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COMPUTER SIMULATION OF INTERFACES: WHAT DO WE NEED TO KNOW?

A. M. STONEHAM and J. H. HARDING

Centre for Materials Research, Department of Physics and Astronomy, University College London,
Gower Street, London, WC1E 6BT, U.K.

Abstract—We analyze some of the key challenges in the computer simulation of interfaces. These fall into three main groups. First, there are challenges associated with charge on insulator surfaces, including charge patches, charge transfer processes, and charges associated with specific defects. These charges are important in phenomena such as sensor action, in tribology and, especially through tribocharging, in safety issues. Secondly, there are problems in epitaxy. Many of the key issues are understood, of course, but both experiment and computer modelling are showing new features. An example is the memory of epitaxy through an amorphous intermediate layer. Thirdly, there are issues concerned with interatomic potentials. In certain cases, following electronic excitation, one cannot always use a potential of the standard sort. However, even for ground state problems, some results are extremely sensitive to details, and especially to the weak long-range terms which are usually regarded as a minor detail. We discuss specifically the growth modes of metals on oxide and halide surfaces. © 1998 Acta Metallurgica Inc.

1. INTRODUCTION

“What do we need to know?” is a wide-ranging question. At one extreme, we want to know about the performance of a surface, how well the processes at that surface achieve what we would like, and whether we could devise a better surface. At the other extreme, we need to know about tools. Have we the capability to model the structures and properties for the varied materials we might wish to consider? Do we have the right ideas to understand what is happening? Here we examine some of the more challenging situations to try to identify some critical themes.

Almost all our examples will relate to interfaces between different media, so we will not consider grain boundaries or other planar defects within a single medium. In materials technology, almost every combination of metal, semiconductor, ionic and organic with each other is to be found (not forgetting the vacuum as a distinct medium). In addition, these may be present in any combination of phases. Applications demand an extremely wide range of properties. Some are mechanical (adhesion, friction and wear, ductility, stress); some are chemical (reactivity, interfacial bonding, materials modification); others involve the mesoscopic structure (nucleation, control of phase or of growth mode). These themes involve behaviour at several length scales: the *atomistic*, which is our theme here, the *mesoscopic*, and the *macroscopic* (or engineering) scale. The mesoscopic scale, where one needs to look at microstructure (such as the grain structure, or the surface roughness profile) has long been a theme in work at Harwell. The linking of atomistic studies to engineering applications usually demands

a proper and explicit treatment of the intermediate length scale. This demand (which is not often satisfied) is increasingly important because of the remarkable new information from atomic scale microscopy, notably atomic force microscopy and its generalisations.

Rather than tackle this wide range of needs, we will discuss specific cases which show how ideas are emerging and which point to more specific technical demands. It is timely to emphasise that modelling spans materials science and engineering. It is not concerned solely with condensed matter physics and chemistry, but includes the engineering of materials, the complete design and manufacturing process, and the monitoring and inspection of materials and processes throughout life.

Three themes emerge repeatedly. The first is that *charged regions or charged species are to be expected in non-metallic systems: simple assumptions of neutrality are often wrong*. The second is that interatomic potentials are really rather good for representing the ground state behaviour of many systems. They are far better than ionic radius notions in describing packing, not least because the polarisability and the short-range repulsive forces are interdependent. However, there are critical cases where the accuracy is not sufficient, and neither empirical nor more fundamental approaches are secure. An example is when the long-range (dispersion) term is important. A third theme involves excited states and materials modification by excitation. Here, reasonably sophisticated electronic structure calculations are essential, although one is often forced to go beyond the methods which are optimal for the ground state.

2. SURFACE CHARGE AND ELECTRON TRANSFER AT INTERFACES

The simplest calculations for surfaces are often predictions of surface energies. They can be for simple surfaces, or for surfaces with steps or more complex structures. Such calculations give a framework for understanding the distinctly more complicated surface structures which are seen in the atomic force microscopy of surfaces. This can help to predict where and how strongly inert species are adsorbed, an important preliminary to some catalytic processes. If we assume that the surface structure is known, how well can charge transfer processes be described? This is one of the cases where the ideas are more important than the techniques for implementing them, although it remains true that understanding of the kinetics of charge transfer is still primitive.

Surfaces are natural places to find large electric fields. There is a dipole at the surface of ionic solids due to the different relaxation and polarisation of anions and cations. Adsorbed species can accept or donate electrons to the substrate to generate further dipoles; this is central to certain oxidation processes. Nor need surfaces be electrically neutral, except on a macroscopic scale. For example, kink sites on simple surfaces like NaCl(100) always have a charge which cannot be saturated by electrons or ions. (The argument, due to Seitz [1], is as follows. Suppose a kink at a ledge ends with a cation, and the kink has charge qe . If an anion of charge $-e$ is added, then the new charge will be $-qe$. Conservation of charge means that $qe - e = -qe$, so that $q = 1/2$: the kink has half-integral charge.)

There are dipole fields at interfaces due to space charges, associated with defects or impurities. Typical space-charge layers extend for 10–100 nm from the surface, and lead to an energy difference of perhaps 0.2 eV and fields of 10^6 – 10^7 V/m. The defect populations associated with space charge can be essential for some processes, for example AgBr microcrystals would have too few interstitials for the photographic process to be effective without space charge [2]. Space charge can be controlled by impurities, by intrinsic defect formation (there will be a surface excess of the defect with the larger formation energy), or by changing the polarisability of the surrounding medium. This can have several consequences. One concerns nanocrystals, small particles of perhaps 100–200 atoms, which have promise in optoelectronic applications. Their performance is strongly influenced by changes in refractive index on the scale of the optical wavelength, and hence is modified by the medium in which they are embedded. A second application relates to controlled adhesion. If the host crystal is surrounded by an unpolarisable vacuum, then charged defects are discouraged from approaching the surface. If there is a metal (or other high-dielec-

tric constant medium) adjacent to the surface, charged defects will be encouraged to approach the surface. Since charge redistribution can be slow (whether by electronic or ionic movement) this leads to ways to control adhesion [3]. The three examples which we describe illustrate different aspects of charge transfer.

2.1. Solid-state gas sensors

These sensors, typically oxides, show an extremely sensitive (and often selective) response to different gases. For example, 100 parts per billion of ozone can be detected [4]. The basic process is certainly one where the detected molecule initiates the transfer of charge to or from the oxide, and this leads to the electrical effects which are observed. But what are the steps in between?

It is natural to approach the problem by looking at the way each of the molecules to be sensed interacts with surfaces or surface features of the oxide. This is actually a very bad way to approach the problem: it is far too easy to rationalise and be deceived. The situation becomes much clearer when one looks at a very large ensemble of data for hundreds of oxides and tens of gases [5]. Several rules become evident, of which the most important is that it is not the interaction of species X directly with the oxide surface which matters, but the interaction of X with a common species (probably O_2^-) which exchanges charge with the oxide substrate. A second rule is that most of the interference with sensor action is associated with adsorbed H_2O . The nature of the interactions with the oxygen-related species and with water is still being resolved, as is the way water molecules aggregate, cluster and react on surfaces [6].

Having decided that a particular species like O_2^- is central, one can check the energetics of charge transfer. Simple calculations confirm that the species should be bound. Calculations [7] based on shell-model interatomic potentials show that electron transfer is exothermic in simple cases (for example MgO: Fe^{2+} will transfer an electron to O_2^- to yield the negative molecular oxygen and a ferric ion.) Far more sophisticated calculations are now possible [8], and the application of self-consistent molecular dynamics to these problems is developing. We note recent observations of the efficient transfer of electrons from surface anions to oxygen atoms or halogen atoms at near-grazing incidence, and their possible explanation in terms of adiabatic transitions [9, 10].

2.2. Metal electrodes for electroluminescent polymers

The injection of electrons from one electrode and of holes from the other are critical steps here. The complications are twofold. There is a straightforward problem, namely that the polymer strands vary in length, in cross-linkages, and curvatures. They therefore have different electron affinities.

Fortunately, these can be calculated, and agree well with electrochemical data [11]. There is a less straightforward problem, in that a single electron has a significant effect on an individual polymer strand, which might only involve 100 carbons. The effect is not just the Coulomb repulsion (a special case of the Coulomb blockade) but deformation, with changes in bonding patterns which need self-consistent molecular dynamics. This means that the charge transfer process (both injection, and transfers from chain to chain) is more complex, and needs more attention. The two problems have a further effect: one should not assume one can predict performance by the simple rules which apply to conventional semiconductors. There is a temptation to model conducting polymers either as isolated single molecules, or as a homogeneous solid like silicon. Neither limit carries the whole story, and mesoscopic modelling appears essential.

2.3. The initial stages of the oxidation of silicon

There are two apparently inconsistent results for the early stages: oxidation is layer-by-layer (in so far as one can define that for an amorphous oxide) and oxidation does not occur at steps, but apparently over the terraces. How can these be reconciled? The most likely explanation [12, 13] argues as follows. To give layer-by-layer growth, there must be some factor which encourages arriving oxygens to settle down at the sites as close to the silicon substrate as possible. This could mean that the oxygen moves over the surface until it finds a deeper site, or perhaps the initial sticking probability is higher at a deeper site. Why should either effect occur? The major factor may be the higher *polarisability* of the silicon, which has a significantly higher dielectric constant than the oxide. If charge transfer to the oxygen is possible, then the *image interaction* will bias the energies so that deeper sites are selected.

3. SURFACE CHARGE: SITUATIONS WITH STATIC CHARGES

In a remarkable experiment, Horn and Smith [14, 15] pressed together mica and silica glass in a way which did not lead to sliding. They found that contact charges were created, of order one electron every 80–320 sites, even for these inert materials. The charges occasionally led to discharges, and contributed to a large cohesive energy across the interface. What this shows is how naive it is to assume that static charges at interfaces will be absent or negligible. The influence of static charges is discussed [16] in a slightly different picture (emphasising work function anisotropies as a source of patch charges) to understand force microscope data.

The observation of discharges is also significant. Indeed, gaseous discharges have been suggested [17]

as an explanation of the anomalous contact charging of polymers where, unlike simple rare gas solids [18], the equilibrium models of charge transfer fail: the charge transferred does not correspond to that which would equalise Fermi levels. There are many other issues relating to contact charging, including controversy as to whether electron or ion transfer is dominant [19].

The development of friction microscopy has stimulated the modelling of the atomic processes at the point of contact. In terms of modelling macroscopic friction, one is assuming the AFM tip mimics a normal asperity [20], and a proper link must be made via mesoscopic features to the engineering phenomenon. Molecular dynamics is a powerful theoretical tool when one is not sure what to expect. What emerges [21, 22] is striking. Charged ions are pushed up from the surface, and there is charged debris. There is no difficulty in understanding the existence of charged patches, or even of net charges on surfaces. The questions which are left unanswered are ones like "What determines the charge Horn and Smith actually saw?" and "If you cleave MgO as precisely as you can, what surface charge patches will there be?"

4. EPITAXY INVOLVING A NON-CRYSTALLINE SOLID

Heteroepitaxy, the growth of one material in a well-defined and coherent way on a substrate of another, involves several well-known ideas. Some involve equilibrium: is the total free energy less when one has a strained but defect-free layer, or is there an energy advantage in having defects? Other ideas are concerned with defect nucleation, for it is clearly possible to have metastable situations as well. Then there are the specific discussions of misfit dislocations, which are the only defects of significance for some systems. For ionic systems, one must look further. Twist grain boundaries, for instance, will normally bring like-charged ions from the two materials into close proximity, so that the lowest energy boundaries will have missing ions (it is confusing to call them defects) or ions with altered charge states [23]. When the dielectric constant of one material is very high, it may be favoured to have different charge states for the ions close to the interface (so NiO joining BaO may have some 3+ charge states as well as 1+). New phases might form; indeed this seems to be the case for Ag/NiO, where what is essentially Ni₂O₃ is the stable form close to the interface [24].

What is more intriguing is the case when the new layer is amorphous. Clearly, the idea of epitaxy cannot apply in a simple form. But there are constraints at the actual interface, and these can have effects. For SiO₂ (which has many amorphous and crystalline phases) on Si, there does appear to be an intermediate layer, perhaps 1nm thick. This can be

rationalised in several ways, some concerned with the growth mode, others associated with the strain energy type of argument which is traditional in talking about epitaxy. An interesting variant is that one cannot use dislocations to reduce misfit; one must therefore either exploit the wide variety of phases, or exploit point defects. Experimentally, it is found [25] that, as one varies the oxidation conditions, the density of P_b centres correlates with interfacial stress. (These centres are essentially dangling Si bonds at the interface, pointing into the oxide; it is likely that there is an Si-Si bond above [26].) This suggests that point defects may be responsible for reducing the misfit, perhaps in conjunction with other factors.

One striking result [27, 28] involves two crystalline media separated by an amorphous layer. In some cases, there appears to be an epitaxial relationship between the two crystalline components. How can this be, when the amorphous layer is over 10 nm thick (say 40 "layers" of atoms)? The obvious mechanisms are unlikely to be effective. One possibility (work in progress by V. J. B. Torres and A. M. Stoneham) is that the effect may be largely what is known as graphoepitaxy. The steps on the substrate carry crystallographic information; the amorphous material will have some memory, with ridges corresponding to those on the substrate, and these will influence the epitaxy of the final crystalline layer. Initial Monte-Carlo calculations suggest the idea is promising.

5. GROWTH MODES OF METAL FILMS ON IONIC SURFACES

The metal-ionic interface (and especially the metal-oxide interface) has long been a centre of attention in applications. Only relatively recently has theory come to grips with the issues ([3, 29-32] are reviews which cite many different approaches). However, the questions addressed have not always been the most important, nor have the systems been relevant to complex technological problems. Certainly, it is good to know the work of adhesion (or, better, the work of immersion, since the work of adhesion contains a metal surface energy whose origin is physically quite different [32]) and the wetting angle, although neither is a very rigorous test. We shall discuss instead whether or not metals on ionics form layers or three-dimensional clusters. The importance here lies in the control of supported metal catalysts and of other special systems like sensors. What emerges is that some predictions are extremely sensitive to the details of the energies. The particular difficulties are common to almost all current approaches whatever the method employed. Clearly, this raises doubts about the modelling of the really complex systems of interest in applications (such as a uranium nuclear fuel containing fission products in contact with an alloy clad). An

example of sensitivity is whether Ag lies above Mg or O on MgO(100). The local density functional predictions agree with experiment: it lies above O. The position with interatomic potentials and the image interaction analysis is interesting: the answer depends very sensitively on the small contribution of the relatively long-ranged dispersion interaction between Ag and O. Now that new developments in LDA should allow better treatments of dispersion forces [33, 34], it may be possible to resolve tricky cases more easily.

There are three main modes of growth possible when a material is deposited on a surface: layer by layer (Frank van der Merwe) growth, island (Volmer Weber growth) and layer then island (Stranski-Krastanov growth). Equilibrium growth is determined by the energetics of the system. We need to compare the energy of a deposited atom in a single layer with that of an atom in a three dimensional cluster to determine the preferred growth mode. However, growth does not often take place at equilibrium. For example, Didier and Jupille [35] have recently grown Ag on a clean MgO surface and found layer-by-layer growth, which contradicts both other experiments and the theoretical analysis. Any model of the growth process must consider diffusion; surface defects are often important. One of the simplest and most successful models of growth is the pair-binding model [36, 37]. Here, the maximum value of the nucleation density, N_x , in the complete condensation limit is given, for two-dimensional growth, by an equation of the form:

$$N_x \sim R^p \exp\{(E_i + iE_d)/(i + 2)kT\}$$

where R is the deposition rate, T is the deposition temperature and E_d the surface diffusion activation energy for the adatom. The quantity $p = i/(i + 2)$, where i is the critical nucleus size, is calculated self-consistently within the model. The model uses the lateral binding energy, $E_j = b_j E_b$ (where E_b is the binding energy of a pair of adatoms on adjacent sites), of arbitrary two-dimensional clusters, and evaluates " i " as that cluster size j (and configuration) which results in the lowest possible nucleation rate and density at the deposition temperature. The model also allows for incomplete condensation, using a more complete expression [37] than the previous equation. This now requires knowledge of the adatom adsorption energy, E_a . The value of N_x , on a perfect, clean, substrate is a sensitive test of E_d and E_b . Higher values of E_b prolong the lower critical sizes, and higher nucleation density, to higher temperatures. It is therefore of interest to attempt to calculate these energies.

5.1. Method of calculation

The methods used here have been widely used to model many other systems involving planar

interfaces [38], grain boundaries [39], metal oxide interfaces [40], and defects at interfaces [41]. The difficulty, as noted above, lies in obtaining a suitable potential model. Obtaining a *reliable* potential is always difficult (see [42] for a general discussion). For metal/oxide potentials, the traditional method of fitting to experimental data is not available and the potential must be calculated.

Some previous attempts have been made to derive potentials [43]. These used the Margenau formulae to estimate the dispersion term and a Lennard-Jones repulsion ($1/r^{12}$) fitted to the interatomic distance (assumed to be the sum of the covalent radii) to obtain the short-range term. The Margenau formulae are completely unreliable for estimating the dispersion energy [44]. However, if the sum of the covalent radii is a reasonable estimate for the silver-ion distance, the repulsion term will tend to cancel out this error. Such a method, however, can scarcely be called reliable. It does however, illustrate a common problem in obtaining and using potentials. A potential model, if it is to be more than a pointless fitting exercise, must be usable over a far wider range of configurations than those for which it has been fitted and tested. This is a particular problem in covalent materials where there is no agreement on the functional form to be used and where bond breaking and reforming may be expected to cause the form of the potential to change for different configurations. These problems are discussed for silicon in [45].

The potentials used here were obtained by two methods (full details are given in [46]). The potentials for the substrates were taken from the literature ([47] for MgO; [48] for NaCl, NaF and [49] for CaF₂). These are empirical fits to experimental data. The potentials between the metal atom and the ions were calculated using the procedure discussed by Pyper and co-workers [44, 50], using an averaging method for the open shell [51]. A shell model was used to simulate the effects of electronic polarisation. The polarisabilities of the metal atoms are taken from [52]. The metal-metal potential was a Morse potential fitted to spectroscopic data [53, 54]. This method is adequate for dimers; however for other clusters a more flexible potential form, taking account of tendency to metallic behaviour, is needed. Although they are fitted to bulk metals, Finnis-Sinclair potentials are often suitable for clusters. Here we use the set of Ref. [55]. Such a

mixed set of potentials is difficult to avoid in problems of this kind. Even if one resorts to calculated potentials, it is difficult to ensure that the level of approximation is the same. The greatest difficulty is to avoid double-counting terms, particularly polarisability effects. The only way to avoid this is to be clear about what a given potential does include and what it does not. This is often easier to see when all the potentials are calculated.

5.2. Results for metal atoms on ionic surfaces

Calculations of the adsorption and migration of single ions have been performed [46, 56]. The comparison with experiment is shown in Table 1. The agreement with experiment is good for the two silver cases on alkali halides where reliable data are available; rather poorer for gold. In some cases (Ag/CaF₂ and Ag/MgO) there is evidence of significant bonding.

We finally address the question of whether two-dimensional or three-dimensional growth should be expected. For Ag/MgO, the calculations point strongly toward metastability, in agreement with experiment. The infinite two-dimensional layer has binding energy $E_a + 4E_b(\infty)$. This is not the same as E_b in Table 1 since that value refers to the silver dimer only. The cohesive energy of bulk silver is 2.95 eV per atom with respect to silver atoms whereas the cohesive energy of a two dimensional Ag sheet is 1.82 eV per atom, assuming the Ag has adjusted to the lattice spacing of MgO. The energy balance is then quite delicate between an Ag island and a monolayer of Ag on MgO. Our earlier MgO/Ag interactions gave a binding of 1.2 eV per atom, which gives very close energies; revised potentials make the three-dimensional islands more stable by about 0.5 eV/atom.

At some point, probably during the formation of the first monolayer, the Ag adatoms prefer to be on top of the Ag(100) layers, rather than on the bare MgO surface. By condensing at low enough temperature, this three-dimensional growth can be prevented by kinetic means. Nearly all the adatoms arrive at the edges of the (initially two-dimensional) clusters by diffusing rapidly over the MgO surface, with a low value of E_d , and bind there. To get on top of the Ag layer, these adatoms need to lose a substantial fraction of E_a before regaining a larger adsorption energy on top of the Ag layer. A simple order of magnitude comparison shows that

Table 1. Values for the rate theory parameters (Experimental results [51] are shown in normal brackets; previous calculations [40, 52] are given in square brackets)

Parameter	E_a (eV)	E_d (eV)	E_b (eV/atom)
MgO/Ag	1.51	0.26	0.75
NaCl/Ag	0.27 (0.41) [0.27]	0.13 (0.19) [0.09]	0.88
CaF ₂ /Ag	0.23	0.1 (0.4-0.5)	0.84
NaCl/Au	0.15(.49) [0.36, 0.62]	0.07 (0.16) [0.13, 0.14]	1.17
NaF/Ag	0.26	0.24	0.82

at room temperature, a 1.5 eV barrier would be large enough to retard these two-dimensional to three-dimensional kinetics substantially (for MgO), whereas 0.35 eV (for NaCl) would be quite ineffective.

Defects on the surface would promote three-dimensional growth; they increase N_x , which decreases the lateral growth rate of each island, and hence allows more time for the three-dimensional jumps to occur and they can provide lower barrier pathways to growth. In metal on metal epitaxy these pathways lead to "re-entrant layer growth" at low temperature, where the lower layer is more stable. Here, they would lead to three-dimensional island growth, since the upper layers are more stable.

6. CONCLUSIONS

The three issues which we have emphasised (surface charges, epitaxy beyond the standard cases, and energetics for which both potentials and other approaches are stretched) are not the only outstanding problems. We have barely mentioned excited state processes, which underpin many applications like laser sputter deposition and secondary ion mass spectrometry. However, the three challenges of charge motion, of extended ideas of epitaxy, and of the way metals grow on ionics, already point to much future work.

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