Part III

Cellular Automata Simulation of Monolayer Surfaces

“The concept of progress acts as a protective mechanism to shield us from the terrors of the future.”

–the words of Paul Muad’Dib

Chapter 6

Methodology Associated with Cellular Automata

6.1 Abstract

Here, a generalised description of the methodology, as implemented in a recently developed cellular automata simulation code, is given. Lennard-Jones potentials are used to calculate local interactions of an argon gas atom incident on a calcium (111) surface. The methodology incorporates the ability to simulate gas atom interactions with an atomically rough calcium (111) surface. Since the code is still in active development, no details of the actual code are presented. If such details are of interest then the code authors, M. O. Zacate and K. J. W. Atkinson, should be contacted directly.

6.2 Introduction

When a specific microstructure is required, it is very difficult and expensive to experimentally determine the optimum process conditions if there are more than a few preparation variables. Consequently, there is considerable interest in predicting the values of system variables via computer simulation. Since microstructure ultimately depends on processes occurring at the atomistic level, it is desirable that such a model be atomistically based if it is to be fully transferable. This should also allow the user to explicitly include the role of all types of chemical and crystallographic defects. Once established it is not hard to envisage how these types of simulation could be extended to simulate complex environmental conditions and thus predict material performance.

A number of atomistic-scale simulation techniques exist that could potentially be used as the basis for predicting microstructural evolution. These include molecular dynamics and energy minimisation, both of which have been highly successful in predicting energetics and structures in metals, ceramics, and semiconductors. As seen in chapters 4 and 5, present computational facilities are not nearly sufficient to allow these methods to become routinely useful predictive tools on scales required for microstructural size and growth times. Excellent work has been conducted by Sayle and co-workers [113–115] using molecular dynamics. They simulate defects in supported molecular clusters involving several thousand atoms for times of 10^{-9} seconds, which is quite an achievement. However, to be truly useful in predicting microstructural evolution, time periods several orders of magnitude longer are required. Monte Carlo (MC) techniques present a tempting alternative since each calculation is concerned with a new configuration. Between each step, an atom is moved to a new position or, possibly, a pair of atoms are swapped. The total energy of this new configuration is then calculated and compared with the energy of the old configuration. On this basis, a decision is made as to whether the system should be updated to the new configuration or remain unaltered. However, even this method becomes computationally challenging when the number of atoms reaches the point necessary to model microstructural evolution. As such, an alternative implementation of a MC-related methodology based on cellular automata (CA) is used here.

Formally, CA are discrete dynamical systems, the behaviour of which are completely specified in terms of local interactions. Typically, the evolution of CA is controlled by updating the state of each discrete cell on the basis of a rule involving only the states of adjacent cells. The entire cell assembly is updated simultaneously in an update step that may be taken to represent a single step in time. Thus, there are three differences between CA and MC methodologies:

- All the cells are updated in a single step in CA.
- The interactions between particles are local, not system wide.
- Each cell does not necessarily have to consist of a single atom at a single site, but may include multiple sites and multiple states.

Having said this, there are variants of MC that assume local interactions and variants of CA that count interactions beyond the nearest neighbour. Thus, the difference between CA and MC can become somewhat blurred.

This methodology extends the work carried out by Zacate *et al.* [116] in using cellular automata techniques to model gas mono layer evolution on an atomically perfect calcium (111) surface. Here, the methodology is modified to take into account the effect of having an atomically rough surface. This methodology is implemented in a newly developed version of the code and in chapter 7, results are presented of argon gas evolution onto rough calcium (111) surfaces.

6.3 Crystallography of the Calcium (111) Surface and its Gas Atom Interaction

α-calcium metal has a face-centred-cubic (f.c.c.) structure so that the (111) surface exhibits a close packing of calcium atoms. These may be regarded as A sites. When an argon gas atom attaches itself to the surface, it will reside in a site formed by three metal atoms since this maximises its interaction with the metal surface. Two sets of interstitial sites exist, which can be regarded as B sites (red) and C sites (blue), as illustrated in figure 6.1.

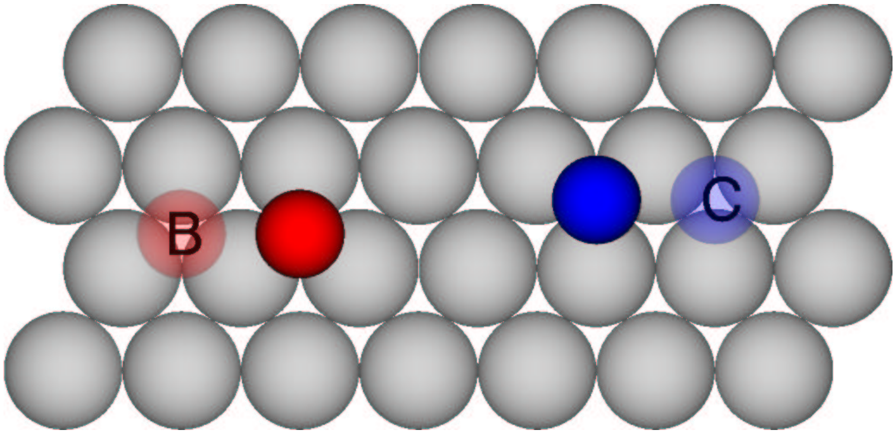

Figure 6.1: Crystallographic structure of the calcium (111) surface indicating the two interstitial sites for argon gas atom adsorption.

The success of the CA approach relies on the ability to define a cell based on the geometry of the system such that the local environment is easily determined and the outcome of a cell event has physical meaning. Examining the (111) surface more closely, it is clear that the distance between an interstitial B site (red sphere) and a nearest neighbour C site (blue sphere) is rather short. Indeed, the argon atoms in figure 6.2 overlap considerably onto the neighbouring sites. As such, if an argon atom resides in a B site, it is not possible for a second argon atom to occupy a nearest neighbour C site due to steric hindrance. It is important to realise that this is true only because of the specific matching of the size of the calcium (111) surface to the size of the argon atoms. By considering this surface condition a cell can be defined that contains a B site and a C site. This cell can only have three states: unoccupied; B site occupied; or C site occupied. Figure 6.2 shows a series of cells on the surface with steric hindrance highlighted in the central cell by the area of overlap between the transparent spheres which represent the relative size of argon atoms. The local environment of a cell can be ascertained by observing the state of the surrounding cells. In figure 6.2, red and blue dots indicate the nearest neighbour equivalent sites that can be occupied by B site (red) and C site (blue) argon atoms respectively. The cells holding the local environment information for the central occupied cell are also outlined, again each cell has a B site and a C site. The simulation code holds the state information of all cells in memory and is thus able to determine the local environment of any argon atom in the simulation during a time step.

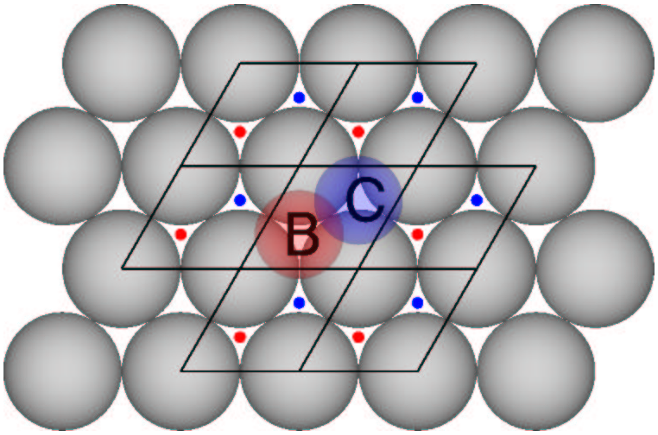

Figure 6.2: The cellular automata cell geometry for the calcium (111) surface indicating the gas atom adsorption sites and geometry of neighbouring cells.

For rough surfaces a calcium atom is fixed in either a B site or a C site. This surface defect atom introduces the same steric hindrance to the local environment that a gas atom would. However, it is introduced at the beginning of a simulation and is not allowed to move. The interaction energy between this calcium defect and the argon gas will be different than that between two argon atoms. As such, the defect will control its local environment throughout the simulation.

6.4 Interaction Energy of an Argon Atom with a Specific Surface Site

6.4.1 Origins of the Interaction

In this methodology, two types of interactions are considered:

- The interaction between inert argon atoms on the surface.
- The interaction between inert argon atoms and the calcium atoms.

Both forms of interaction have two physical origins: electron cloud overlap repulsion and van der Waals attraction. Lennard-Jones potentials, as described in chapter 2 (equation 2.6), are used to describe the interaction.

6.4.2 Atomic Interactions on the Surface

Using pair potentials it is possible to derive the general case for calculating the interaction energies that define the stability of a gas atom at a specific site on a surface. Consider an isolated gas atom, g, on a surface site. It will have an interaction with each substrate surface atom, s, such that the interaction, $\Phi_{g,s}$, is,

$$\Phi_{g,s} = (A_{g,s} r_{g,s}^{-12} - B_{g,s} r_{g,s}^{-6}) \tag{6.1}$$

where $r_{g,s} = r_g + r_s$, is the sum of the gas and surface atom radii, respectively. $A_{g,s}$ and $B_{g,s}$ are parameters of the Lennard-Jones potential which describe the gas-surface atom interaction. The interaction energy between two gas atoms on the surface, $\Phi_{g,g}$, is given by,

$$\Phi_{g,g} = (A_{g,g}r^{-12} - B_{g,g}r^{-6}) \tag{6.2}$$

where $A_{g,g}$ and $B_{g,g}$ are parameters of the Lennard-Jones potential which describes the gas-gas interaction, and r is the distance between surface sites. It should be noted that here the separation of the gas atoms, r, is defined by the substrate. To simplify the analysis further, for each surface gas atom only the following interactions are considered: first those between the surface gas atom and substrate atoms, second with the nearest sterically unhindered equivalent neighbour site gas atoms, or third with any substrate defects (i.e. a substrate atom that is not part of the perfect atomic plane below). The final type of interaction is between the surface gas atom, g, and a surface defect atom, d. The interaction, $\Phi_{g,d}$, is similar to that with the substrate and the distance is again fixed by the surface crystallography similar to the gas-gas interaction,

$$\Phi_{g,d} = (A_{g,s}r^{-12} - B_{g,s}r^{-6}) \tag{6.3}$$

where r, $A_{g,s}$ and $B_{g,s}$ are as above. Given these general interactions it is possible to calculate the total attachment energy, Φ_a, of a gas atom in specific local environments that may occur on the surface,

$$\Phi_a = n_{g,s}\Phi_{g,s} + n_{g,g}\Phi_{g,g} + n_{g,d}\Phi_{g,d} \tag{6.4}$$

where $n_{g,s}$ is the number of surface atoms that a gas atom rests against when located on the surface; $n_{g,g}$ is the number of nearest sterically unhindered equivalent neighbour sites which are occupied by gas atoms; and $n_{g,d}$ is the number of nearest sterically unhindered equivalent neighbour sites which are occupied by surface defect atoms. Obviously, $n_{g,g}$ + $n_{g,d}$ cannot exceed the number of local equivalent sites. For the calcium (111) surface $n_{g,s} = 3$ and $(n_{g,g} + n_{g,d}) \leq 6$. This attachment energy is used to determine the probabilities of events occurring, which forms the basis for the time evolution of the surface. This link between the local atomic structure and the probability for adsorption or desorption is the key feature of this model. The computational effort is greatly reduced by realising that there are a finite number of possible values for Φ_a, fixed by the crystallography of the system. These are evaluated at the beginning of the simulation and then used in a look-up table, thus greatly reducing the number of mathematical operations per simulation cycle.

6.5 The Gas Evolution Process

This methodology aims to simulate gas atom evolution onto a metal surface by using simple models of adsorption and desorption. Additional simplifications are imposed: the gas is not allowed to grow beyond a monolayer, no surface diffusion is allowed and periodic boundary conditions are employed.

6.5.1 The Desorption Process

Assuming a single-step activated process, the probability, P_{des}, that desorption occurs between time t and $t+dt$ is given by,

$$P_{des} = \lambda e^{-\lambda t} dt \tag{6.5}$$

where the desorption rate, λ, is given by [116],

$$\lambda = g\nu_0 e^{\frac{-\Phi_a}{kT}} \tag{6.6}$$

where g is a geometric factor taken to be unity, ν_o is the attempt frequency, Φ_a is the environmentally dependent attachment energy defined in equation 6.4, k is Boltzmann's constant and T is temperature. Thus, the probability that any given atom desorbs during a single time period, τ, is

$$P_{des} = \int_0^{\tau} \lambda e^{-\lambda t} dt = 1 - e^{-\nu_0 \tau e^{-\frac{\Phi_a}{kT}}} \tag{6.7}$$

As such T is a variable in the simulations. To a good approximation, the attempt frequency is equivalent to the vibrational frequency of the gas atom on the surface. Thus,

$$P_{des} = 1 - e^{e^{\frac{-\Phi_a}{kT}}} \tag{6.8}$$

where the time step is equivalent to the vibrational frequency. To relate the results to time, the characteristic attempt frequency can be calculated by fitting a harmonic function to the energy profile of a gas atom at a site with all neighbouring sites occupied. For argon this is 4.45 x 10^{-10} s^{-1}. However, since the interaction energy varies according to the number of neighbouring occupied sites, such an analysis is imprecise. Therefore, the results are best reported in time steps rather than in seconds. Nevertheless 100,000 steps will represent approximately 10^{-6} seconds.

6.5.2 The Adsorption Process

During each time step, the number of gas atoms that strike the surface is defined by f_N (the flux), such that,

$$f_N = \frac{(\text{number of atoms striking surface})}{(\text{number of surface sites}) \cdot (\text{time step})} \tag{6.9}$$

The flux thus becomes another variable in the simulation. The incoming atoms are assumed to have a Maxwellian distribution of kinetic energies, ε:

$$n(\varepsilon) = \left(\frac{1}{kT}\right) e^{\frac{-\varepsilon}{kT}} \tag{6.10}$$

The fraction of incoming atoms that adhere to the surface depends on the substrate's ability to dissipate enough kinetic energy for the colliding atom to become trapped in the potential well of the site. Thus, the following assumptions are made:

- any atom with a kinetic energy less than Φ_a will become trapped.

- there is no energy barrier against adsorption i.e. electric field.

Thus, the probability that an incident gas atom sticks, P_{ads}, in a potential well of depth Φ_a is,

$$P_{ads} = \int_0^{\Phi_a} \left(\frac{1}{kT}\right) e^{\frac{-\varepsilon}{kT}} d\varepsilon = 1 - e^{\frac{-\Phi_a}{kT}} \tag{6.11}$$

6.6 The CA Rule Set

The CA simulation is implemented in three stages per time step. The first stage randomly assigns energies to all atoms present on the surface, subject to a Boltzmann distribution at the target temperature, and removes them according to their desorption probability. The second stage randomly assigns incident atoms an interaction site and energy, again subject to a Boltzmann distribution at the target temperature, and adds them according to their adsorption probability. The third stage updates the periodic boundary conditions of the edges of the surface.

6.6.1 Desorption Stage

For the desorption stage, each atom on the surface prior to the adsorption stage is considered for desorption. The probability that each atom desorbs is given by $P_{des}(n_{g,g}, n_{g,d})$, where $n_{g,g} + n_{g,d}$ is the number of occupied nearest neighbour equivalent sites prior to the adsorption stage.

6.6.2 Adsorption Stage

During the adsorption stage N lattice sites, calculated from the flux, are randomly selected, representing locations where the atoms strike. A specific location is identified by the particular CA cell in which it is located and by the label B or C, indicating the lattice site within the cell. Rather than report the number of atoms incident on the surface per time step, N, the flux, f_N, is given because it scales with the number of surface sites (defined as the number of CA cells).

Two possibilities are considered for each lattice site assigned in the flux stage, depending on the occupancy of the lattice site. If the position is already occupied, the incoming atom striking that position does not adhere to the surface. If the position is empty, the probability of sticking depends on the neighbourhood of the site. For example, if there are one or more gas or defect atoms already located in positions that sterically hinder the site under consideration, the adsorption probability is zero and the atom will not adsorb. Otherwise, the atom adsorbs with a probability, $P_{ads}(n_{g,g}, n_{g,d})$, which is a function of the number of equivalent neighbours prior to the adsorption stage. Note that the considered neighbourhood is that which existed before any adsorption occurs.

6.6.3 Potential Parameters

The interaction parameters used for the Lennard-Jones pair potential are taken from the earlier work of Zacate *et al.* [116]. Briefly the $B_{g,s}$ and $B_{g,g}$ parameters are determined from the polarisabilities of the interacting atoms via the Slater Kirkwood formula [117]. The $A_{g,g}$ parameter was chosen to reproduce the lattice parameter of Ar. For the Ca-Ar interaction the $A_{g,s}$ parameter was chosen so that the minimum of $\Phi_{g,s}$ corresponds to a radius given by the sum of the argon radius and the calcium radius.

Table 6.1: Parameters for the Lennard-Jones potential used to described the interaction between argon gas atoms and the calcium (111) surface.

Interaction	A (eV Å^{12})	B (eV Å^{6})
Ca-Ar	$64,447.4$	40.90
Ar-Ar	$53,845.3$	40.90

6.6.4 Cellular Automata Simulation Techniques and Results

As previously mentioned, the code used for this study is still in development and as such it is in the early stages of application. Procedures for interpreting and representing the output from the code are also continually in development. The output produced is purely descriptive of the cell status for a sample of steps. This data can be interpreted pictorially or statistically. A pictorial representation, in the form of an image, at specific time steps presents the surface arrangement of argon on the surface. A series of these images can be converted into a digital movie which shows the evolution of the surface with time. Statistics of surface coverage give an indication of the general behaviour of the surface but not its structure. The advance made in this present work was to enable the setting up of a specific surface prior to the start of the simulation. Additionally the code was modified to take into account interactions with substrate atoms on the surface in gas atom sites. The incorporation of these two aspects have allowed the simulation of gas atoms adjacent to surface defects to be studied in chapter 7.

6.6.5 The Random Number Engine

As is obvious from the above method this technique depends critically on the quality of the random numbers generated by the code. This in turn is dependant upon the implementation of the random number generator function, the choice of constants for the arithmetic and the number of calls made to the function. On this issue, “Numerical Recipes in C” [118] was consulted and it was determined that the internal ‘random’ function used in the C compiler on the calculation machine (an SGI R1000, IRIX 6.x) was quite sufficient for this simulation. The generator is based on the portable routine proposed by Knuth [119]. It should be noted that this implementation is not consistent across all platforms and compliers and, as such, the current code is not truly portable. For full portability the random number generator should be internalised within the code itself.

6.7 Further Work

This code is in the early stages of its implementation and further conceptual advances are expected. Thus, there are many areas that could be advanced. The code, while written in C, requires some reorganisation to bring it in line with best coding practise. Documentation is minimal and until a stable version is reached, it is difficult to see how this can be rectified. The documentation that does exist is in the form of comments in the source code itself. As a purely technical exercise, it is recommended that reorganisation and documentation be implemented before any further code development takes place, thus giving a stable code release.

The simulation routines are quite efficient, however, the routines for reporting simulation results are not. Currently the code outputs everything, rather than that data which is useful. A rationalisation of this strategy should go some way to removing this as a bottleneck, thereby yielding a speed benefit. There are also several ancillary programs and scripts which interpret the code output. These have been written on an *ad hoc* basis when required. As such, there is much overlap and again rationalisation is recommended.

There are two major advancements which would boost the functionality of this code. Firstly, implementation of growth of the gas layer into the 3^{rd} dimension and secondly generalisation of the code for different cell geometries. The first issue would extend the capability of the code and, in conjunction with the second, would extend the range of systems which could be simulated. Neither of these require any advance in the methodology but do present significant coding challenges. A minor development to the code would be to allow the simulation conditions (temperature or flux) to be varied over the simulation. This would allow the non-steady state conditions to be simulated. For example, a domain structure could be evolved for a period of time under constant temperature and gas flux conditions, then heated. Continuing this idea, and as a move towards simulating real conditions, the population of gas atoms could be fixed. Thus, the gas flux would vary as a function of the number of atoms on the surface during any time step. This could vary during the simulation to replicate experimental conditions where a sample is initially in a vacuum but then subject to the gradual introduction of a gas.

In the case of the methodology there are several developments that should be tackled. The introduction of surface diffusion is an important issue, and one that is perhaps most important if low fluxes and high temperatures are simulated. Under these conditions it is reasonable to assume that surface diffusion will become an important process compared to adsorption and desorption events. Currently, the method of dealing with what happens when an incident atom strikes a sterically hindered site is not satisfactory. There is the possibility that such an event may cause some local rearrangement of the blocking atoms. This is likely to be true if there are few neighbours surrounding the blocking atom acting to stabilise it on the surface. Currently interactions are very local and as new systems are investigated then interactions with non-adjacent neighbours may become important and should be accounted for. Implementation of such routines is likely to cause a significant slow down of the simulation which may ultimately reduce the effectiveness of the current methodology. This is of course a dilemma that faces all modern simulation techniques.