First principles calculations of monolayer compressibilities

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October 26, 2018

Abstract

We perform high quality, first principles calculations of the properties of Pb and Tl isolated monolayers. Among these, we consider the equilibrium lattice constant, the two dimensional compressibilities and the electronic density. Comparison is made with previous results obtained using more simplified models. The present results represent an improvement concerning the calculated compressibilities; these remaining still lower than the measured values. We speculate that the latter could be due to some corrugation of the monolayer, not considered in the present modeling.

Keywords: work function, local pseudopotentials, density functional calculations.

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1 Introduction

The application of in-situ surface X-ray scattering techniques to the study of electrochemical systems has contributed to the elucidation of the structure of metal monolayers adsorbed at underpotential [1, 2, 3, 4, 5, 6]. Among these systems is particularly interesting the case of sp metals adsorbed at underpotential on dense substrate faces like Ag(111) and Au(111). In these cases, the adlayer presents an incommensurable structure, whose lattice constant varies with the applied electrode potential. The monolayer is built with a lattice constant which is smaller than that expected from the bulk structure. This contraction of the adsorbed monolayer has been theoretically explained by Leiva and Schmickler [12] by means of a jellium model with pseudopotentials, using the density functional formalism to write down the energy of the system. In the case of the detachment of a single slab from the bulk, it was found that the electronic density of the isolated layer expanded in the direction perpendicular to the lattice plane. This relaxation, concomitant with a decrease of the nearest neighbor distance between the ion cores in the slab, occurs because the absence of the ions of neighboring planes sitting on hollow sites reduces the electronic pressure in the direction perpendicular to the slab. In the case of the experiments, it was found that when the potential is shifted cathodically, more atoms are packed into the adsorbed monolayer, with the concomitant decrease of the lattice constant. From this experimental information, the 2D isothermal compressibility $K_{2D}$ is estimated to be in the range of 1.2 to 1.9 Å²/eV. A first estimation of this compressibility in terms of a free electron model yielded values in the order of 0.5 Å²/eV, that is, considerably lower than in the experiment. Recent calculations by Leiva and Schmickler [13] using a more sophisticated jellium-pseudopotential model also rendered values which were low as compared with the experiment. It is the purpose of this work to perform high quality, first principles calculations for some of the systems addressed above, which should clarify if the relatively low theoretical compressibilities are due to simplifications in the model or to some other aspects so far not taken into account. We consider here the cases of Pb and Tl, which are the systems for which a wealth of information exists.
Figure 1: Schematic illustration of the supercell geometry employed in this work in order to represent a single layer of a metal isolated in vacuum.

2 Model and calculation method

In these preliminary calculations we only consider a metal slab isolated in vacuum, which we contract isotropically, thus obtaining the energy as a function of the distance between nearest neighbors.

We performed two sets of calculations. One of them was performed by means of a computer code developed by one of us [14], which solves an effective one dimensional Schrödinger equation in the presence of averaged local pseudopotentials [15] within the density functional approach [18]. Within this model, which will be referred as 1-D model onwards, the electronic density is a function of the distance perpendicular to the metal surface. The other set of calculations was performed with the complex computer code fhi96md [8], developed at the Fritz-Haber-Institut by Scheffler and coworkers. In this case, the geometry actually corresponds to that of a periodic supercell as schematically shown in Figure 1 and the pseudo electronic density contains the full three dimensional features outside a selected core region. We shall refer to the results obtained by this method as those of the 3-D model. The geometry of the nuclei is contained in a supercell, which is periodically repeated as a lattice. Thus, the coordinates of a nucleus or its periodic image $R_i$ will be
\[ R_i = \tau_i + R \]

where \( \tau_i \) represents the position of nucleus “i” inside the supercell and \( R \) is a lattice vector. The compact surface structure subject of the present studies was represented by a simple hexagonal lattice. In order to ensure that the results of the calculation accurately represent an isolated surface, the vacuum region was varied and the convergence of the energy was monitored. We found that a distance of five times the distance between nearest neighbors is adequate for the present purposes. Since the features of the computational method are extensively described in the reference given above [8], we just give here a short comment on those aspects that are relevant for the present application. This program is also based on the density-functional formalism[18], where the variational problem of a many-particle Schrödinger equation is transformed into a variational problem of an energy functional \( E[n(r)] \), where we represent the electron density of the system with \( n(r) \), in short \( n \). The energy equation of the electronic system is then usually written as:

\[
E[n] = T_s[n] + E^H[n] + E^{e-nuc}[n] + E^{xc}[n] + E^{nuc-nuc}
\]

where \( T_s[n] \) is the functional describing the kinetic energy of a system of non interacting electrons with density \( n(r) \) , \( E^H[n] \) is the Hartree energy, calculated from the corresponding potential \( V_H(\vec{r}) \) and \( E^{xc}[n] \) is the so called exchange and correlation energy. In the present case we have used the so called local density approximation (LDA) to the exchange and correlation energy, which applies locally the results for the homogeneous electron gas obtained by Ceperley and Alder [9] in the parameterization of Perdew and Zunger [10]. The remaining terms correspond to the electron-nuclei (\( E^{e-n} \)) and nuclei-nuclei (\( E^{nuc-nuc} \)) electrostatic interaction. The electronic density \( n(r) \) is obtained through the self-consistent solution of the corresponding Kohn-Sham equations:

\[
\left[-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})\right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})
\]

where \( V_{ext}, V_H \) and \( V_{xc} \) are the external potential, the Hartree and the exchange-correlation potentials respectively, which are given by:

\[
V_H(\vec{r}) = \int d\vec{r} n(\vec{r}) \frac{n(\vec{r})}{|\vec{r} - \vec{r}'|}
\]
and

\[ V_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)} \]

Thus, \( n(r) \) is given by:

\[ n(r) = \sum_{i}^{occ} f(i) |\psi_i(r)|^2 \]

where \( f(i) \) is the occupation number of state \( i \). Instead of considering the whole electronic system for the calculation of the properties of the slab, the effect of the core electrons and the nuclei on the valence electrons were replaced by suitable pseudopotentials, constructed according to the schemes of Hamann [16], which were generated and tested for their transferability [17] using the code developed by Fuchs et al. [19]. This involves checking for the absence of ghost states, which may appear as consequence of using Kleinman and Bylander [20] fully separable ab initio potentials and monitoring the logarithmic derivatives of the solution radial Schrödinger equation at energies close to that of the selected reference state.

3 Chemical potential. Equilibrium condition.
Compressibility

When referred to the bulk deposition potential of metal \( A \), the potential \( \Phi(\Theta) \) at which a certain coverage of \( A \) on a substrate \( S \) is obtained can be written as [21]:

\[ \Phi(\Theta) = \mu_{A,A} - \mu_{A,S}[\Theta] \] (1)

where \( \mu_{A,A} \) and \( \mu_{A,S}[\Theta] \) denote the chemical potentials of the \( A \) atoms in the bulk phase and when are adsorbed on \( S \) respectively. We stress the fact that this latter quantity is a function of the coverage degree. In the usual electrochemical potentiostatic experiment, a given potential is usually set and a coverage degree is thus obtained. The calculations follow the reverse order. In this case a certain configuration (coverage degree, nearest neighbor distance) of the system is considered, and the chemical potential \( \mu_{A,S}[\Theta] \) (and thus the potential) can be calculated.

For the discussion below, we remind the fact that we are calculating the ground state properties of an electron gas (\( T=0 \)), so that our free energies are obtained from energy calculations of the system. If we denote with \( F_{A,S} \)
the free energy of the substrate/adsorbate system, $\mu_{A,S}[\Theta]$ can be calculated from:

$$\mu_{A,S}[\Theta] = \frac{\partial F_{A,S}}{\partial N_A}$$

(2)

where $N_A$ represents the number of adsorbed atoms of type A and constant temperature, area and volume are assumed for taking this derivative. Eq. 2 can be also written in terms of the free energy per unit surface $F_{A,S}^s = F_{A,S}/S$ and the atomic surface $a$:

$$\mu_{A,S}[\Theta] = \frac{\partial F_{A,S}/S}{\partial N_A/S} = \frac{-a^2 \partial F_{A,S}^s}{\partial a}$$

(3)

A simple relationship between the chemical potential $\mu_{A,S}[\Theta]$ and the binding energy per atom $E_{A,S}^s$ can thus be obtained by considering that in the present case $F_{A,S}^s = E_{A,S}^s$. Eq. 3 turns into:

$$\mu_{A,S}[\Theta] = -a^2 \frac{\partial E_{A,S}^s}{\partial a}$$

(4)

This equation could also have been formulated in terms of the binding energy per adsorbate atom $E_{\text{bind}}$, which can be calculated from $E_{A,S}^s$ and the corresponding energy per unit surface of the pure substrate $E_{S}^s$ according to

$$E_{\text{bind}} = a(E_{A,S}^s - E_{S}^s)$$

(5)

In the present calculations $E_{A,S}^s$ will be considered to be equal to the energy per unit surface of the isolated slab, since the contribution of the substrate will be ignored.

Using now eqs. 4 and 5 we obtain :

$$\mu_{A,S}[\Theta] = E_{\text{bind}} - a \frac{\partial E_{\text{bind}}}{\partial a}$$

(6)

All chemical potentials and binding energies reported in this paper have been referred to the energy of the ion cores and the valence electrons infinitely separated from each other. The corresponding values referred to the energy of neutral atoms can be obtained by adding the proper ionization energies.

We now turn to analyze the equilibrium condition in order calculate the lattice constant of the adsorbed monolayer. The pressure of a thermodynamic system can be calculated from:

$$P = -\frac{dE}{dV}$$

(7)
where $E$ and $V$ are the energy and the volume of the system respectively. The constant entropy restriction was left out because we are considering the zero temperature case. In the case of three-dimensional solids, setting in this equation $P = 0$ provides a way of predicting the density of a metal if an expression for $E$ is available [22]. In the present case, where we are considering the isotropic compression of an adsorbed monolayer, it is suitable to state the problem in terms of the area as the extensive coordinate and its conjugate force, usually called spreading pressure [23], that we denote with $\phi$. Thus, in the zero temperature case the analog of eq. 7 becomes:

$$\phi = -\frac{\partial E}{\partial S}$$

(8)

where constant temperature and volume are assumed for taking this derivative. Thus, we shall employ the condition:

$$\frac{\partial E_{\text{bind}}}{\partial a} = 0$$

(9)

to predict the equilibrium lattice parameter of the monolayer.

The 2D isothermal compressibility of the Tl monolayer was calculated according to the usual definition [23]:

$$\kappa_{2D} = -\left(\frac{\partial a}{\partial \mu}\right)_T$$

(10)

which is the same as that employed by Toney et al. [7] to get the experimental values from the dependence of $a_{nn}$ on the applied potential.

## 4 Results and discussion

In addition to the logarithmic derivatives and the hardness monitoring, a further test of the transferability of the pseudopotentials that is usually performed consists in calculating the equilibrium lattice constant and bulk modulus of the metal considered. We performed these calculations for Pb and Tl, obtaining the results given in Table 1. As can be seen from the comparison with the experimental values found in the table the agreement is very good, not only in the lattice constant but also in the bulk modulus.

Energy calculations as a function of the nearest neighbor distance $a_{nn}$ for Pb and Tl isolated slabs are shown in Figure 2. The $a_{nn}$ values at the
Figure 2: Energy as a function of the distance between nearest neighbors for single Pb and Tl monolayers isolated in vacuum. Results obtained with local pseudopotentials, 1-D model a)Pb, b)Tl. Results obtained with non-local pseudopotentials, 3-D model, c)Pb, d)Tl.
minimum, along with the compressibility $K_{2D}$ obtained through numerical differentiation of these results are shown in Table 2. For the sake of comparison, we show in both cases the results obtained by means of the self-consistent calculation employing local pseudopotentials and the one-dimensional solution of the effective Schrödinger equation. The curves obtained with the local pseudopotentials show a steeper increase of the energy in the neighboring of the energy minimum, which is the reason for the outcoming relatively low compressibilities. As discussed below, the stiffness of the one-dimensional model may be understood in terms of a lack of relaxation of the electronic density in the direction parallel to the surface. In this respect, the introduction of the real three dimensional structure of the electronic density brings a considerable improvement over the calculated compressibilities.

Figure 3 illustrates some differences concerning the electronic density that appear between the 1-D model and the more sophisticated 3-D model calculations. In the case of the 3-D model, the electronic density was averaged in the direction parallel to the surface (say, the x-y plane) and a one-dimensional electronic density was obtained according to:

$$n(z) = \frac{\int \int n(x, y, z)dx dy}{\int \int dx dy}$$  \hspace{1cm} (11)$$

It is observed that while the nonlocal pseudopotentials concentrate more electronic density on the center of the metal slab, the Ashcroft -empty core-
Figure 4: a) Contour lines of the electronic density within a Pb surface unit cell. b) Contour plots of the electronic density in a plane perpendicular to the surface unit cell, containing two nearest neighbor atoms. c) Plot of the electronic density in the line joining two atoms in surface unit cell as shown in the inset $\rho_{\text{mean}}$ indicates the average electronic density of bulk Pb. Thick point dashed lines in the contour plots show the isoelectronic line corresponding to the value of the average valence electronic density of the bulk metal.
pseudopotentials show a depletion there. On this basis only, and thinking in terms of a free electron gas, it could appear that the Ashcroft pseudopotentials should yield a higher compressibility, since the electron gas with the lower electronic density should yield the higher compressibility [24]. However, the results of the computations can be understood if we consider the electronic density in the x-y plane, as shown in Figure 4a, where we have plotted the contour lines of the electronic density within the layer. Figure 4b shows similar contour plots for a plane perpendicular to the x-y plane, containing two nearest neighbor atoms. Figure 4c shows a plot of the electronic density in the line joining two atoms in surface unit cell as shown in the inset. It can be appreciated that the electronic density *in-between* the atoms is lower than the average electronic density $\bar{n}$, thus producing a concomitant higher compressibility of the layer as compared with that of a homogeneous electron gas with density $\bar{n}$.

Figure 5 shows the nearest neighbor distance as a function of the chemical potential, calculated according to the formulation of the previous section. The chemical potentials are referred to the chemical potential of the layer for $\phi = 0$. These curves are the theoretical analog of the experimental nearest-neighbors vs potential curves. Note that the Tl curves show a larger curvature, a fact which is in qualitative agreement with the experimental findings. These curves should actually not be attainable from the electrochemical experiment for $(\mu - \mu_{eq}) > 0$, since this would correspond to a negative $\phi$ (stress) of the monolayer, which would produce an exponential

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**Figure 5:** Nearest neighbor distance between the atoms in the monolayer as a function of the chemical potential, a) Tl, b) Pb.
increase of the number of defects and thus the breakdown of the monolayer.

5 Conclusion

While the present theoretical compressibility values are in qualitative good agreement with other previous estimations and show an important improvement towards agreement with the experiment, they are still too low as compared with the measured values. Although the presence of a substrate may deliver some contribution to the compressibilities, we expect that an adsorbed monolayer should be even less compressible than an isolated one, because of the contribution of the valence electrons of the substrate. Thus, we think that the relatively high compressibility values measured may be related to some other aspect of the experiment so far not taken into account. A small corrugation of the monolayer under compression could explain this fact. This should be considered in the future modeling of these systems.

6 Acknowledgments

All calculations were done in a DIGITAL AlphaStation workstation donated by Alexander von Humboldt Foundation (Germany). A fellowship (C.S.) and financial support from the Consejo de Investigaciones Científicas y Técnicas de la Provincia de Córdoba, financial support from the Consejo Nacional de Investigaciones Científicas y Técnicas, the Secretaría de Ciencia y Técnica de la Universidad Nacional de Córdoba and language assistance by Pompeya Falcón are also gratefully acknowledged.
Table 1: Comparison between the theoretical predictions and the experimental results for the lattice constant and the compressibility of the bulk metal. The experimental results were taken from ref. [25]. We find a theoretical $c/a$ ratio for Tl of 1.6; the experimental value is 1.599.

| Metal | $a(\text{th})/\AA$ | $a(\text{exp})/\AA$ | $B(\text{th}) \times 10^{-12} \text{ dyn/cm}^2$ | $B(\text{exp}) \times 10^{-12} \text{ dyn/cm}^2$ |
|-------|---------------------|----------------------|--------------------------------|--------------------------------|
| Pb    | 4.98                | 4.95                 | 0.530                           | 0.488                           |
| Tl    | 3.47                | 3.46                 | 0.344                           | 0.359                           |
Table 2: Nearest neighbor distance values ($a_{\text{min}}$) and 2D compressibilities $K_{2D}^{\text{min}}$ obtained at the minimum of the energy vs nearest-neighbor curve. The theoretical values correspond to the one-dimensional (th1) and to the three-dimensional (th2) calculation respectively. The experimental values (exp) were taken from ref. [6] and correspond to the adsorption of the metals on Ag(111) and Au(111) surfaces.

| Metal | $a_{\text{min}}^{(\text{th1})}/\text{Å}$ | $a_{\text{min}}^{(\text{th2})}/\text{Å}$ | $a_{\text{nn}}^{(\text{exp})}/\text{Å}$ |
|-------|----------------------------------|----------------------------------|----------------------------------|
| Pb    | 3.314                            | 3.271                            | 3.33-3.43                        |
| Tl    | 3.349                            | 3.212                            | 3.39-3.50                        |

| Metal | $\kappa_{2d}^{\text{min}}^{(\text{th1})}$ | $\kappa_{2d}^{\text{min}}^{(\text{th2})}$ | $\kappa_{2d}^{(\text{exp})}$ |
|-------|----------------------------------|----------------------------------|----------------------------------|
| Pb    | 0.48                             | 0.53                             | 1.52-1.88                        |
| Tl    | 0.28                             | 0.72                             | 1.25-1.69                        |
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