

# End of 2nd year report: Progress

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## 1 Comparison to proposals in 1st year report

In my 1st year report I proposed to examine three areas during my second year. However, one of these areas - ‘the effect of concentration gradients at surfaces’ - proved to contain far more interesting results than was initially suspected. As a result it is this and related areas which have dominated my attention this year, while the other two proposed areas of study have been largely ignored. I will now outline the results I have obtained in the last year.

## 2 Inhomogeneous disorder and surfaces

Almost all previous *ab initio* studies of disordered alloys have concerned themselves with those which have what I shall refer to as *homogeneous disorder*. In this type of disorder the probability  $c_A$  of finding an  $A$  atom at any particular site is the same for all sites in the alloy - where here we are considering the binary alloy  $A_xB_{1-x}$ . This is not the case in *inhomogeneous disorder*. In the type of inhomogeneous disorder which I considered, sites in each monolayer of the system generally had different values of  $c_A$ . Assigning different concentrations to different monolayers in this way allows a wide range of systems to be examined in which  $A$  and  $B$  atoms interfuse at an interface. I have used the correlated-charge model (CCM) to obtain the following results for such systems.

### 2.1 List of results

- I have derived analytic expressions for variance and average of potentials and charges in each monolayer, given any concentration profile in bulk or at a surface.
- I have derived analytic expressions for how the potential in each layer varies with its local environment, given any concentration profile in bulk or at a surface.
- For systems of ultra-thin films, the trend that the average potential potentials in each layer follows as the film ‘melts’ and interfuses into its surroundings agrees well with *ab initio* predictions.

- I have conducted simulations of surface systems using the CCM to simulate core-level XPS spectra. Systems simulated include:
  - $n$  monolayers of  $A$  deposited on pure  $B$ , with various degrees of interfusion into the bulk of  $B$
  - Various surface segregation profiles - in which the concentration profile oscillates and decays from a maximum at the surface.
- The potential  $V^i$  and charges  $Q^i$  of sites of the same species in the surface region fall on a straight line with a slightly different gradient than for bulk sites. This reflects the link between the gradient of the  $Q - V$  relation and the nature of the screening - which is necessarily different between surface bulk sites.
- The scatter of  $(Q, V)$  points about the  $Q - V$  line for sites near the surface region is larger than in the bulk - where it basically vanishes. This may indicate a problem with the self-consistency between a site's charge and its potential at the surface region in the CCM. This may indicate that, just as in the same way that including the charge-transfer effects from more distant sites improved the self-consistency for bulk sites in the CCM, a generalisation of the CCM may be required in which charge transfer between two sites depends not only on their separation, but how far each is from the surface.
- I have conducted simulations of bulk systems using the CCM to simulate spectra. Systems simulated include:
  - Isolated ultra-thin films of  $A$  atoms embedded in a  $B$  metal, with various degrees of interfusion into the  $B$  metal.
  - Periodic systems of ultra-thin films of  $A$  atoms embedded in a  $B$  metal, with various degrees of interfusion into the  $B$  metal.
- All spectra results indicate that it should be possible to quantify the amount of interfusion which occurs.
- The amount of 'disorder broadening' due to the range of core-level binding energies in the inhomogeneously disordered systems examined was often larger than the maximum disorder broadening observed in homogeneous systems. This is not obvious.

### 3 Beyond binary alloys

Only binary alloys can be considered within the CCM. I have generalised the CCM to enable it to include any number of alloy components by appealing to the idea that the magnitude of charge transferred between different species  $A$  and  $B$  depends on the electronegativity difference between them. In this way alloys such as  $A_x B_y C_z$  can be considered.

### 3.1 List of results

- I have derived analytical expressions for the mean and variance of the charges and potentials for sites belonging to each species for homogeneously disordered alloys as a function of the concentrations of each species (e.g.  $x, y$  and  $z$  in  $A_xB_yC_z$ ).
- I have derived analytical expressions for the potential of a site as a function of its local environment in such alloys.
- I have derived an expression for the Madelung energy of such alloys, again as a function of the concentrations of each species. This enables a ‘Madelung energy phase diagram’ to be created given the electronegativities of each species in the alloy. This expression however is only for the simplest form of the CCM - in which only interactions between nearest neighbours are considered.
- I have performed preliminary computational simulations of such alloys. Out of what I have compared to the analytical predictions, there is agreement.

## 4 Properties of the charge model if all shells are included

The CCM does not take into account the effect of charge transfer between sites which are separated beyond a certain predetermined cut-off distance. In reality there will be a finite amount of charge transfer between all sites, regardless of their separation. This corresponds to setting the cut-off distance to infinity in the CCM. I have discovered that the CCM in this limit, which I shall refer to as the I-CCM, has some interesting properties.

### 4.1 List of results

- In the I-CCM there are two free parameters, one determining the amount of charge transfer ed between  $A$  and  $B$  atoms - which depends on the elements  $A$  and  $B$  represent, and the other determining the nature of the screening - which was discovered by Ruban and Skriver in *ab initio* calculations to be universal. Continuously varying the parameter which governs the nature of the screening spans a continuum of possible screening distributions. This is not obvious from the normal CCM.
- The distribution of screening charge about an impurity in the I-CCM in the continuous limit has a Yukawa form - which is the form found within the Thomas-Fermi approximation.

- The distribution of screening charge follows the same trend as another prominent model for alloys, the BZW model, as the equivalent free parameter in the I-CCM is varied. Other results I have hint at other possible links between the I-CCM and the BZW model - which itself closely resembles a tight-binding model.
- The potential  $V^i$  and  $Q^i$  for all  $A$  sites  $i$  in any alloy (not just disordered) with proportions  $A_x B_{1-x}$  in the I-CCM obey the formula  $V^i = aQ^i + k(x)$ , where  $a$  is a constant of the model. Note that the intercept of the resulting so-called  $Q - V$  relation depends only on the proportion of  $A$  and  $B$  atoms, but not where they are in the alloy. This is analogous to the universal  $Q - V$  relation discovered by Ruban and Skriver in *ab initio* calculations.