

# First stages of epitaxial growth studied by rate equations or MC approaches

## I. Introduction

This project concerns the analysis of the growth on surface using rate equations or Monte-Carlo approaches.

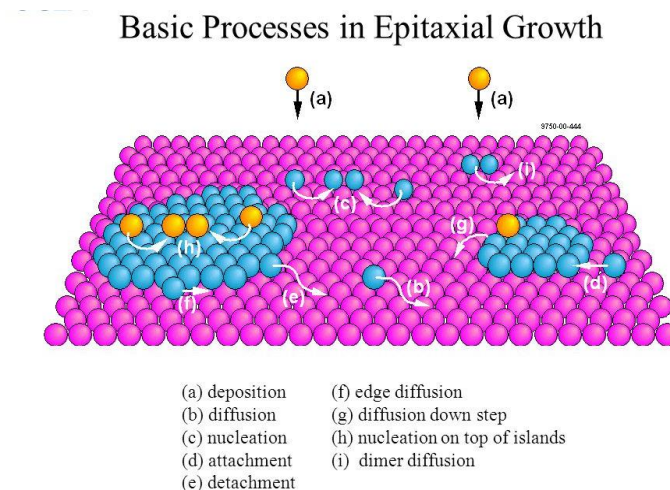
There are several tasks to be done which are more or less connected to each other. A team manager should be assigned and the number of persons allocated per task should be discussed carefully. Of course they should not be assigned randomly but tasks should be given to the « right » persons, i.e. taking into account their expertise, their programming skills, the time they can spend to the dedicated task or even their lazyness and courage ! It is like in real life ! It is a team worm with advantages and inconvenients to work inside a real team !

## II. The model

In this project, we want to look at the growth phenomena using a rate equation approach and a Kinetic Monte-Carlo approach. We will use the usual deposition, diffusion, aggregation model to mimick them.

### Adsorption on a surface:

Adsorption is a 2D phenomena which occurs on the surface of a material. The main process which occur are depicted in Figure 1



Here, adsorption of atoms will be done on a rectangular terrace of area ( $L \times L$ ). The lattice geometry is chosen to be a square of unit side. Thus,  $L^2$  defines the total number of accessible adsorption sites. Atoms (we will call them also monomers) from the gas phase are deposited randomly on single sites of the 2D lattice with a flux  $F$  ( $s^{-1}$ ), and they can diffuse from a site to an adjacent one with a diffusion coefficient  $D_1$  ( $s^{-1}$ ). We assume that only monomers on the surface can move in the present work. When two monomers occupy adjacent sites, they form an irreversible, fixed, dimer, and so on, in order to produce growing

motionless islands. For small coverages (less than 0.1) we can avoid double layer growth but not for larger coverages.

The diffusion coefficient  $D_1$  per surface area unit is fixed to  $10^4 \text{ s}^{-1}$ . The flux  $F$  has to be varied from  $5 \cdot 10^{-6}$  to  $10^4$  monolayer  $\text{s}^{-1}$  in order to sample a wide set of  $F/D_1$  values.

### The rate equation model for adsorption

The time variation of the mean density of monomers in monolayer per second unit on a surface is approached by the equation

$$\frac{dn_1}{dt} = F - 2k_1D_1n_1^2 - k_2D_1n_1n - k_3Fn - 2k_3Fn_1 \quad (1)$$

where the first term on the right-hand side of Eq.1 creates the monomers on the terrace and the second and third terms describe the loss of monomers that nucleate or aggregate to the island, respectively. The fourth and fifth terms correspond to direct impingement of deposited monomers onto monomers or islands.

The parameters  $k_1$  and  $k_2$  can be related to the efficiency of monomer-island and monomer-monomer collisions in the nucleation process, respectively.  $k_3$  can be related to the efficiency of monomer-monomer collisions between one deposited monomer and one monomer already adsorbed on the surface.

The time evolution of the island density is approached by the equation

$$\frac{dn}{dt} = +k_1D_1n_1^2 + k_3Fn_1 \quad (2)$$

where the right-hand side terms characterize the formation of an island due to monomer-monomer collision on the surface and to direct collision between one deposited atom and a monomer on the surface, respectively.

Note that, compared to Eq.1, a factor 2 disappears due to the fact that these two processes create only one island, while two monomers disappear.

We can add an equation describing the mean island size  $s$  defined as the ratio of the density  $n_i$  of atoms in the islands over the density of islands  $n$ . The density  $n_i$  follows the rate equation :

$$\frac{dn_i}{dt} = +2k_1D_1n_1^2 + k_2D_1n_1n + k_3Fn + 2k_3Fn_1 \quad (3)$$

The time behavior of  $s(t)$  can be obtained from the knowledge of  $n_i$  and  $n$ .

Note that Eqs.1 and 2\_ form the basis of the RE approach since they are intrinsically coupled, while Eqs. 3 only serves to define observables which depend on the data extracted from the previous Eqs. 1 and 2.

We can estimate  $k_1$ ,  $k_2$  and  $k_3$  independently using subsidiary simple simulations.

### **Task 1. Determination of parameter $k_1$**

To determine  $k_1$ , we must calculate the number of collisions between monomers deposited on a (LxL) surface. The monomer density should remain very small.

For a given (LxL) value and a small number of deposited monomers, make a large number of random diffusions  $N_{\text{dif}}$  for the monomers, with no possible aggregation i.e., when two monomers collide, they are randomly redeposited on the surface.  $k_1$  is equal to the ratio between the number of collisions between monomers and the number of diffusions.

Goal : give an estimate of  $k_1$

Pay attention to the influence of :

- Size of the system (LxL)
- Conditions at the limits of the simulation box
- Number of diffusion allowed  $N_{\text{dif}}$
- Number of independent calculations
- Chosen density of monomers on the surface  $n_1$

### **Task 2. Determination of parameter $k_2$**

The same kind of trivial simulations can be performed to estimate the efficiency of collisions  $k_2$  between a monomer and a fixed point island, which is in fact the diffusion efficiency of a single monomer. On a (LxL) surface, we thus must calculate the mean number of visited sites after  $N_{\text{dif}}$  random diffusions of a single monomer. The monomer density should remain very small.

For a given (LxL) value and a small number of deposited monomers, make a large number of random diffusions  $N_{\text{dif}}$  for the monomers.  $k_2$  is equal to the mean number of visited sites after  $N_{\text{dif}}$  random diffusions.

Goal : give an estimate of  $k_2$

Pay attention to the influence of :

- Size of the system (LxL)
- Number of diffusion allowed  $N_{\text{dif}}$
- Number of independent calculations
- Chosen density of monomers on the surface  $n_1$

### **Task 3. Determination of parameter $k_3$**

We can also estimate the efficiency of direct collision between a deposited atom and a monomer already deposited on the surface. The density of deposited monomers should remain small.

For a given ( $L \times L$ ) value and a small number of deposited monomers, make a large number of random depositions  $N_{\text{dep}}$  for the monomers.  $k_3$  is equal to the ratio between the number of collisions between deposited/adsorbed monomers and the number of deposition events.

Goal : give an estimate of  $k_3$

Pay attention to the influence of :

- Size of the system ( $L \times L$ )
- Number of deposition  $N_{\text{dep}}$
- Number of independent calculations

#### Task 4. Resolution of the rate equations

Numerical solution of Eqs. 1 and 2 look simple but you will not have time to wait for the determination of  $k_1$ ,  $k_2$  and  $k_3$  values by your colleagues. You should prepare the code in advance and anticipate for the numerical problems you can face.

Try to solve this coupled differential equations using different  $F/D_1$  values. Make sure that for large  $F$  or  $D_1$  values you can easily explain the numerical results you have obtained.

Goal : development of the rate equation solution program

Pay attention to the influence of :

- Time step  $\Delta t$
- $F/D_1$  values
- Number of deposition  $N_{\text{dep}}$
- Number of independent calculations

#### Task 5. Coadsorption of species that can mix

In this task, we consider the coadsorption of two species A and B, i.e. that two species can be deposited with the same flux  $F$  ( $\text{s}^{-1}$ ) on a rectangular terrace of area ( $L \times L$ ). We will deposit the same amount of A and B species. The lattice geometry is always a square of unit side. A and B atoms can diffuse from a site to an adjacent one with diffusion coefficient  $D_A$  ( $\text{s}^{-1}$ ) and  $D_B$  ( $\text{s}^{-1}$ ). We also assume that only monomers can move in the present task. When two monomers (A or B) occupy adjacent sites, they form an irreversible, fixed, dimer, and so on, in order to produce growing motionless islands. For small coverages (less than 0.1) we can avoid double layer growth but not for larger coverages.

- Determine the new rate equations satisfied by monomers (A and B) and islands
- If needed, contact your colleagues who did tasks 1-3 for  $k$  values you need to know

The flux  $F$  is chosen at  $10^{-2}$  monolayer  $\text{s}^{-1}$ . The diffusion coefficient  $D_A$  per surface area unit is fixed to  $10^4 \text{ s}^{-1}$ . The diffusion coefficient  $D_B$  has to be varied in order to sample a wide set of  $D_B/D_A$  values.

- Contact your colleague who did tasks 4 for solving your equations

Pay attention to the influence of :

- Time step  $\Delta t$
- $D_B/D_A$  values
- Number of deposited particles
- Number of independent calculations

### Task 6. Coadsorption of species that can react

In this task, we consider the coadsorption of two species A and B, i.e. that two species can be deposited with the same flux  $F$  ( $s^{-1}$ ) on a rectangular terrace of area ( $L \times L$ ). We will deposit the same amount of A and B species. The lattice geometry is always a square of unit side. A and B atoms can diffuse from a site to an adjacent one with diffusion coefficient  $D_A$  ( $s^{-1}$ ) and  $D_B$  ( $s^{-1}$ ). We also assume that only monomers can move in the present task. When two monomers (A or B) occupy adjacent sites, they react and form a new molecule C. This one can move with the lowest diffusion coefficient (compare  $D_A$  and  $D_B$ ). When monomers A-A, A-B, A-C, B-C are on adjacent sites they form irreversible, fixed, dimer, and so on, in order to produce growing motionless islands. For small coverages (less than 0.1) we can avoid double layer growth but not for larger coverages.

- Determine the new rate equations satisfied by monomers (A,B and C) and islands
- Contact your colleagues who did tasks 1-3 if needed for k values you need to know

The flux  $F$  is chosen at  $10^{-2}$  monolayer  $s^{-1}$ . The diffusion coefficient  $D_A$  per surface area unit is fixed to  $10^4 s^{-1}$ . The diffusion coefficient  $D_B$  ( $D_B \leq D_A$ ) has to be varied in order to sample a wide set of  $D_B/D_A$  values.

- Contact your colleague who did tasks 4 for solving your equations

Pay attention to the influence of :

- Time step  $\Delta t$
- $D_B/D_A$  values
- Number of deposited particles
- Number of independent calculations

### Task 7. Kinetic Monte-Carlo code

Another way to obtain the monomer and island densities together with the size of the islands formed on the surface is to build a Monte-Carlo code which takes into account for the main processes (Deposition, Diffusion and Aggregation)

For a given ( $L \times L$ ) surface, you can randomly deposit particles with a frequency  $F(s^{-1})$ . Between two successive deposition events, all the monomers can make diffusion jumps (compare  $D$  and  $F$ ). When monomers make collisions they stick irreversibly to make a dimer. Monomers can also diffuse and stick to an island. We will investigate only low coverage values (10% of a layer at maximum)

How will you take into account temperature  $T$  for the MC configurations to be allowed or not ?

Goal : development of the KMC program

Pay attention to the influence of :

- $F/D_1$  values
- (LxL) surface area
- Number of independent calculations
- ...

**Of course, you will have no time to investigate all the situations proposed here (basic model, coadsorption of species that can mix, that can react...) for KMC simulations. Make choices and justify them.**

**Note : You will certainly face some numerical problems connected to**

- convergence criteria
- size of the systems you can simulate
- number of configurations you can calculate.

**Probably numerical tricks will be needed here.**

**Enjoy it!**