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First-principles calculations of the screening of electric fields at the aluminium(111) and (110) surfaces

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Abstract. Using a self-consistent pseudopotential technique we calculate the distribution of screening charge at the Al(111) and (110) surfaces with perpendicular applied electric fields of up to $5 \text{ V } \text{\AA}^{-1}$ (with the metal charged positively). With increasing magnitude of the field the centre of gravity of the screening charge (the electrical surface) moves into the metal, although much less so than for the jellium model at the corresponding density. The major peak in the screening charge density profile narrows as the field is increased, in qualitative agreement with the results for the jellium model at a similar density and range of applied fields.

1. Introduction

The physics of metal surfaces under applied electric fields is relevant to a number of experiments and phenomena such as field ion and field emission microscopy, scanning tunnelling microscopy, second-harmonic generation and metal/electrolyte interfaces. Classically an applied field is perfectly screened at the surface and the response of the system may be idealized as the formation of an induced surface charge density at the interface. At the atomic level the screening charge density is not distributed homogeneously over the metal surface, and perpendicular to the surface it is spread out over a region which is a few Ångströms thick.

There have been a number of self-consistent calculations of the potential and screening charge density at metal surfaces including the effects of applied electric fields. The first such calculations were performed by Lang and Kohn [1], who studied jellium surfaces. Work on jellium models has continued with self-consistent studies by Gies and Gerhardt [2], Schreier and Rebentrost [3], and Weber and Liebsch [4], as well as a number of non-self-consistent calculations. Serena *et al* [5] studied a modified jellium model which included the planar average of the ionic pseudopotentials, thereby, capturing some of the effects of the ionic lattice while retaining the simplicity of solving only one-dimensional equations for the electronic structure of the surface. There have been rather few self-consistent calculations including the full three-dimensional nature of the problem. The first such calculation appears to have been that of Ho *et al* [6], who studied the Ag(110) surface (a more recent calculation for this surface was performed by Fu and Ho [7]). Calculations for the Ag(001) surface have been performed by Kolb *et al* [8] and by Aers and Inglesfield [9]. Some calculations for aluminium surfaces have been reported: by Inglesfield for the Al(001) surface [10], and by Finnis for the Al(111) surface [11].

Very recently some calculations have been performed including applied electric fields for surfaces with adatoms [12].

We have performed calculations for the Al(111) and (110) surfaces, including applied electric fields of up to 5 V \AA^{-1} (with the metal charged positively). The main purpose of this work was to study the tunnelling process which generates positive ions in the field ion microscope. The electron potentials obtained from these calculations were used to calculate the electron tunnelling rate from an imaging inert gas atom into the metal surface [13]. These calculations also give a wealth of data about the linear and non-linear response of the surfaces to the applied field, and it is the purpose of this paper to describe and discuss this information.

2. Theory of electrical surfaces

Consider a model of a semi-infinite conductor with a smooth surface, such as the standard jellium model, and let z be the coordinate normal to the surface. Suppose that an electric field of magnitude F is applied perpendicular to the surface. This field is perfectly screened by the formation of a layer, close to the physical surface, of screening charge whose areal density has magnitude $F/4\pi$. Suppose we define the electrical surface to be the plane at z_0 at which the electric field appears to originate. The meaning of this definition becomes clear on studying figure 1. The screening charge is present only in the region between z_A and z_B close to the physical surface. Deep inside the bulk (to the left of z_A in figure 1) the potential can be taken to be zero, and far to the right of z_B the potential is $F(z - z_0)$, where z_0 is yet to be determined. Suppose that the change in the potential across the region where the screening charge exists is ΔV , then from figure 1 we immediately see that the position of the electrical surface z_0 is given by

$$z_0 = z_B - \Delta V \partial z / \partial V \quad (1)$$

where the derivative in the second term on the right-hand side of equation (1) is taken in the region to the right of z_B so that

$$\partial V / \partial z = F = 4\pi \int_{-\infty}^{\infty} \rho(z) dz \quad (2)$$

where $\rho(z)$ is the screening charge density, and we have used the fact that the screening charge density is non-zero only between z_A and z_B in setting the upper limit of the integral to infinity. The change in the potential across the screening charge density is found by integrating Poisson's equation:

$$\Delta V = 4\pi \int_{-\infty}^{z_B} \int_{-\infty}^{z''} \rho(z') dz' dz'' \quad (3)$$

Performing the z'' integration in equation (3) by parts and using equations (1) and (2) yields

$$z_0 = \int_{-\infty}^{\infty} z \rho(z) dz / \int_{-\infty}^{\infty} \rho(z) dz \quad (4)$$

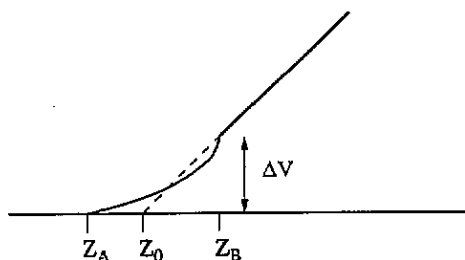


Figure 1. The electrostatic potential in the direction perpendicular to a semi-infinite conductor with an applied electric field. The screening charge density is non-zero only in the region between z_A and z_B . Deep in the bulk of the conductor (to the left of z_A) the potential is taken to be zero. Far out in the vacuum region (to the right of z_B) the potential has the form $F(z - z_0)$, where z_0 is the position of the electrical surface. ΔV is the potential step across the region where the screening charge density is non-zero.

so that the plane at z_0 at which the electric field appears to originate is identical to the centre of gravity of the screening charge density.

We now turn our attention to the case of surfaces with regular atomic structure, for which the screening charge density is a periodic function within the surface plane. By Fourier transforming Poisson's equation within the surface plane we can see immediately that the electrostatic potential due to the in-plane variations in the screening charge density falls off exponentially on either side of the layer of screening charge. Therefore the above arguments concerning z_0 are unaffected and the results hold for the case of a regular lattice of ions as well as for jellium type models.

The results given above were previously obtained by Lang and Kohn [14], although our presentation is a little different from theirs. Our simple derivation stresses the point that the equivalence of the definitions of the electrical surface as the centre of gravity of the screening charge density and the plane of origin of the electric field holds for any strength of the uniform electric field and whether a lattice of atoms is present or not.

3. Self-consistent pseudopotential calculations for Al(111) and (110) surfaces

The details of our calculations are identical to those given in [13], and here we give only a brief summary. We used a self-consistent pseudopotential technique to calculate the screening charge density at Al(111) and Al(110) surfaces, including perpendicular applied electric fields of up to 5 V \AA^{-1} (with the metal charged positively). For both the Al(111) and (110) surfaces we used a supercell technique with a unit cell containing a slab of metal consisting of six atomic layers of Al, and the equivalent of six layers of vacuum. We quote results for the distribution of screening charge only for the case where the atomic positions are chosen to be those of truncated bulk aluminium, i.e. without surface relaxation, although we will give a brief discussion of the effects of surface relaxation. The potentials and valence electron wavefunctions were expanded in a plane wave basis set containing all waves up to 9 Ryd in energy. Brillouin zone integrations were performed by sampling on regular grids in reciprocal space, containing 384 sampling points in the zone for the (111) surface calculations and 160 points for the (110) case. We

employed the Ceperley–Alder form of the local-density approximation (LDA) for the exchange–correlation potential [15], and for simplicity we used a local pseudopotential to represent the Al^{3+} ions, which had been successfully in previous calculations [16]. The electric fields were included by adding a thin sheet (with a Gaussian profile of width 0.529 \AA) of negative charge in the centre of each vacuum region, and varying the position of the Fermi level in the metal until charge neutrality was obtained for the unit cell as a whole. Consequently the potential and charge density in the centre of the metal slab are hardly disturbed from those of the bulk form while the external electric field is fully screened by the build up of screening charge at the surfaces, which occurs via a depletion of electrons. The Friedel oscillations in the electronic and screening charge density are quite weak for a metal of the density of aluminium ($r_s = 2.07$) and their truncation due to the finite thickness of the slabs is not expected to affect our results significantly.

4. Results and discussion

In [13] we gave contour maps of the screening density for the Al(111) and (110) surfaces with a field of 2 V \AA^{-1} , which show that the screening charge tends to build up on top of the surface atoms, as was previously found by Inglesfield for the Al(001) surface [10]. The planar averages of the screening charge density show similar features to those for jellium surfaces given in [1–3], and therefore we will not reproduce them here.

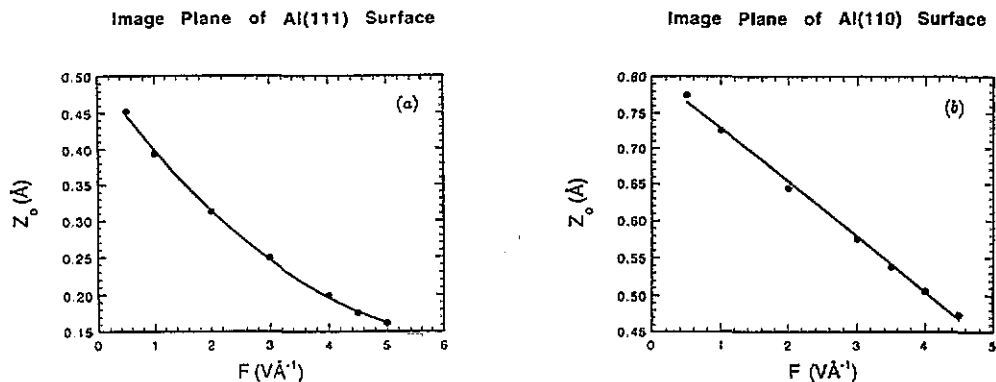


Figure 2. The position of the electrical surface, z_0 , plotted against the magnitude of the applied field for (a) the Al(111) surface, and (b) the Al(110) surface. z_0 is measured with respect to the geometrical surface (see text). The full curves indicate the results of equations (5) and (6).

In figure 2 we plot the position of the centre of gravity of the screening charge density as a function of the applied electric field for the Al(111) and (110) surfaces. The data for the (111) surface are well fitted by a quadratic form

$$z_0 = 0.50 - 0.11F + 0.0085F^2 \quad (5)$$

where z_0 is measured in \AA outwards from the geometrical surface, which is defined to be one half of the interplanar separation ($d_{111} = 2.34 \text{ \AA}$) outside the top layer

of atomic nuclei. The field F is measured in V \AA^{-1} and the sign convention is that positive F corresponds to charging the metal positively. The data for the (110) surface show some curvature but are reasonably well fitted by the linear relation

$$z_0 = 0.80 - 0.075F \quad (6)$$

where again z_0 is referred to the geometrical surface and $d_{110} = 1.43 \text{ \AA}$. The use of a linear fit results in a zero-field position of z_0 which is a little too close to the surface and in a slight underestimate of the magnitude of the linear coefficient, but the quadratic coefficient is much smaller than for the (111) surface and we have chosen to neglect it in this case.

The zero-field value of z_0 for the (111) surface is in reasonable agreement with the value of $z_0 = 0.43 \text{ \AA}$ due to Finnis [11], which was obtained by calculating the potential energy of a point charge outside of the surface and extrapolating to the value for a vanishingly small charge. Because of the significant positive quadratic term in equation (5) the extrapolation procedure used by Finnis is likely to underestimate the true zero-field value of z_0 . Inglesfield [10] has calculated z_0 for the Al(001) surface and obtained a value of $z_0 = 0.58 \text{ \AA}$ with an applied field of 0.514 V \AA^{-1} . Our results for the (111) and (110) surfaces suggest that the zero-field result should be only slightly further from the surface (about 0.05 \AA) than this value. The zero-field value for z_0 for jellium at a density of $r_s = 2$, which is close to that of aluminium, is $z_0 = 0.85 \text{ \AA}$ [1, 3, 4] and therefore, as noted previously by Inglesfield [17], the atomic structure of the surface pulls the electrical surface inwards with respect to the jellium value.

There is some evidence that the position of z_0 is tied not to the geometrical edge but to the position of the outer layer of atomic nuclei [5, 11, 18, 19]. Using our data along with those of Inglesfield [10] we can test this conjecture for the Al(111), (110) and (001) surfaces. When referred to an origin on the outermost plane of nuclei we have

$$z'_0(111) = 1.67 \text{ \AA} \quad z'_0(110) = 1.52 \text{ \AA} \quad z'_0(001) = 1.59 \text{ \AA} \quad (7)$$

The near equality of these values is further evidence to support the above conjecture. Serena *et al* [5] calculated the position of the electrical surface at Al(111), (110) and (001) surfaces using a self-consistent LDA technique and a modified jellium model which included the planar average of the ionic pseudopotentials. Their result for the positions of the electrical surfaces referred to an origin on the outermost nuclei are also only weakly dependent on the surface orientation, but their numerical values are shifted outwards from ours by about 0.17 \AA .

The field dependence of the distribution of screening charge is related to the phenomenon of second-harmonic generation at surfaces [4]. An important quantity is the dependence of the position of the electrical surface on the magnitude of the applied field. Calculations of this dependence were reported in [2-4] for jellium, but the only previous calculation for a surface with atomic structure that we are aware of was by Aers and Inglesfield [9] for the Ag(001) surface. Our results show that for both the (111) and (110) surfaces the electrical surface moves inwards with increasing magnitude of the applied field. For jellium at a density of $r_s = 2$ Weber and Liebsch [4] obtained a coefficient of linear variation of z_0 with applied field of $-0.20 \text{ \AA}^2 \text{ V}^{-1}$, which is significantly larger in magnitude than the values of $-0.11 \text{ \AA}^2 \text{ V}^{-1}$ and

$-0.075 \text{ \AA}^2 \text{ V}^{-1}$ that we have found for the Al(111) and (110) surfaces. This indicates that the atomic structure of the surfaces results in screening charge densities which are much stiffer than the corresponding jellium model. A similar result was found previously by Aers and Inglesfield [9] for the Ag(001) surface; they obtained a linear coefficient which was about three times smaller than the value for jellium at a density of $r_s = 3$. Aers and Inglesfield proposed that this difference is due to the exclusion of the screening charge density from the ion cores, which therefore tends to pin the screening charge. It would be interesting to perform calculations on the planar averaged pseudopotential model used by Serena *et al* [5] to see whether it gives screening charge densities of greater stiffness than the jellium model.

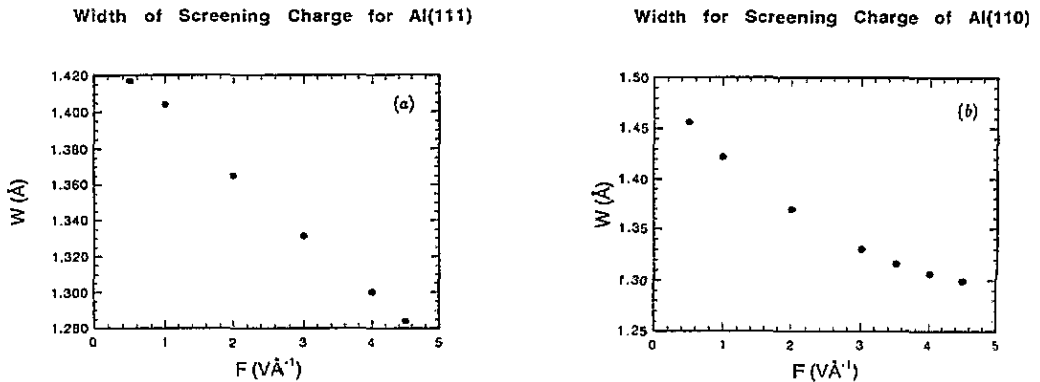


Figure 3. The full width at half maximum of the major peak in the screening charge density plotted against the magnitude of the applied field for (a) the Al(111) surface, and (b) the Al(110) surface.

The optical properties of a charged metal surface are dependent upon the width of the layer of screening charge. In figure 3 we give the full width at half maximum (FWHM), W , of the first peak in the screening charge density, in which the majority of the screening charge resides, as a function of the applied field, for the (111) and (110) surfaces. In each case W decreases with increasing field; for the (111) surface W falls essentially linearly with the field, while for the (110) surface the curve falls less rapidly at high fields. It might seem surprising that W decreases with increasing field, and indeed the asymptotic behaviour at extremely large fields must be that W increases with field; however it is clear that we are very far from this asymptotic regime. Our results are in qualitative agreement with the jellium results of Gies and Gerhardt [2]. For $r_s = 2$, which is close to the average valence density of aluminium, they found that W decreased from 1.501 \AA at a field of 0.91 V \AA^{-1} to 1.427 \AA at a field of 2.73 V \AA^{-1} .

It is interesting that our results show that W falls less rapidly at high fields for the (110) surface than for the (111) surface. The distribution of screening charge density over the surface is not uniform, and the screening charge tends to build up on top of the surface atoms. Because the density of atoms within the surface layer is smaller for the (110) surface than the (111) surface the build up of screening charge on top of the surface atoms will be larger for the (110) surface. This effect can be seen in the plots of the screening charge density for the Al(111) and (110) surfaces with a

field of 2 V \AA^{-1} shown in figure 3 of [13]. We might say that at a fixed applied field the effective electric field felt by an atom in the (110) surface is greater than that felt by an atom in the (111) surface. The larger accumulations of screening charge density for the (110) surface appear to bend around the atomic nuclei, indicating that they are inhibited from penetrating further into the surface rather more than is the case for the (111) surface. It seems likely that this effect is due to the exclusion of the screening charge from the ionic cores mentioned earlier.

It is worth mentioning that the applied field and screening charge density exert forces on the atomic nuclei, which cause relaxations of their positions. Dramatic effects can result at a metal–vacuum interface; for instance a large electric field may remove atoms from the surface in a process known as field evaporation, which has been observed in field ion microscope experiments. The low-temperature evaporation field of aluminium is approximately 3.3 V \AA^{-1} [20], and therefore some of the calculations reported in this paper are for fields at which the surfaces considered are not stable! We have performed a number of calculations for both the Al(111) and (110) surfaces with applied electric fields and incorporating full relaxation of the positions of the atomic layers in the slab. The results show that the slab dilates with increasing field, but the electrical surface, when measured with respect to the position of the outermost atomic layer is almost unaffected by these relaxations, which gives further evidence that the position of the electrical surface is tied to the positions of the surface atomic nuclei.

5. Summary

We have performed self-consistent plane wave pseudopotential calculations of the screening charge density for the Al(111) and (110) surfaces with perpendicular applied electric fields of up to 5 V \AA^{-1} (with the metal charged positively). The screening charge density piles up on top of the surface atoms. The density of surface atoms is lower for the (110) surface and consequently, for a fixed applied field, the effective electric field felt by an atom in the (110) surface is greater than that felt by an atom in the (111) surface. With increasing magnitude of the applied field the centre of gravity of the screening charge density moves deeper into the metal, but much less so than for the corresponding jellium model. For the (111) surface this effect is strongly non-linear in the applied field, whereas it is much less so for the (110) surface. The centre of gravity of the screening charge density appears to be pinned to the position of the outer layer of atomic nuclei rather than the geometrical surface (equivalent jellium edge). The major peak in the screening charge density profile narrows as the field is increased, in qualitative agreement with the results for jellium surfaces in this range of fields; however, at very high fields the width of the peak must increase.

Acknowledgments

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