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# A Model for Sequential First Order Phase Transitions Occuring in the Underpotential Deposition of Metals

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## Abstract

A model for the underpotential deposition of metals that occurs in stages is introduced. In this model the deposition takes place as a sequence of first order phase transitions of the adsorbate. In this application we study the underpotential deposition of Cu on a Au(111) surface in the presence of sulfate ions. The voltammogram of the deposition shows two sharp spikes which are reproduced by our model.

# 1 INTRODUCTION

Voltammograms<sup>1</sup> of underpotential deposited films on perfect single crystal surfaces contain sharp spikes.<sup>2-6</sup> Such spikes seem to occur also in polymer film formation.<sup>7-8</sup> In earlier work, we discussed the possibility of explaining these spikes as the result of first order phase transitions occurring in the surface.<sup>9,10</sup> There are a number of conditions that have to be met to obtain sharp spikes in the voltammogram. These include chemical equilibrium, the degree of perfection of the substrate (a single crystal in most cases), and the scanning rate of the voltammogram. Ideally the width of the voltammogram is due to diffusion processes,<sup>1</sup> so that slow scanning rates would be best to observe these spikes. The area under the spike is proportional to the change in coverage of the surface, which is not necessarily equal to the ideal coverage. As was discussed in earlier work,<sup>9,11</sup> second order phase transitions, such as the one occurring in the hard hexagon lattice gas model, are also possible. However, these transitions would be very hard to see in a voltammogram, because of the vanishingly small area of the spike associated with a second order transition.

We have recently studied a statistical mechanical model for adsorption on electrode surfaces that includes the lateral interactions of the adsorbates.<sup>9,10</sup> In this model we use exact results for two dimensional lattices that tell us when a first or a second order phase transition will occur. We also show that a first order phase transition corresponds to a sharp spike in the voltammogram.<sup>10</sup>

In some systems, more than one spike has been observed to occur in the voltammogram during the deposition process. In particular, a voltammogram with two sharp spikes has been observed during the underpotential deposition of copper on the (111) surface of gold in the presence of sulfate ions.<sup>2</sup> This system has been recently studied by a number of in-situ techniques.<sup>12-16</sup> While we do not have a complete and clear picture yet, the recent scanning tunnel microscope and atomic force microscope experiments seem to indicate that there is a  $\sqrt{3} \times \sqrt{3}$  structure that exists between the two underpotential deposition peaks at 0.07 and 0.22 volts. There seems to be evidence also that there is sulfate adsorption,<sup>17</sup> which undoubtedly plays an important role in the underpotential deposition. Unfortunately, careful measurements of the fraction of occupied surface are not at hand. A preliminary measurement of the relative area of the two spikes of the voltammogram seems to show

that this ratio is 1 to 2.<sup>18</sup> We have constructed a physically reasonable model which is consistent with the near edge EXAFS,<sup>11</sup> and which exhibits two first order phase transitions corresponding to a voltammogram with two spikes of this relative area. For a reasonable choice of parameters, it can be made to agree with the experimentally obtained one. Treating incommensurate structures such as the ones recently postulated<sup>12,13</sup> is certainly possible in our theory, but we could not use the simple and exact results of two dimensional lattices. Our model is simple and versatile, and can be adapted to other circumstances, such as different lattices or adsorption sequences.

## 2 THE MODEL

In our model for the underpotential deposition of Cu on Au(111) in the presence of high concentrations of sulfuric acid we assume that a well defined sequence of events takes place:

- First, the sulfate ions that are adsorbed form a  $\sqrt{3} \times \sqrt{3}$  lattice on the gold surface.
- Copper ions are then adsorbed on the free adsorption sites, which form a honeycomb lattice.
- Finally the adsorbed sulfate ions are replaced by copper ions .

We assume that the sulfate binds to the gold (111) surface in such a manner that the sulfur is directly on top of the adsorption site for the copper, three of the sulfate oxygens being above and directly associated with the three gold atoms of the surface, which form a triangle about the adsorption site. Packing considerations indicate that two sulfate groups cannot be adsorbed onto neighboring adsorption sites. The sulfate ions will thus form a  $\sqrt{3} \times \sqrt{3}$  film by occupying one of the three triangular sublattices  $\Lambda_T$  of the full triangular lattice of adsorption sites. One can show from statistical mechanics that an order-disorder transition will accompany this adsorption (or desorption) process. However, since there is no change in the adsorption coverage at the transition ( rather a change in the adsorption rate ), there should be no observable spike in the voltammogram. This type of  $\sqrt{3} \times \sqrt{3}$  sulfate film is illustrated in Fig. 1. The gold atoms are represented by large white disks, the adsorption sites by small black disks. Each adsorbed sulfate ion is represented by a set

of three lines centered at the adsorption site and ending at the three associated gold atoms. Each line represents a S-O bond. The vacant adsorption sites form a honeycomb lattice  $\Lambda_H$ .

As the potential bias becomes less positive, copper atoms will be adsorbed onto the surface and discharged. To model this deposition process, we construct a statistical mechanical model for the interaction of a solution of copper ions with a gold (111) surface which contains the  $\sqrt{3} \times \sqrt{3}$  sulfate film.

As was done before, the adsorption sites in the model are considered to be sticky points (to which atoms are either chemically bound or not) with a stickiness parameter  $\lambda_T$  for the sites on  $\Lambda_T$ , the triangular sublattice of adsorption sites which are associated with the sulfate groups, and with a stickiness parameter  $\lambda_H$  for sites on the vacant honeycomb sublattice  $\Lambda_H$ .

This sticky site model can be shown to be equivalent to a two dimensional lattice gas<sup>9, 19, 20</sup> of copper atoms which have a fugacity

$$z_T = \lambda_T \rho_1^0(0, \Psi) \quad (1)$$

if adsorbed on  $\Lambda_T$ , and a fugacity

$$z_H = \lambda_H \rho_1^0(0, \Psi) \quad (2)$$

if adsorbed on  $\Lambda_H$ . Here  $\rho_1^0(0, \Psi)$  is the number density of copper ions at contact with the surface under a potential bias  $\Psi$ . Here

$$\Psi = \beta \epsilon [\psi(0) - \psi_{pzc}], \quad (3)$$

where  $\epsilon$  is the elementary charge,  $\beta = 1/kT$ ,  $\psi(0)$  is the potential at the electrode surface, and  $\psi_{pzc}$  is the potential of zero charge. At 25°C

$$\Psi = 38.922V, \quad (4)$$

where  $V$  is the potential in volts. We approximate  $\rho_1^0(0, \Psi)$  as<sup>10</sup>

$$\rho_1^0(0, \Psi) = e^{-\beta \epsilon \Psi} \rho_1^0(0, 0), \quad (5)$$

where  $\tilde{z}_1 = 2$  is the electrovalence of the copper ions in solution. When two copper ions are adsorbed on sites  $i$  and  $j$ , separated by a distance  $r_{ij}$ , they interact in the equivalent lattice gas with an interaction energy which is equal to the potential of mean force

$$w(r_{ij}) = -kT \ln[g_2^0(r_{ij})]. \quad (6)$$

where  $g_2^0(r_{ij})$  is the pair correlation function of two copper atoms in the adsorption plane. We should remark that this pair correlation function is quite different from the pair correlation function of the copper ions in the bulk, since they already form part of the metal electrode.

We shall calculate the properties of the two dimensional lattice gas using the following simplifying assumptions: if two copper atoms are adsorbed on neighboring sites of  $\Lambda_H$ , their interaction energy is

$$w_H = -kT \ln[g_2^0(d)]. \quad (7)$$

and if they are adsorbed on neighboring sites of  $\Lambda_T$ , then they interact with an energy

$$w_T = -kT \ln[g_2^0(\sqrt{3}d)]. \quad (8)$$

Otherwise we shall assume that there is no interaction between adsorbates. This approximation decouples the adsorption process on the two sublattices, and consequently simplifies the calculation. ( We will include the interactions between atoms adsorbed on  $\Lambda_T$  and atoms adsorbed on  $\Lambda_H$  in a forthcoming publication.)

We shall now use some ideas introduced in Ref.(10) to calculate the adsorption isotherms for our model. We use the first 8 terms in the low  $z_T$  series approximation to the free energy<sup>21, 22</sup> to construct a Padé approximant to  $\theta_T$ , the fraction of sites of  $\Lambda_T$  which are occupied by copper atoms. This Padé approximant,  $\theta_{T,l}$ , is best at low  $z_T$  and is constructed to be the natural extension of the Langmuir isotherm which includes interactions between atoms adsorbed on neighboring sites. Using symmetry considerations we then construct a Padé approximant  $\theta_{T,h}$  which is best at high  $z_T$ . The explicit form of these Padé approximants is given in Ref.(10).

When the lateral interactions are turned off,  $g_2^0(\sqrt{3}d) = 1$  and both  $\theta_{T,h}$  and  $\theta_{T,l}$  are equal to the exact isotherm,  $\theta_T$ , which is, in this case, identical with Langmuir's isotherm.

The isotherm  $\theta_T$  is a smooth function of  $z_T$  for all values of  $g_2^0(\sqrt{3}d)$  which are less than the critical value 3.<sup>9</sup> For values exceeding 3, there is a first order phase transition with a corresponding jump in the fraction of occupied sites  $\theta_T$ .

In order to construct a single approximation to  $\theta_T$  which is valid for all values of  $z_T$ , we use a switching function

$$\eta(y_T, s_T) = (1/2)\{1 + \text{Erf}[(y_T - 1)s_T]\}, \quad (9)$$

where  $\text{Erf}$  is the error function, and

$$y_T = z_T^{-1} g_2^0(\sqrt{3}d)^{-3} \quad (10)$$

is a variable which becomes unity at the first order phase transition.<sup>9</sup> The parameter  $s_T$  is a measure of the sharpness of the switching function and is introduced in order to account for a variety of line broadening factors, especially diffusion and the degree of crystallinity of the surface, which are not included explicitly in our present treatment of the model. We then construct the single continuous approximation

$$\theta_T = \eta(y_T, s_T)\theta_{T,l} + [1 - \eta(y_T, s_T)]\theta_{T,h}. \quad (11)$$

In a similar fashion we use 8 terms in the low  $z_H$  approximation to the free energy of a lattice gas on the honeycomb lattice  $\Lambda_H$  to construct a Padé approximant  $\theta_{H,l}$  which is best at low  $z_H$  and a Padé approximant  $\theta_{H,h}$  which is best at high  $z_H$ . The fraction of sites of  $\Lambda_H$  occupied by copper atoms is then approximated as

$$\theta_H = \eta(y_H, s_H)\theta_{H,l} + [1 - \eta(y_H, s_H)]\theta_{H,h}. \quad (12)$$

where

$$y_H = z_H^{-1} g_2^0(d)^{-3/2} \quad (13)$$

is a variable which is unity at the phase transition of  $\Lambda_H$ .

The fractional coverage of the full lattice  $\Lambda_T \cup \Lambda_H$  is then given as

$$\theta = (2/3)\theta_H + (1/3)\theta_T. \quad (14)$$



The change in  $\theta$  at a phase transition is roughly equal to the measured area under the corresponding spike of the voltammogram.

As was discussed in our earlier work,<sup>10</sup> a phase transition will appear in the voltammogram as a sharp peak in the intensity  $I$ . If the scanning rate is constant and we neglect diffusion and double layer effects,<sup>1</sup> the intensity of the current in the voltammogram can be obtained by differentiation as

$$I(\Psi) = \frac{\partial \theta}{\partial \Psi} \frac{d\Psi}{dt}. \quad (15)$$

In Fig. 2 we show a voltammogram which is obtained using

$$\begin{aligned} \lambda_T \rho_1^0(0.0) &= 9.1. \\ \lambda_H \rho_1^0(0.0) &= 5.2 \times 10^5. \\ g_2^0(d) &= 14. \\ g_2^0(\sqrt{3}d) &= 3.1. \\ s_T &= 5. \end{aligned} \quad (16)$$

and

$$s_H = 2.$$

The intensity is given in units of the sweep rate  $|dV/dt|$ . This voltammogram is very similar to the one obtained experimentally for the underpotential deposition of copper on a (111) surface of gold in the presence of sulfuric acid.<sup>2</sup>

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## FIGURE CAPTIONS

Figure 1: The  $\sqrt{3} \times \sqrt{3}$  sulfate phase on the (111) face of gold. Gold atoms are represented by large white disks, the adsorption sites for sulfate and copper are depicted as small black disks, and the adsorbed sulfate groups are depicted as sets of three lines emerging from the adsorption sites to the neighboring gold atoms.

Figure 2: A voltammogram with two sharp peaks corresponding to two first order phase transitions in the model.

Figure 1

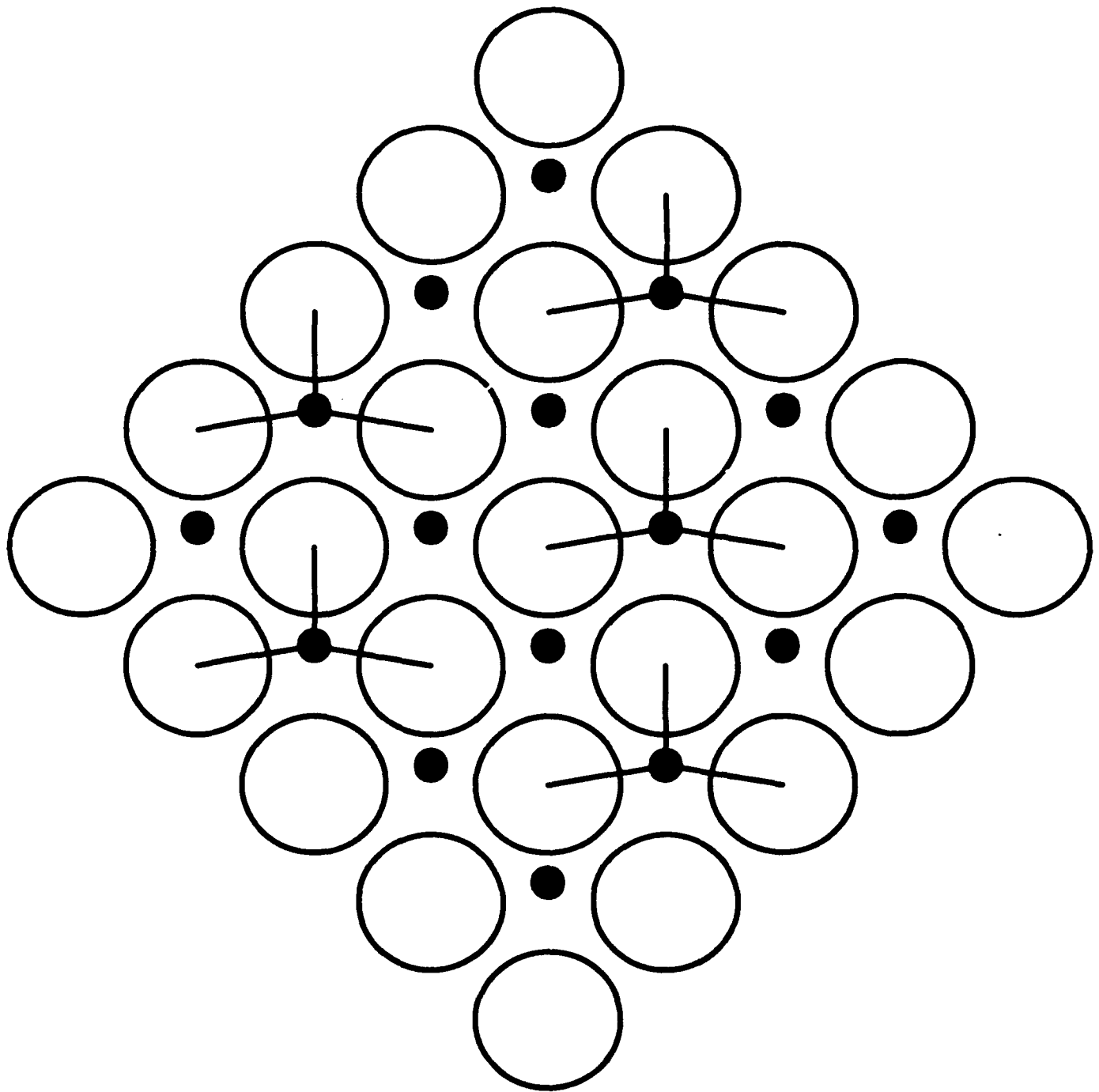


Figure 2

