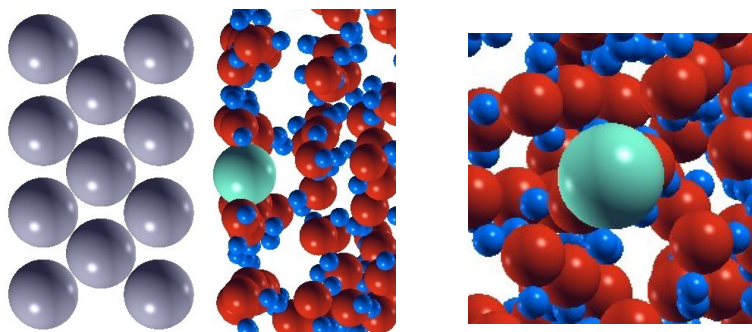


Figure 1: Snapshot of a Ag<sup>+</sup> ion positioned in the potential minimum near the surface. Left panel: side view; right panel: top view without the metal atoms.

Figure 1 show a snapshot from the molecular dynamics calculations for the case where the ion is at the minimum of the potential of mean force. As can be seen from the two views presented, at this position it is surrounded by a stable solvation cage.

## Technicalities of the DFT Calculations

All quantum chemical calculations were performed using the DACAPO code [6], which utilizes an iterative scheme to solve the Kohn–Sham equations of density functional theory self-consistently. A plane-wave basis set is used to expand the electronic wave functions, and the inner electrons were represented by ultrasoft pseudopotentials [7], which allows the use of a low energy cut-off for the plane-wave basis set. An energy cut-off of 400 eV, dictated by the pseudopotential of the metal, was used in all calculations. The electron–electron exchange and correlation interactions were treated with the generalized gradient approximation (GGA) in the version of Perdew, Burke and Ernzerhof [8]. The Brillouin-zone integration was performed using a  $8 \times 8 \times 1$   $k$ -points Monkhorst–Pack grid [9] corresponding to the  $(1 \times 1)$  surface unit cell. The surfaces were modeled by a  $(2 \times 2)$  supercell with four metal layers and eight layers of vacuum. Dipole correction was used to avoid slab–slab interactions [10]. The first two layers were allowed to relax, while the bottom two layers were fixed at the calculated nearest-neighbor distance. The optimized surfaces (pre-relaxed) in the absence of the Ag atom were used as input data to carry out the calculations to study the approach of the silver atom to the metal electrode. For each system, we performed a series of calculations for a single silver atom adsorbed on a four-fold hollow site, and varied its separation from the surface. The pre-relaxed surface was kept fixed while the Ag atom was allowed to relax in the  $xy$ -coordinates during these calculations. At each position we calculated the adsorption energy, and the DOS projected onto the 5s orbital of silver.

The energy to detach an atom from the kink site position and to move it to the terrace was obtained from the nudged elastic band method [11]. To perform this calculation the surface was modeled by a  $(4 \times 4)$  supercell with four layers. The top layer was used to create the defect. All other parameters are the same as for the DFT calculations.

## Interaction of the silver 5s orbital with the silver Ag(100) surface.

In order to understand the details of the interaction between the silver ion and the silver surface, we have calculated the density of states (DOS) of the Ag atom’s 5s orbital as it approaches the surface (see Fig. 2). Over the range shown in the figures, the atom is not spin-polarized. At larger distances the DOS is centered at the Fermi level and is half-filled, as is to be expected. However, even at a distance of 3.5 Å it is substantially broadened and exhibits a tail extending to lower energies caused by the interaction with the  $sp$  band. At a distance of 2.5 Å the DOS has already become very broad, and largely follows the  $sp$  band. The DOS of the adsorbed atom is very similar to the  $sp$  band, and shows the same peak near -5.6 eV with respect to the Fermi level. These densities of states show no visible inter-

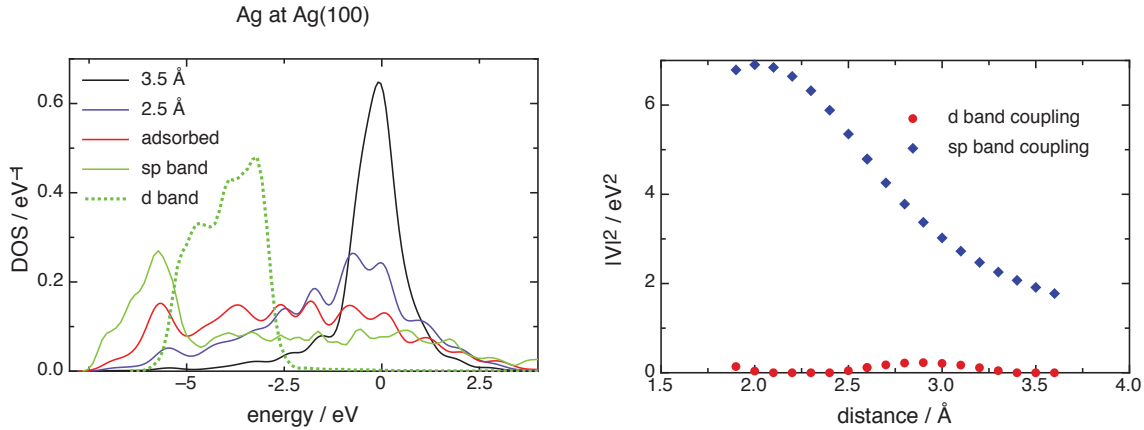


Figure 2: Left: Electronic density of states of a Ag atom at various distances from the Ag(100) surface; the Fermi level has been taken as the energy zero. Right: Coupling constants with the silver  $d$  and the  $sp$  bands.

action with the silver  $d$  band, which lies well below the Fermi level. From these DOS we evaluated the coupling constants, or rather their square  $|V|^2$ , of the 5s orbital with the  $sp$  and with the  $d$  band of silver (see Fig. 2). The coupling to the  $d$  band is very small, but the interaction with the  $sp$  band is very strong and long ranged.

### Interaction with the $d$ band

As noted in the main text, the 5s orbital of the silver atom interacts only very weakly with the  $d$  band of silver. However, the 4d orbital of the silver atom interacts with the silver  $d$  band, and there is some interest in studying this interaction. Figure 3 shows the density of states of a silver atom approaching a Ag(100) surface. When the atom is at a distance of 3 Å, its DOS is substantially broadened, and has roughly a Lorentzian shape. As expected, its center lies well below the Fermi level. When the atom is adsorbed, its  $d$  orbital merges with the  $d$  band of the substrate. Since all of the DOS lies well below the Fermi level, there is no sizable contribution of the  $d$  orbital to the adsorption bond.

### Calculation of the free energy surface

We consider only the 5s valence orbital of silver, which bonds to the silver surface. The problem is therefore equivalent to the adsorption of hydrogen on metals, for which we have developed our own theory [13]. The electronic part of the problem

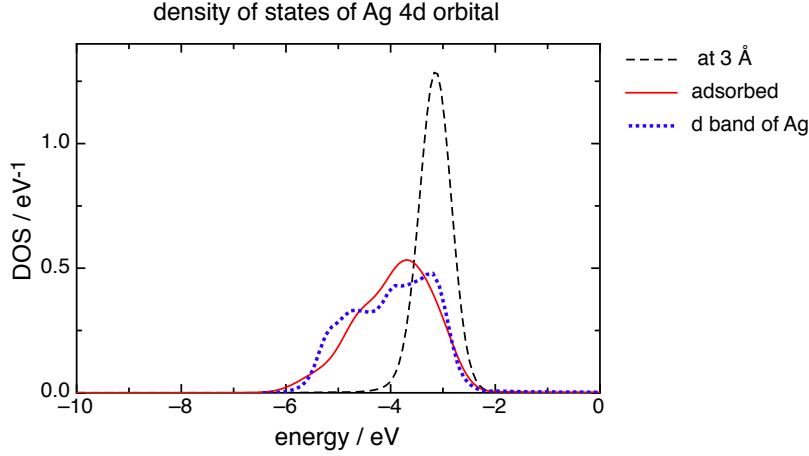


Figure 3: Density of states of a silver atom above a Ag(100) surface at a distance of 3 Å and in the adsorbed state.

is the same, but the treatment of the solvent is different. To make this supplement self-contained, we briefly state the Hamiltonian. We denote with the index  $a$  the silver 5s orbital, by  $\epsilon_a$  its energy, and by  $n_a$  the corresponding number operator; the metal states are labeled  $k$  and thus have energies  $\epsilon_k$  and number operators  $n_k$ . The reaction takes place so close to the surface that spin polarization plays no role. We can therefore write the electronic part of the Hamiltonian in the form:

$$H_{\text{el}} = \epsilon_a n_a + \sum_k \epsilon_k c_k + \sum_k [V_k c_k^\dagger c_a + V_k^* c_a^\dagger c_k] \quad (1)$$

The last term effects electron exchange between the metal and the reactant;  $c^\dagger$  denotes a creation and  $c$  an annihilation operator. Of course, the 5s orbital can take up two electrons.

The solvent terms of our Hamiltonian are:

$$H_{\text{sol}} = \frac{1}{2} \sum_\nu \hbar \omega_\nu (q_\nu^2 + p_\nu^2) + (1 - n_a) \sum_\nu \hbar \omega_\nu g_\nu q_\nu \quad (2)$$

where  $\nu$  labels the phonon modes,  $q_\nu$  and  $p_\nu$  are the dimensionless coordinate and momentum operators, and in the last term  $g_\nu$  is the interaction constant of the charge with the mode  $\nu$ ;  $n_a$  is the occupation operator for the 5s orbital of silver. After transformation to a single generalized solvent coordinate  $q$  and normalization these terms are transformed to [12]:

$$H_{\text{sol}} = \lambda(q^2 + p^2) + 2\lambda q(1 - n_a) \quad (3)$$

where  $\lambda$  is the energy of reorganization familiar from Marcus theory. In electron transfer theory, the solvent modes are divided into a slow (nuclear) part and a fast (electronic) part. The energy of reorganization comprises only the slow part. The interaction with the fast part is [13]:

$$V_f = (1 - \langle n_a \rangle) \lambda_f \quad (4)$$

where  $\lambda_f$  is the interaction energy with the fast part. Note that the fast part couples via the expectation value of the occupation operator  $n_a$ . The sum of the two terms gives the free energy of solvation:  $\lambda + \lambda_f = \Delta G_{\text{solv}}$ . The division in two parts is given by the Pekar factor, which for water is practically 1/2. Therefore we have set:  $\lambda = \lambda_f = \Delta G_{\text{solv}}/2$ . Our simulations give the free energy of solvation, and hence  $\lambda$  and  $\lambda_f$  as a function of the distance, and we have used these in the calculation of the free energy surfaces. Thus the rough estimates for  $\lambda$  as a function of the distance that we employed in our previous works have been replaced by the values calculated from molecular dynamics. Finally, the electrode potential couples to the charge on the reactant, and gives an extra term  $(1 - \langle n_a \rangle) e_0 \phi$ , where  $\phi$  is the potential difference between the potential in the solution and the metal.

The electronic part of the Hamiltonian can be solved by Green's function techniques familiar from Anderson-Newns theory. In particular, this gives a formal expression for the density of states (DOS) of the silver atom's 5s orbital in front of the silver surface. We obtain the electronic parameters of our model by fitting this expression to the DOS obtained from DFT.

While the Anderson-Newns model gives a consistent description of the system, it suffers from the neglect of many-body terms. To compensate for this defect, we calculate the energy of the silver atom as a function of the distance both from DFT and from our model. The difference  $\Delta E$  is the error of our model for an occupation of  $\langle n_a \rangle = 1$ , which is in equilibrium with a solvent configuration of  $q = 0$ . During the reaction the occupation changes from 0 to 1. We assume that the error in the electronic energy is proportional to the occupation of the valence orbital:  $\Delta E(q) = \Delta E(q = 0) \times \langle n_a \rangle$ . This linear interpolation is obviously correct for the two limits  $\langle n_a \rangle = 1$  and  $\langle n_a \rangle = 0$ .

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