

Chapter 7

Simulation of Gas Monolayers on Rough Surfaces

This chapter uses a recently developed version of a cellular automata based code to simulate the interaction of an argon gas flux with both perfect and defective calcium (111) surfaces. Temperature is a variable with a constant flux of 8%. The evolution of 10^4 surface sites over approximately 10^{-6} seconds with very modest computing facilities is achieved. In these simulations, the formation and growth of domains is observed. However, the rate of growth is not a well-behaved function of temperature, but instead exhibits a critical region in which the growth rate suddenly falls to zero. Surface defects, as defined by the degree of surface roughness, are also shown to have a dramatic effect on domain growth morphology.

7.1 Introduction

Continuing the development of a CA model to describe microstructural evolution, this chapter describes the results of work for a simple atomistic simulation of gas evolution onto defective calcium (111) surfaces. The methodology applied in the code has been previously described in chapter 6. Simulation runs result in the formation and growth of domains, with the domain growth rate increasing as a function of simulation temperature. Previous results with an earlier version of this code [116] revealed that the domain size increases as a function of the flux of atoms incident on the surface. However, for the results presented here, the flux rate was held constant at eight percent (i.e. the number of gas atoms that were allowed to interact with the surface corresponded to eight percent of the total number of surface sites).

During a simulation run when the first few gas atoms impinge on the surface they may reside in either B or C sites (defined in chapter 6). As more atoms collect, patches or islands of B- and C-type atoms form. The distance between two neighbour B-type gas atoms (i.e. in nearest neighbour equivalent sites) is the same as between two neighbouring C-type gas atoms (i.e. where $R = 2r_{Ca}$, see figure 7.1). However, the distance between neighbouring B- and C-type atoms is greater. This results in a surface area with a lower density of gas atoms, termed a growth fault. In three dimensions, this would give rise to a stacking fault. Faults are important to the stability of a gas atom on the surface since the interaction energy of gas atoms is lower when they interact over longer distances. Therefore, atoms adjacent to growth faults have a lower attachment energy. This is the driving force that results in the formation and growth of islands of gas atoms that occupy only one type of site.

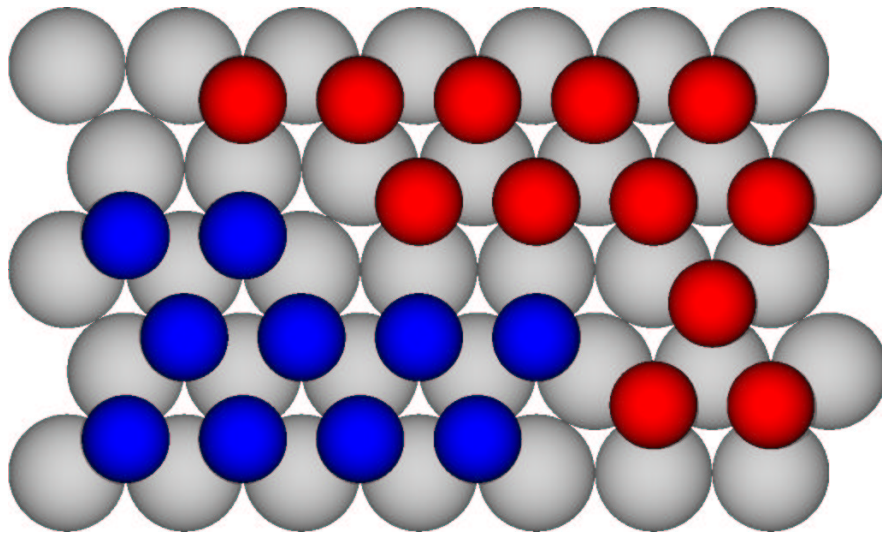


Figure 7.1: Argon gas atom domain boundaries on a calcium (111) surface.

7.2 Results

In this chapter four different surfaces: a perfect surface and three rough surfaces, as illustrated in figure 7.2, are simulated. Simulations were run for 100,000 time steps. Each surface was 100 by 100 atoms and subjected to an 8% argon gas flux. Gas morphology information was collected at four temperatures (90K, 100K, 120K and 140K) and is presented pictorially for the four test groups.

The first group of results show argon gas evolution onto a perfectly flat calcium (111) surface. Subsequent results show gas evolution onto various types of calcium surface roughness; however, in each case, the degree of roughness, characterised by the number of additional calcium atoms on the (111) surface, is constant at 10% coverage. Thus, when it is assumed that the additional calcium atoms are randomly distributed, as shown in figure 7.2a, one in every 20 surface sites contains a calcium atom (the maximum number of surface sites that could be occupied is 50%, which would correspond to 100% coverage). The opposite scenario was also considered, in which all additional calcium atoms aggregated to form a hexagonal (i.e., roughly spherical) island occupying only B

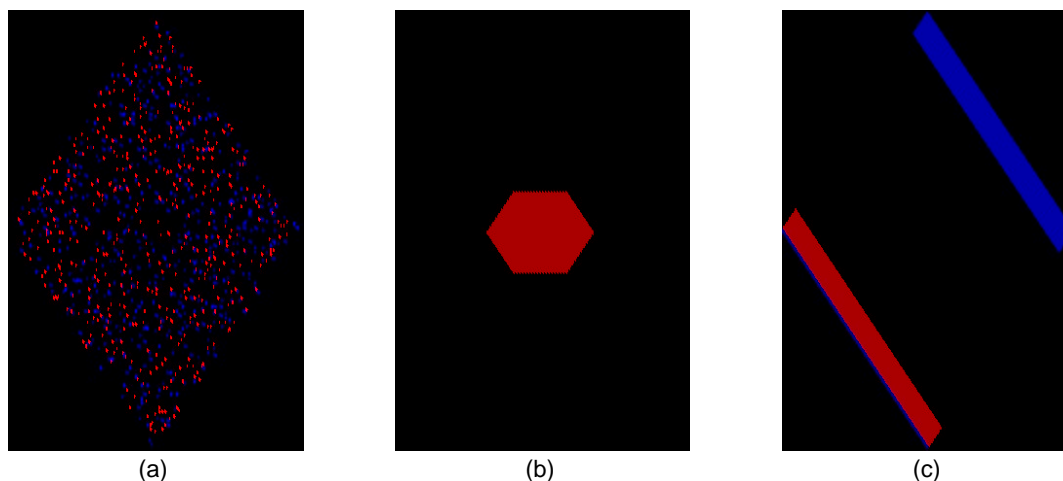


Figure 7.2: Pictorial representation of the atomically rough surfaces before the simulation begins: a) distributed roughness b) hexagonal feature c) canyon feature. (Fixed calcium B site occupied cells are dark red, fixed calcium C type occupied cells are dark blue.)

sites as shown in figure 7.2b. Nevertheless, such an island still has a very small radius, much smaller than the size of a typical microstructure. Therefore, in the final group of results, the additional atoms form a canyon-like structure that has an effectively infinite radius of curvature, as shown in figure 7.2c. The hexagon feature of the third group should therefore be considered as an intermediate radius structure. Results for each type of surface are presented in figures 7.3-7.6 each in the form of a matrix of surface domain structure snapshots. There are two variables in the matrix: time, t , in simulation steps, increasing across the page (at $t=100$, $t=1,000$, $t=10,000$, $t=100,000$) and temperature, in Kelvin, increasing down the page (at 90K, 100K, 120K and 140K). While these static 'snap shots' of the surface are sufficient to understand the processes involved, they do not convey the time evolution well. This data has been presented in a previous electronic publication [120]¹ which contains animated movies of the same data. It is recommended that this be read alongside figures 7.3-7.6.

¹also mirrored at <http://abulafia.mt.ic.ac.uk/JOM-e/Atkinson-9908/Atkinson-9908.html>

A separate series of simulations were run for only 10,000 time steps but at a wider range of temperatures (10 degree intervals from 70K to 170K). Here only statistical data was collected. For each set of conditions five runs were simulated each with a different random seed for the random number function. The random number generator in the code is responsible for assigning sites, adsorption events and atom energies. The average coverage statistic (over the five runs) versus temperature is presented graphically in figure 7.7. The coverage statistic is defined as the percentage of the surface covered by argon after 10,000 time steps.

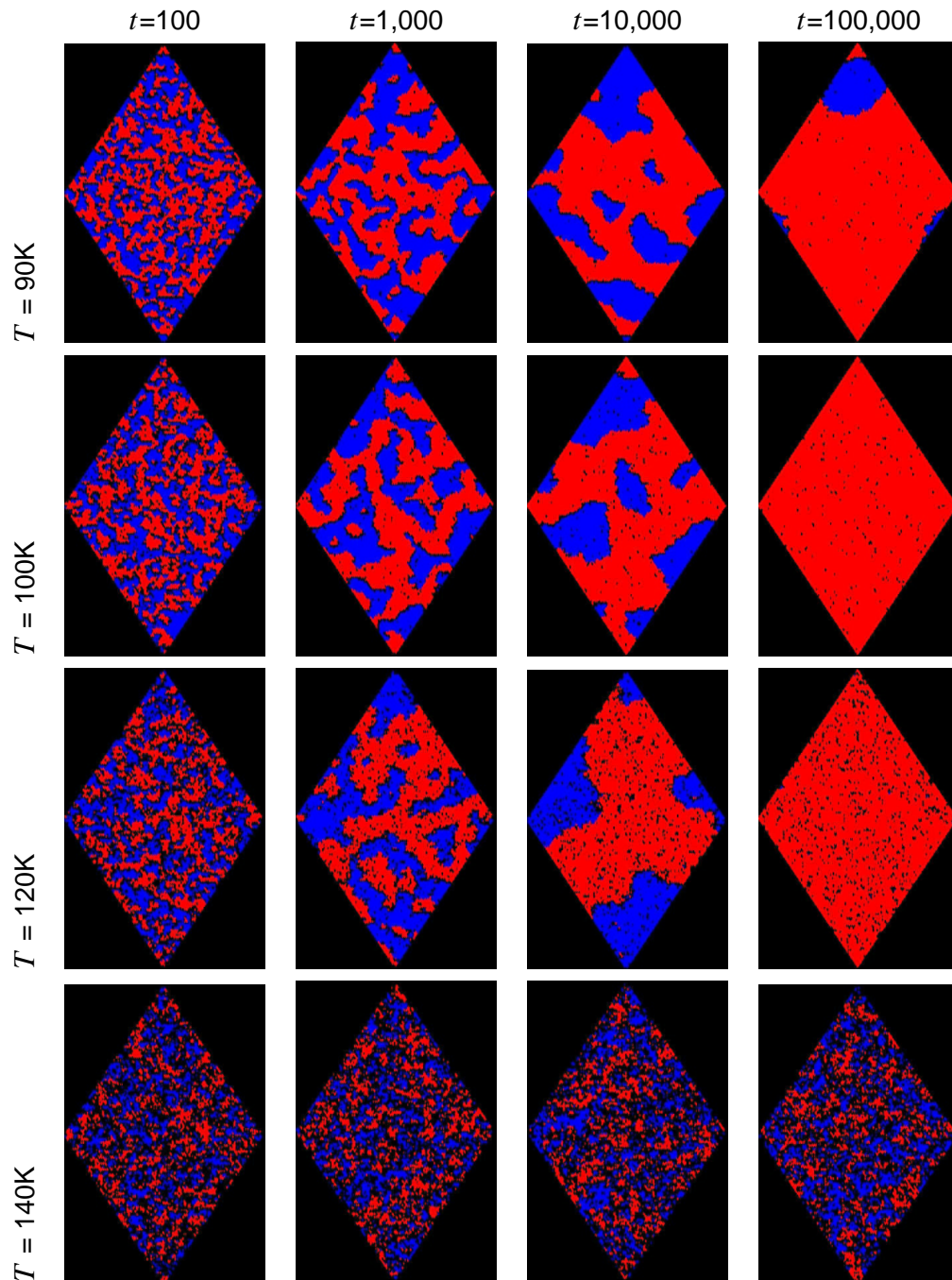


Figure 7.3: Pictorial representation of the argon domain structure evolution on a perfect calcium (111) surface (argon B site occupied cells are red, argon C type occupied cells are blue).

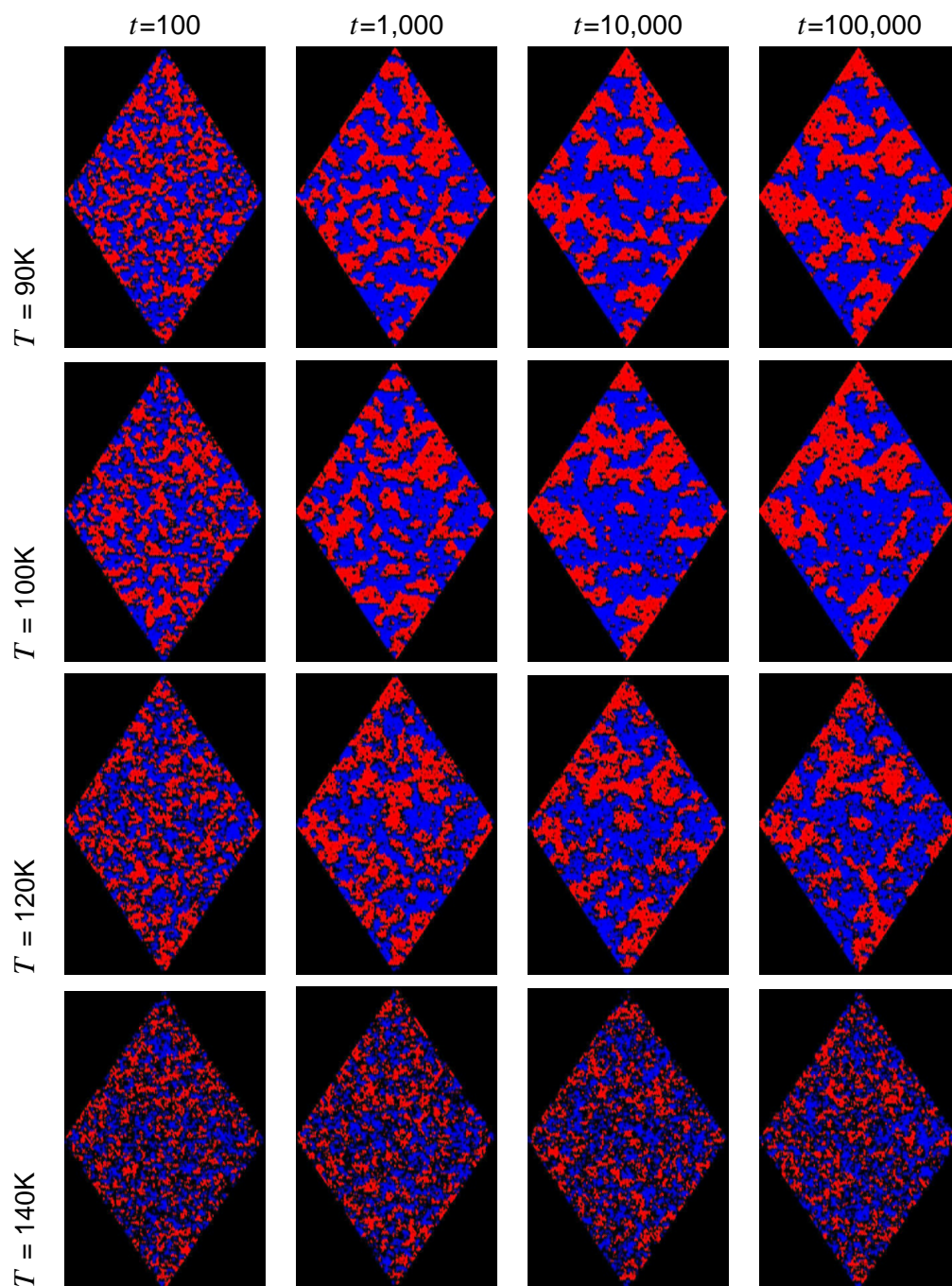


Figure 7.4: Pictorial representation of the argon domain structure evolution on a calcium (111) surface with distributed roughness (argon B site occupied cells are red, fixed calcium B site occupied cells are dark red, argon C type occupied cells are blue, fixed calcium C type occupied cells are dark blue).

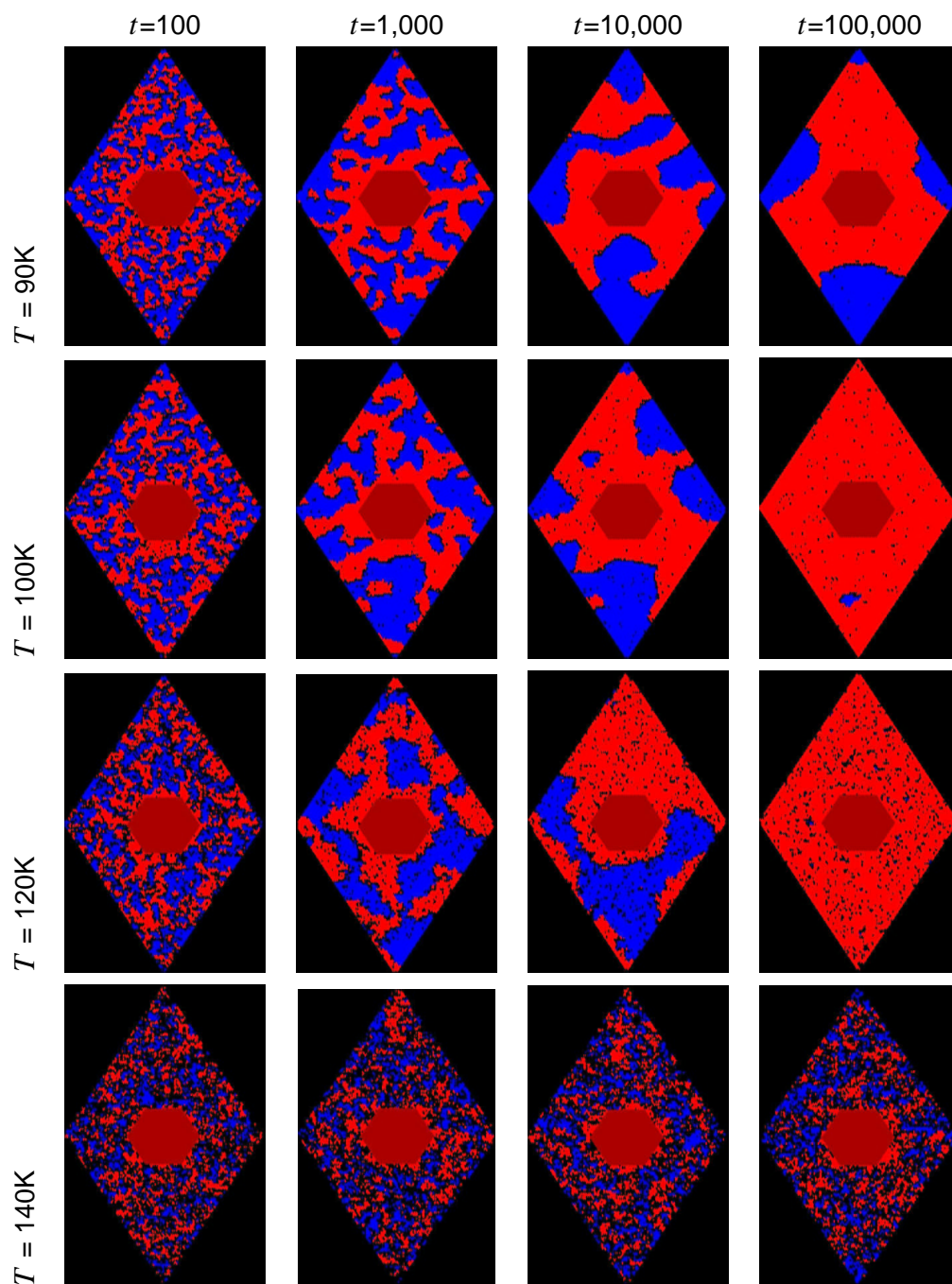


Figure 7.5: Pictorial representation of the argon domain structure evolution on a calcium (111) surface with a hexagonal calcium feature (argon B site occupied cells are red, fixed calcium B site occupied cells are dark red, argon C type occupied cells are blue, fixed calcium C type occupied cells are dark blue).

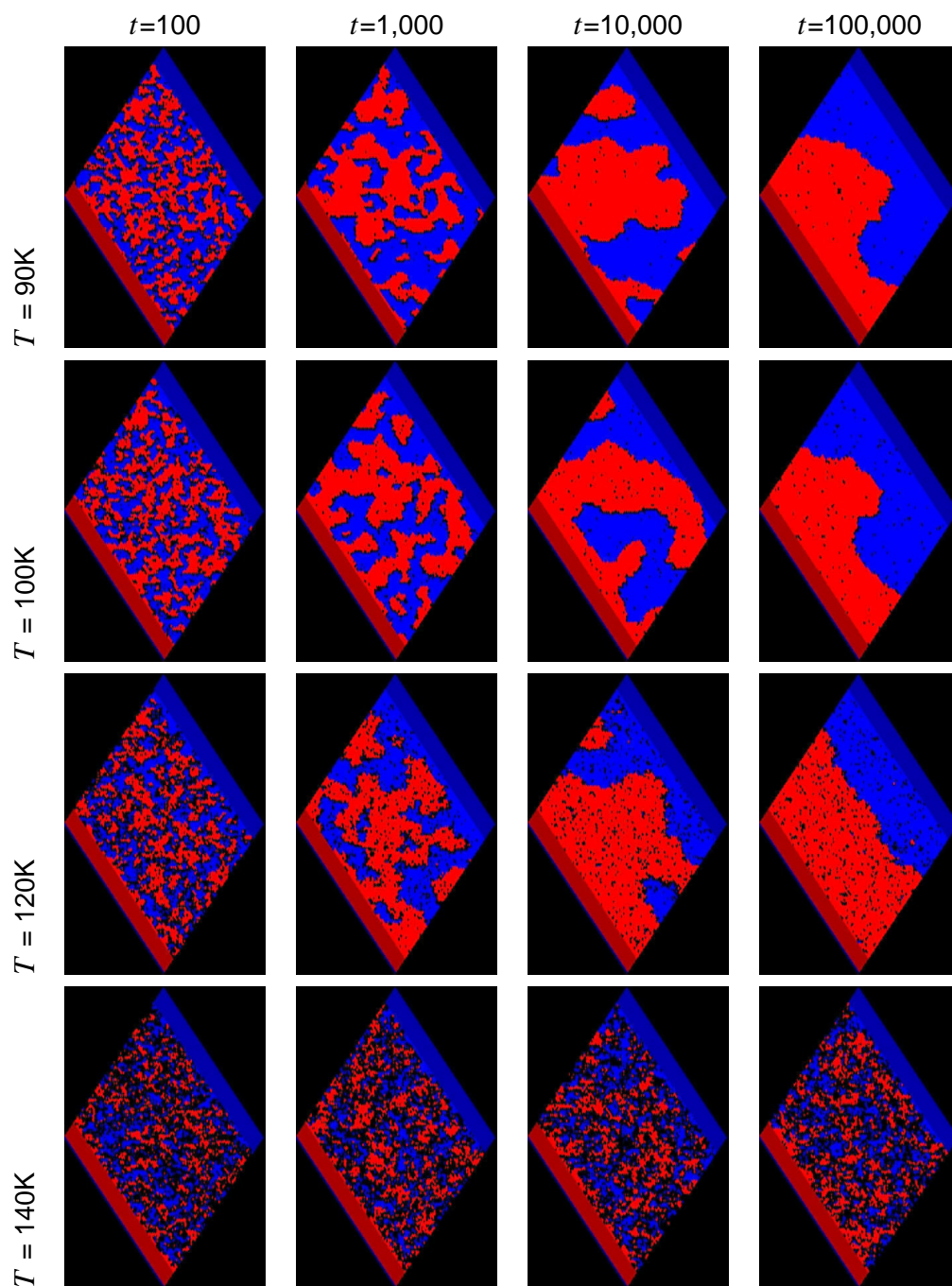


Figure 7.6: Pictorial representation of the argon domain structure evolution on a calcium (111) surface with a canyon calcium feature (argon B site occupied cells are red, fixed calcium B site occupied cells are dark red, argon C type occupied cells are blue, fixed calcium C type occupied cells are dark blue).

7.3 Discussion

7.3.1 The Perfectly Flat Surface

Starting with a perfectly flat surface, the coverage initially increases as a function of time while empty surface sites become occupied. Once the majority of sites are occupied (at an 8% flux, this occurs in a matter of a few tens of time steps), the arrangement of gas atoms on the surface begins to evolve. This is characterised by domain growth, with the smaller domains being consumed. The rate of domain growth can be quantified by considering the coverage after 10,000 time steps (figure 7.7). This shows that below 115 K the surface is 90% covered by gas atoms, but above this temperature there is an abrupt reduction in the coverage. Indeed, the reduction is so abrupt that it might be described as a critical phenomenon.

The generally constant coverage below 115 K is the result of an interplay between two processes. At the lowest temperatures, there are still a number of growth faults after 10,000 time steps, which, given their lower site density, reduce the overall coverage. In addition, there are a small number of missing gas atoms in the interior of the gas-atom domains (i.e. point defects). This is apparent in figure 7.3 (t=10,000@90K). As the temperature rises, there are fewer growth faults but more point defects (see, for example, figure 7.3 (t=10,000@100K) and figure 7.3 (t=10,000@120K)). Nevertheless, the surface is effectively stable since each gas atom is surrounded by a majority complement of its nearest equivalent neighbours.

Once the temperature reaches 120K to 130K, the coverage reduces rapidly. The rate at which atoms leave the surface becomes sufficiently high that each gas atom has a significantly smaller complement of nearest equivalent neighbours. Consequently, the energy required to remove each gas atom, Φ_a , is smaller, and gas atoms more readily desorb from the surface. This is the origin of the dramatic reduction in surface coverage

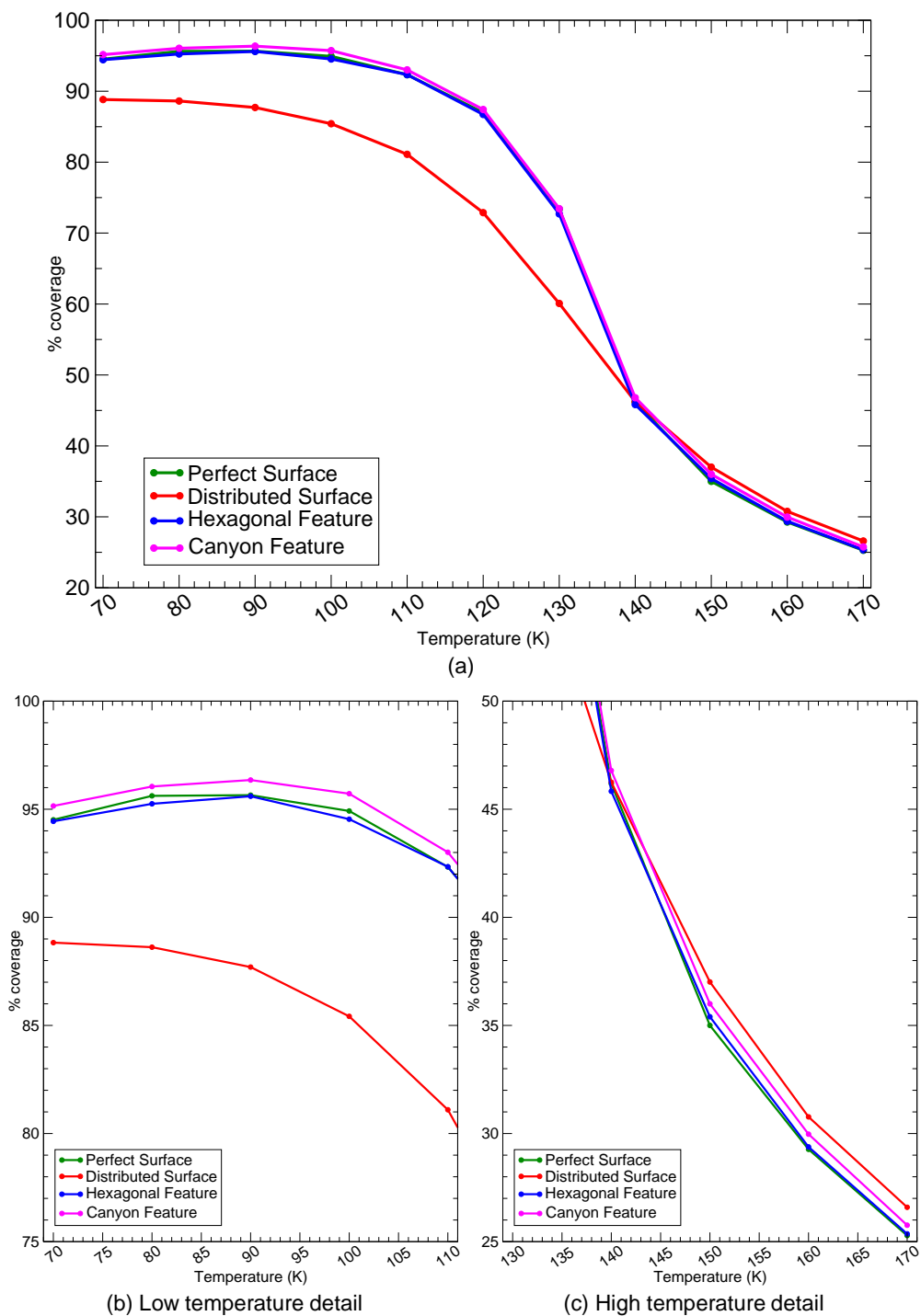


Figure 7.7: The coverage at 10,000 time steps for perfect and imperfect 100 x 100 atom surfaces at varying temperature: a) full data set b) detail at low temperature c) detail at high temperature.

rather than exponential decay, which would be expected purely on the basis of increasing temperature.

7.3.2 The Randomly Distributed Surface

The surface with randomly distributed roughness (see figure 7.4) shows a different coverage vs. temperature behaviour than the perfect surface. This is characterised by lower coverage at low temperatures (see figure 7.7). As the temperature is increased, there is immediately a gradual reduction in coverage. By 140 K, the coverage for this surface is effectively the same as for the other surfaces, because the gas-atom coverage of all surfaces is highly unstable.

Consider the development of the distributed rough surface at 90K seen figure 7.4. After 100 time steps, the distributed rough surface morphology is very similar to that of the perfect surface. Even after 1,000 time steps, these rough and perfect surfaces are fairly similar, although some domain growth has occurred. After 10,000 time steps, the surfaces are quite different, with the domain size growth of the distributed roughness surface being effectively arrested. It is tempting to state that the domain size has been pinned, but by 100,000 time steps there is some indication that more growth has occurred, although the effect is small considering the number of time steps has increased by an order of magnitude.

An interesting observation is that for the distributed roughness surface, the domain size at 1,000 time steps and beyond is greater than the distance between the defect surface calcium atoms (see, for example, figure 7.4 ($t=10,000@100K$)). Consequently, each domain contains a number of additional calcium atoms. Furthermore, the surface calcium atoms occupy both B and C sites within each domain; clearly, the additional calcium atoms are not simply acting as classical nucleation points. The reason the domain

structure becomes contained in the way that it does is a complex interplay between the specific surface roughness distribution and the initial random deposition process over the first few hundred time steps.

7.3.3 The Hexagonal Surface Feature

Figure 7.5 presents data for the hexagonal feature. In this case, the variation in coverage is practically identical to that found for the perfect surface (see figure 7.7). However, in figure 7.5, it was observed that, to a certain extent, the growth proceeded from the hexagon. Hence, it is interesting that this did not have an effect on the overall coverage after 10,000 time steps. The hexagon may affect the initial nucleation and growth, but this is a local process which, after a certain point, becomes unimportant to the slower growth process. Similarly, the small amount of enhanced B site coverage around the hexagon at 140 K did not lead to enhanced coverage, and the surface remains unstable. One important feature of this surface is that the coverage always evolves towards a single B site dominated domain.

7.3.4 The Canyon Surface Feature

The observations of the canyon feature suggest that there are a number of characteristics in common with the hexagonal feature (see figure 7.5). For example, the existence of the feature causes nucleation and growth of same-site gas atom structures over the first 1,000 time steps adjacent to the feature; this stabilises the growth of the single-site domains. However, in figure 7.7, the canyon simulation shows essentially the same coverage at 10,000 time steps as does the hexagon and perfect surfaces. Again, the existence of a feature has a strong influence on what initially nucleates and grows, but not on the overall coverage after the initial growth period.

Because the canyon feature is composed of two different site features opposite each other, the result is the growth of two different site domains. The 90K, 100K, and 120K simulations after 10,000 time steps yield domain structures that are inter-growths. The remaining 90% of the simulation time (i.e. to 100,000 time steps) is required for a clear bimodal domain structure to develop. By comparing the 90K, 100K, and 120K simulations, it is clear that at the higher temperature, the structure is more developed toward some form of equilibrium. Because of the equivalence in the energetics associated with B- and C-site gas atom absorption and the nature of the periodic boundary conditions, such a straight equal-proportioned domain structure might be expected; however, this type of simulation would also allow investigations on the extent of the boundary fluctuation as a function of temperature and gas-atom flux.

7.4 Conclusions

This study bridges three orders of scale in both the spacial and time dimensions; from atomistic to microstructural simulations, resulting in new insights into the growth of surfaces. Despite the apparent simplicity of this model system, qualitative analyses of data, such as in figure 7.7 can conceal the complex interplay of physical processes that result in microstructural evolution. As models become more sophisticated and include multiple physical processes, it will become harder to identify the underlying causes responsible for such dramatic effects on surface evolution. Consequently, the analysis tools that interpret large volumes of simulation data will be as important as the simulation methods themselves. However, as simulation methods become more proficient, it will still be important to be able to extract physical understanding.

There is a strong incentive to develop simulation methods that accurately predict physical phenomena independently of experiment. Given the overwhelming complexity of

real systems, this approach may not be the most effective. A more practical alternative is to adjust a representative set of atomistically derived parameters for the CA rule set in order that a limited number of experimental microstructures are accurately reproduced. Such a procedure would provide a simple check for the validity of the model and effectively provide a more accurate simulation. Ideally, the parameters would only need fine adjustments to reproduce the experiment, thereby preserving the atomistic interpretation of phenomena associated with the microstructural evolution. Furthermore, this approach would avoid over parameterisation and an unnecessarily complex model. Once the parameters are calibrated to a set of well-characterised experimental data (i.e. where process variables, such as temperature and flux, are well known), the process variables could then be varied in the CA simulations to determine the optimal experimental conditions for producing a prescribed microstructure.

7.5 Further Work

It is easy to envisage areas of further work with this code, however, it will be dictated by developments in the methodology and code itself. It is difficult to predict the next direction that development will take and so comments here are mainly concerned with what is achievable with the current version of the code. Possible methodology and coding advances have already been discussed in chapter 6.

With the current code, recent increases in CPU power mean that the limit is now 1000 by 1000 sites simulated for 10^7 time steps (equating to approximately 10^{-3} seconds). Thus, larger and longer simulations should be run to see if new behaviours are observed at larger size and longer time scales. It would be interesting to increase the number of time steps by at least another order of magnitude (compared to that used here) to see if the retarded growth, seen for the distributed surface, is indeed 'pinning' or a significant

retardation of growth rate. Thus, the term 'pinning' is relative and simulations should be repeated for longer periods.

In the case of distributed surface roughness the effect of varying the percentage of distributed roughness on the surface may reveal a transition between the rough surface 'pinning', seen here, and the continual evolution seen in the perfect surface. The question would be: How much roughness is needed to 'pin' a surface domain structure?

Other work should consider the effects of varying island feature curvature and size to study the effect on domain evolution. Additionally, different calcium island shapes could be considered (triangle, square and higher order polygons). Yet another alternative would be to study line type defects. Results from the canyon feature suggest that it may be interesting to study the interaction of domain fronts. With the ability to simulate larger surfaces, this could be achieved by constructing several island features on one surface. Finally, other distributions of surface roughness, intermediate between the totally random and condensed features presented in this work, would be possible to implement.

It is apparent in this study that the surface is quickly saturated and the majority of the simulation time evolves the domain structure. As such, there is not an established nucleation and growth regime. The study of very low flux rates may reveal this alternative type of behaviour and is the subject of current investigations.

With advances in the code would come the possibility to study different cell geometries. These alternative cells would be applicable to other systems. For example, staying with monolayer systems, the adsorption of carbon monoxide molecules onto a metal could be considered. Simulation in the 3rd dimension would allow more complex defect structures and multilayer growth to be studied.