

ATOMISTIC MODELLING OF THE METAL/OXIDE INTERFACE WITH IMAGE INTERACTIONS

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Abstract—We calculate the interfacial energy and lowest energy relative position for an Ag (001)/MgO (001) interface. The dominant image terms and short-range repulsions are included in full, and the MgO ions are relaxed to equilibrium using the MIDAS code. An essential new feature is the suppression of charge density fluctuations with wave-vectors greater than a (Fermi wavevector) cutoff. Our results show that the powerful methods based on interatomic potentials, widely used for ionic systems, can be extended to metal/ionic interfaces.

Résumé—On calcule l'énergie interfaciale et la position relative d'énergie minimale pour une interface Ag(001)/MgO(001). On tient compte pleinement des termes images dominants et des répulsions à courte distance et les ions MgO sont placés en position d'équilibre en utilisant le code MIDAS. Le nouvel aspect essentiel de ce modèle réside dans la suppression des fluctuations d'ondes de densité de charges qui ont un vecteur d'onde plus grand que celui de le vecteur de coupure (vecteur d'onde de Fermi). Nos résultats montrent que les méthodes puissantes basées sur les potentiels interatomiques, largement utilisées pour le systèmes ioniques, peuvent être étendues aux interfaces métal/substance ionique.

Zusammenfassung—Wir berechnen die Grenzflächenenergie und die relative Position mit geringster Energie für eine Grenzfläche Ag(001)/MgO(001). Die dominierenden Bildterme und die kurzreichende Abstoßung werden vollständig berücksichtigt; die MgO-Ionen werden mit dem MIDAS-Code bis zum Gleichgewicht relaxiert. Ein wesentliches neues Merkmal ist die Unterdrückung von Ladungsdichte-Fluktuationen mit Wellenvektoren größer als eine obere (Fermi-Wellenvektor-) Grenze. Unsere Ergebnisse belegen, daß die leistungsfähigen, auf interatomaren Potentialen beruhenden Methoden, die vielfach für ionische Systeme benutzt werden, auf metallisch/ionische Grenzflächen übertragen werden können.

1. INTRODUCTION

Surfaces and interfaces dominate many of the technologically important processes in solid materials, such as catalysis, sintering, bonding and oxidation. Atomistic modelling of materials, especially using interatomic potentials within the shell model, has made a significant contribution to the understanding of the structure and property of these planar defects in ionic crystals [1, 2]. The majority of such calculations have, however, been on surfaces or on internal interfaces within a single material. One exception is the BaO/NiO interface, which has been modelled successfully [3]. Work on metal/oxide interfaces has been restricted by the complex nature of the interactions involved since there are competing energy terms [4]. Some work has concentrated on the electronic structure of the metal/ceramic interface [5, 6].

However, Stoneham and Trasker [7] have argued, and verified by restricted calculations [3, 8], that the dominant term in the adhesion is Coulombic, from the interaction of the oxide ions with their images in the metal. This opens the possibility for calculation at the HADES level, based on interatomic potentials and hence modelling with accuracy sufficient for useful application to materials since, e.g. to systemat-

ics of wetting and to the morphology of metal particles on oxide substrates.

These early image calculations considered only unrelaxed configurations, whereas previous experience demonstrated that relaxation can play an important role in determining the structure and energy of defects in ionic materials. In order to minimize the energy of the interface with respect to the ionic coordinates, it is necessary to include both the repulsive interactions between the metal cores and the oxide ions and also the screening of the oxide ion image interactions. This screening, which is known to occur in real metals at atomic scale distances, led to technical problems which have now been overcome. In this paper we demonstrate a method whereby the screened image interaction can be calculated directly, by removing the short wavelength fluctuations from the induced charge distribution, and use this method to calculate the relaxed structure of an MgO/Ag interface.

2. IMAGE INTERACTIONS

Classical electrostatics offers a simple solution to the problem of a point charge outside a continuum dielectric. In the case of a metal, which has an infinite

dielectric constant, a point charge at a distance z_0 from the metal surface induces a charge density ρ on the metal surface given by

$$\rho(r) = z_0 q / 2\pi(z^2 + r^2)^{3/2}$$

where r is the distance parallel to the surface. The resulting potential V at a site (r, z) is equivalent to the potential of a charge of q situated at a distance z inside the surface, i.e.

$$V(r, z) = -q/[r^2 + (z + z_0)^2]^{1/2}.$$

The classical image potential appears to be a reasonable description for the interaction between a charge and a metal surface down to the scale of interatomic distances (about 2 Å) [9] but the continuum dielectric model breaks down at closer distances. The primary reason for the failure of the model is the assumption that the charge-distribution is unrestricted, so that there is no energy cost for rapid variation of charge density in space. In a real metal, however, only charge distributions with wavelengths longer than the Fermi wavelength are permitted, so rapid fluctuations in the charge distribution cannot occur. This wave-vector cut-off gives rise to several effects, notably the familiar Friedel oscillations. Finnis's [10] approach, based on metal atomic polarisabilities, also gives an energy term restricting rapid charge density variations.

2.1. Image interactions with a cut-off wavevector

Willis [11] has calculated the minimum energy charge distribution induced by a point charge outside a metal when the wave vectors of the fluctuations are less than or equal to the Fermi-wavevector (K). The resulting potential has the form

$$V(r, z') = -q/(r^2 + z'^2)^{1/2} + (q/2\pi) \times \int_0^{2\pi} d\Theta \{ \exp[-K(z' + ir \cos \Theta)] / [z' + ir \cos \Theta] \}$$

where $z' = z + z_0$. The integral in this expression, which gives the correction to the classical result, can be calculated numerically for any value of z and r . The solution for $z = 0.3$ and r ranging from 1 to 6 is plotted in Fig. 1. The integral decreases in magnitude and oscillates as r increases. These oscillations correspond precisely to the Friedel oscillations. The integral also decreases in magnitude as z' increases.

It is clear that when $Kz' \gg 1$ the integral (1) is small and the potential can be described by the usual classical result. Also, in the particular case where $r = 0$, the potential becomes

$$V(0, z') = -(q/z')[1 - \exp(-Kz')].$$

We note that this has the same form as that taken for the energy by [12] for an ion interacting with its own image charge. They estimated the screening parameter (their λ) using local density calculations. Here, however, we have obtained the generalization of the Jennings and Jones formalism for the situ-

ations when r is not zero, therefore we can calculate the interaction energy between an ion and the image charge of a different ion. Such a generalization is necessary when a lattice of ions is to be modelled.

2.2. Characteristic screening lengths

It is interesting to compare the values of λ estimated by Smith *et al.* [13] for a number of different metals, fitting to experimental results, with the values of the Fermi wavevector K calculated from the experimental measurements of the plasma frequency [14]. These are given in Table 1.

Thus the values of K and λ vary somewhat in detail but they are similar in magnitude. For the first series transition elements (Cu, Ni), K is some 10% smaller than λ ; for the heavier elements, K exceeds λ by about 5%, with no significant dependence on column in the periodic table. The approach outlined in this paper, therefore, gives a straightforward method for estimating the screening parameter for any metal based on the readily-observable plasmon energy and provides an extension to the Jennings and Jones formula for indirect interactions.

3. THE CALCULATION OF INTERFACIAL ENERGIES

The program used to model the metal oxide interface is a modified version of the Harwell MIDAS Code, which has been used extensively to model both surfaces and grain boundaries. In order to model metal/oxide interfaces it is necessary to include the interactions between the oxide ions and the array of image charges. When the perpendicular separation between the ion and the image is greater than $2a$ (where a is the interionic distance of the oxide) the classical image potential is used, but at smaller separations it is necessary to include the corrections discussed above. For the direct ($r = 0$) interactions the corrections are calculated analytically, but the corrections for the indirect terms must be calculated numerically. The corrections are neglected for parallel separations of more than $6a$.

The modified program was used to model the MgO/Ag interface. Ag is an f.c.c. metal with a lattice parameter of 4.086 Å and MgO has a rocksalt structure with a lattice parameter of 4.212 Å. We have adjusted the lattice parameter of Ag to obtain a commensurate structure. The energy required to expand the Ag lattice has been neglected in the calculation. Only the (001) Ag/(001) MgO interface has been considered to date, but the method is also applicable to other interfaces. A diagrammatic representation of the interface is shown in Fig. 2. A rigid ion model was used for MgO with the repulsive potentials fitted by Sangster and Stoneham [16] to bulk crystal data.

In order to complete the model we require a knowledge both of the repulsive interaction between the metal and of the ceramic and the position of the

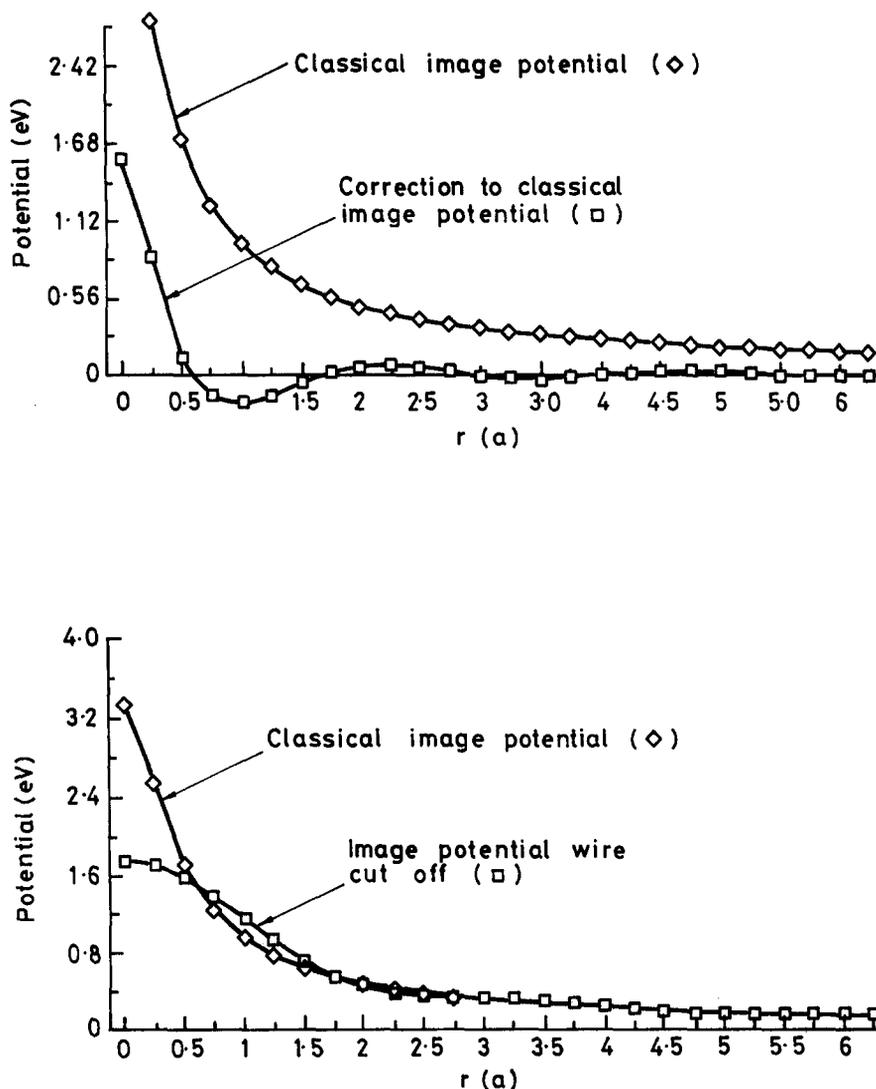


Fig. 1. The classical image potential and the screening integral [the two terms in the expression for $V(r, z')$] plotted for $z = 0.3$.

image plane with respect to the metal. The position of the image plane was taken from an analysis of experiment to be 1.26 \AA from the outer plane of metal cores [13]. We assume that the important part of the repulsive interaction is between the metal cores (modelled as Ag^+) and the Mg^{2+} and O^{2-} ions. Two methods of calculating these have been attempted. An electron gas calculation gives a very large repulsive term, so large that the interface fails to bind. We have therefore used the more accurate Hartree-Fock methods developed by Wood and Pyper [17, 18]. Here the relativistic ion wavefunctions appropriate for the crystal environment are first calculated, and these

wave functions are then used to calculate interionic interactions at the Hartree-Fock level. Correlation and damped dispersion terms are then added to this result. The results are shown in Fig. 3. The electron gas calculation fails because, since it is based solely on the density, it includes interactions between orbitals that are forbidden by the symmetry of the wave functions [18].

The metal cores were fixed during the calculation but 4 layers of oxide ions were relaxed explicitly to equilibrium. The perpendicular distance between the oxide and the metal in the initial configuration was the one with the lowest relaxed energy.

Table 1. Screening wavevectors (atomic units): K is the Fermi wavevector derived from the observed bulk plasma frequency and λ is estimated from surface data

	Cu	Ag	Au	Ni	Pd	Pt	W
λ	1.17	1.18	1.25	1.21	1.23	1.18	1.18
K	1.05	1.25	1.29	1.07	1.27	1.24	1.24

4. RESULTS AND DISCUSSION

Table 2 summarizes the relaxed energies of the interface for various initial configurations (i.e. various perpendicular separations between the metal and the oxide), with the Mg^{2+} ion directly above the metal

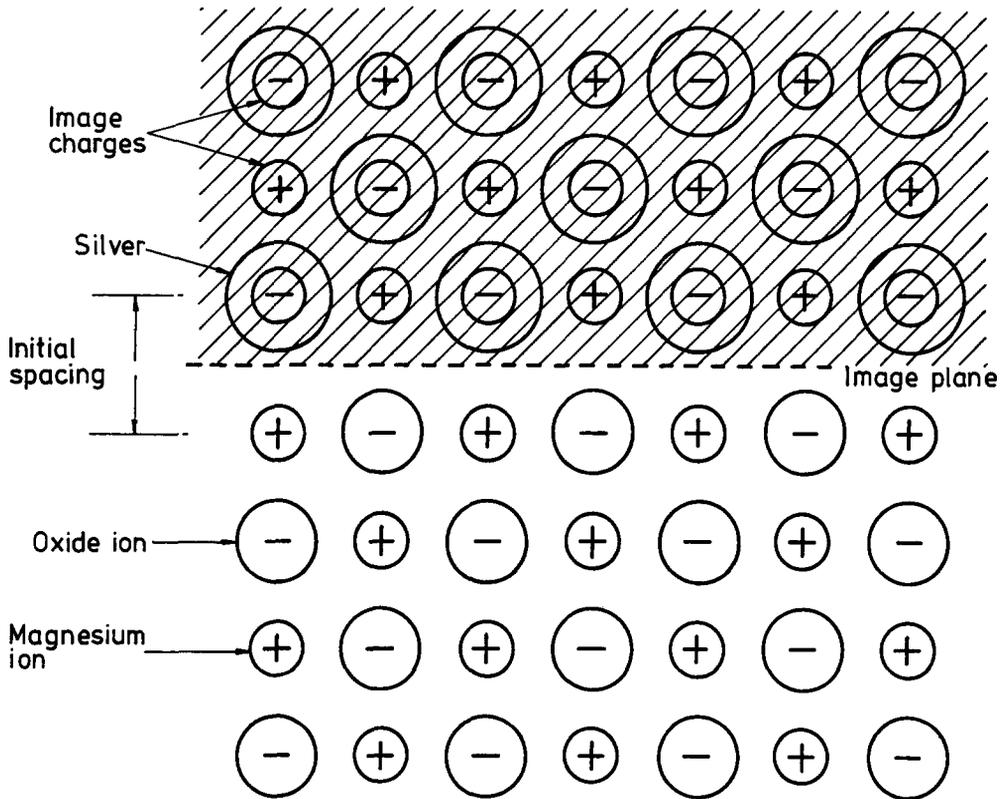


Fig. 2. Unrelaxed configuration of ions and metal cores. The lateral and perpendicular displacement of the oxide is varied but the distance between the metal cores and the image plane is fixed.

core (Fig. 2). In addition to the total final energy we have included the separate components energy we have included the separate components of the Coulomb and repulsive energy. The coordinates of the outer plane ions after relaxation are included to give an indication of the degree of distortion of the

oxide near the interface. The equivalent energies and coordinates for a free (001) MgO surface are also presented for comparison.

We note that as the oxide approached the metal the repulsive energy increases and the Coulomb energy decreases, giving a minimum in the total energy

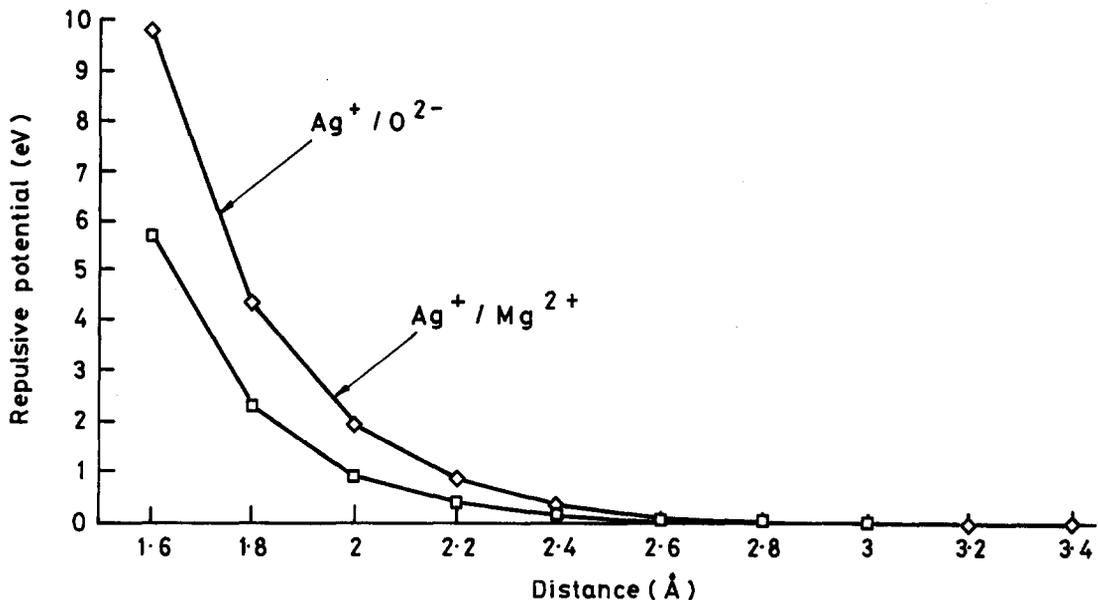


Fig. 3. The potential calculated for the repulsive interaction between the Ag⁺ and O²⁻ ions (□) and the Ag⁺ and Mg²⁺ ions (◇).

Table 2. Ag/MgO (100) interface with Mg ions above the silvers. Distances are in units of the MgO interionic spacing (2.106 Å) and energies in eV. The initial separation is the distance of the (unrelaxed) outer MgO plane from the outer Ag plane. The relaxed ion displacements are relative to this unrelaxed plane and are positive for ion motion into the oxide

Initial separation	Outer oxide coordinates		Repulsive energy	Coulomb energy	Total energy
	Mg	O			
0.95	0.052	0.049	28.81	-192.92	-164.11
1.00	0.021	0.009	28.10	-192.24	-164.14
1.05	-0.020	-0.032	27.42	-191.57	-164.15
1.10	-0.062	-0.073	26.79	-190.92	-164.13
1.15	-0.103	-0.113	26.20	-190.30	-164.10
1.20	-0.144	-0.155	25.66	-189.71	-164.05
Free surface	-0.006	-0.006	27.34	-191.09	-163.75

for an initial separation of $1.05a$. Also, as one might expect, the dilation of the oxide increases as the oxide is moved away from the metal. The energy difference between the most stable interface and the free surface is 0.42 eV which represents a binding energy of the interface of 0.76 Jm^{-2} .

Equivalent calculations were carried out for the cases where the Ag metal cores were over the O^{2-} ion and over the hole (midway between 2.0 surface ions). In the first case, the minimum energy configuration was found for an initial separation of $1.15a$ with a corresponding binding energy of 0.21 Jm^{-2} . The smaller binding energy and the larger separation are both a direct result of the harder potential of the O^{2-} ion Ag interaction. However, the case where the metal cores are over the holes has a minimum energy configuration for a metal-oxide separation of $1.1a$ with a corresponding binding energy of 0.83 Jm^{-2} . Thus our model predicts that the most stable configuration of the MgO/Ag interface has the Ag cores over the gaps in the MgO lattice, in effect a "lock-in" structure. This result appears to contradict the conclusions of the electronic structure calculations which seem to indicate a minimum energy configuration for the metal cores over the oxygen ion [5, 6], though the energy difference we predict is very small ($0.04 \text{ eV/molecular unit}$). Such electronic calculations involve only thin layers of metal (up to 5 planes) for which image effects may not be fully included. Their primary contribution to the stability of the boundary comes from bonding between the metal and oxygen, and this accounts for the stable configuration. In the present model, on the other hand, the bonding results from the image charges and the metal cores introduce only repulsive forces. Thus the configuration which brings the oxide ions close to the image plane whilst maximising the distance between the ions and the metal cores is the most stable one. We are not aware of any experimental evidence about the lateral translation of the Ag/MgO bicrystal which would favour one or other model.

5. CONCLUSIONS

In this paper we have demonstrated that a credible and practical image potential can be calculated simply

by removing all short wavelength fluctuations from the induced charge distribution. The resulting expression which agrees well with electronic structure calculations, gives us a method for extending the Jennings and Jones screening formalism from direct ion image interactions to indirect (ion-different image) interactions. Such an extension is necessary when considering a lattice of ions near a metal surface. We have used the method to produce an atomistic model of an Ag/MgO interface. We found that the attractive interaction between the oxide ions and their images was strong enough to overcome the repulsive interaction between the oxide ions and the metal cores, therefore a stable interface was produced.

The general conclusion reinforces our earlier views: the dominant terms in metal/oxide energetics are Coulombic, dependent on the ionic charges of the oxide, with a weaker dependence on the metal which can be defined largely through its Fermi wavevector (some generalisation is needed for reactive systems, Ref. [19]). To date the method has been used to model only one type of interface, but we plan to use it for other Ag/MgO interfaces, and compare their relative stability. We also hope to extend the formalism to model isolated point defects near the interfaces and small islands of metal on oxide surfaces. These calculations would have direct relevance to many important processes, such as the control of wetting and radiation-enhanced adhesion.

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