A realistic Kinetic Monte Carlo approach for two-component deposition processes

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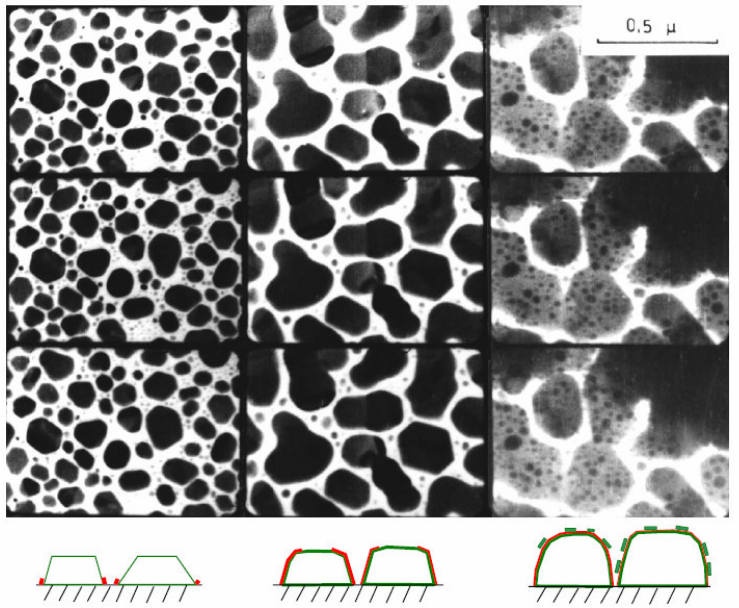
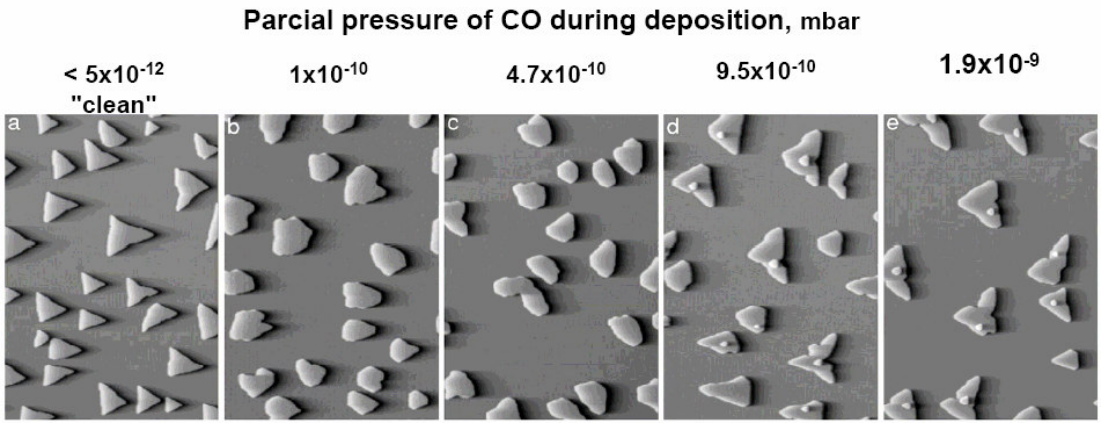
Motivation

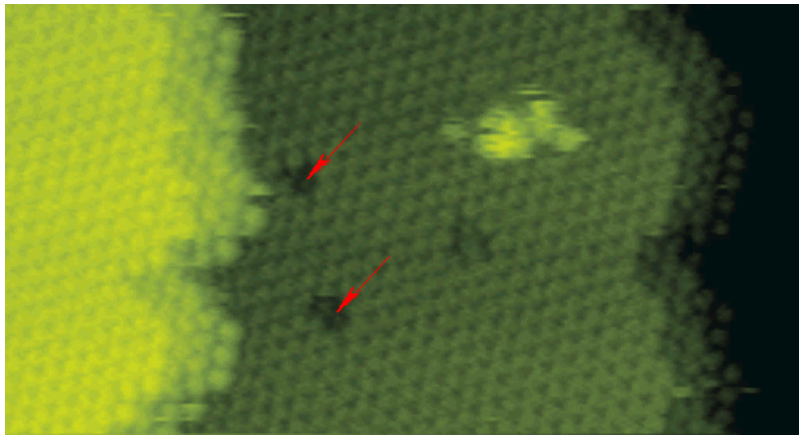
-Modelling two-component deposition processes (segregation, covering layers, etc….)

*growth of carbon doped indium films (in situ TEM experiment, **Pocza** et. al, Jpn. J. Appl. Phys., Suppl. 2, Part 1, 525, 1974)*



-Studying the effect of impurities on surface growth kinetics





Key experiment on contamination effect: influence of CO adsorption on the growth of Pt on Pt(111) surface at 400 K

*(M. **Kalff,** G. **Comsa**, Th. **Michely**, PRL 81(1998)1255)*

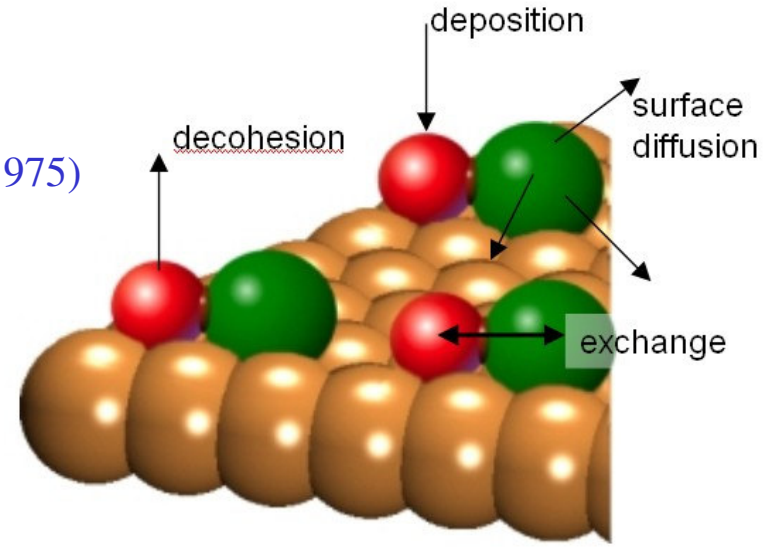
surface of a growing ferritin crystal in the neighborhood of defects (three unfinished crystal layers are visible, with the higher layer colored in brighter yellow)

*from **S.T. Yau** and **P. G. Vekilov***

The classical Kinetic Monte Carlo approach

(kinetic MC → resident time MC or BKL MC)

Bortz, Kalos, Lebowitz; J. Comp. Phys. vol. 17, 10 (1975)



-stochastic simulation on a fixed lattice (L x L)

- fast (much faster than Molecular Dynamics simulations)

-usually a simple 2D simulation (one growing layer on a substrate)

-the following microscopic processes are incorporated:

- **deposition of atoms**
- **surface diffusion of the atoms**
- **decohesion of atoms**
- **direct exchange between neighbouring atoms of different type (?)**

-each process is characterized by a given rate (*R*)

1. deposition rate (number of particles of type *X*, deposited on the surface in unit time) (F_X → the deposition flux for species *X*)

$$R^X_{dep} = F_X \cdot (L \times L)$$

2. surface diffusion rate of species *X*

(k_0 the attempt frequency ≈ vibration frequency of atoms, $E^X_{I \to F}$ is the energy barrier for jumping on a neighbouring site)

$$R^X_{diff} = k_0 \exp(-\frac{E^X_{I \to F}}{kT})$$

3. decohesion rate of atoms of type *X*

($E^X_{tot(I)}$ → total binding energy of atom at site *I*)

$$R^X_{dec} = k_0 \exp(-\frac{E^X_{tot(I)}}{kT})$$

4. direct exchange rate between atom of different species

(E_{ex} → a phenomenological potential barrier characterizing this exchange)

$$R_{ex} = k_0 \exp(-\frac{E_{ex}}{kT})$$

T: the temperature, k: the Boltzmann constant)

A specific example: studying impurity decorated islands for a two species deposition process

M. Kotrla, J. Krug, P. Smilauer, Surface Science 454-456 (2000) 681-685; PRE vol. 62, 2889 (2000)

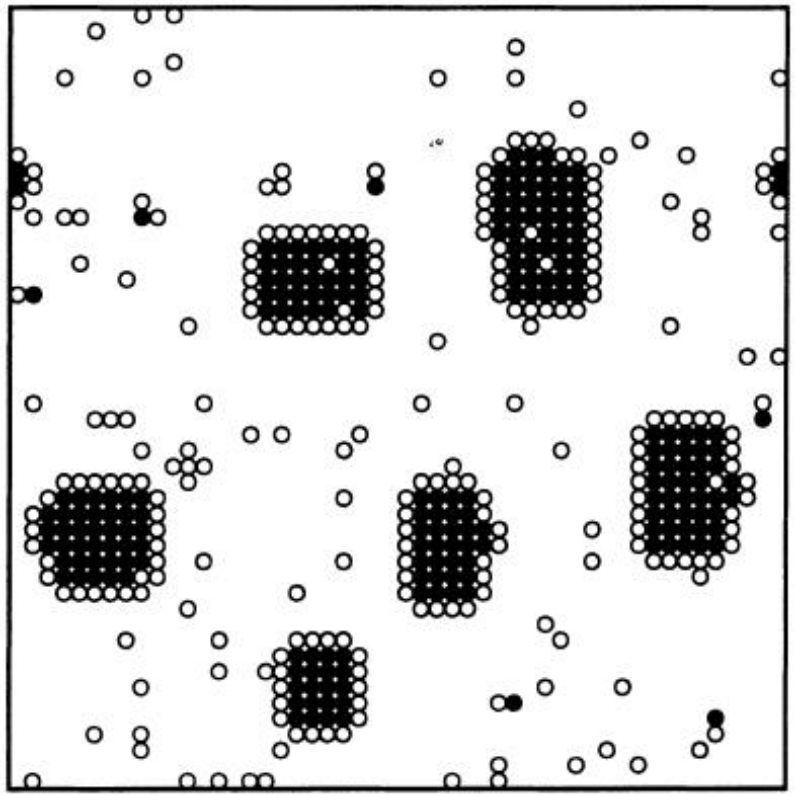
- Co-deposition of species **A** (adatoms) and **B** (impurities) on a planar surface composed by the **A** atoms
- Simulating the case when the two species segregate and impurities decorate the islands formed by the adatoms
- 2D KMC simulation (square lattice) with $F_A=F_B$
- The energy barriers for surface diffusion are defined in function of the nearest neighbours and depends only on the initial state!

$$E^X_{I\to F} = \sum_{Y=A,B} (n_0^Y E^{XY}_{sub} + n_1^{XY} E^{XY}_n)$$

- E_{sub}^{XY} : the hopping barrier for a free X atom on a substrate atom Y
- n_0^Y : 1 if the substrate is of type Y and 0 otherwise
- n_1^{XY} : number of nearest neighbour X-Y pairs
- E_n^{XY} : the contribution to the barrier energy from a X-Y pair

-Direct exchange ($E_{ex} \neq 0$) is necessary in order to get impurity decorated islands!

(an energy bias favoring segregation is not sufficient to obtain configurations with impurities at island edges)



Simulation parameters:

$E_{sub}^{AA}=0.8$ eV; $E_{sub}^{AB}=0.1$ eV; $E_{sub}^{BA}=1.0$ eV; $E_{sub}^{BB}=0.1$eV

$E_n^{AA}=0.3$ eV; $E_n^{AB}=E_n^{BA}=0.4$ eV; $E_n^{BB}=0$ eV; $E_{ex}=1.0$ eV

$F_A=F_B=0.004$ML/s; $T=500$ K, $k_0=10^{13}$ Hz

Eliminating the direct exchange

The unrealistic direct exchange is not necessary for the segregation of the two components (this is a first approximation only for a more complicated exchange process blocked by oversimplified geometries)

Other possibilities to realize this exchange through diffusion processes should be included!

Modifications relative to the classical algorithms:

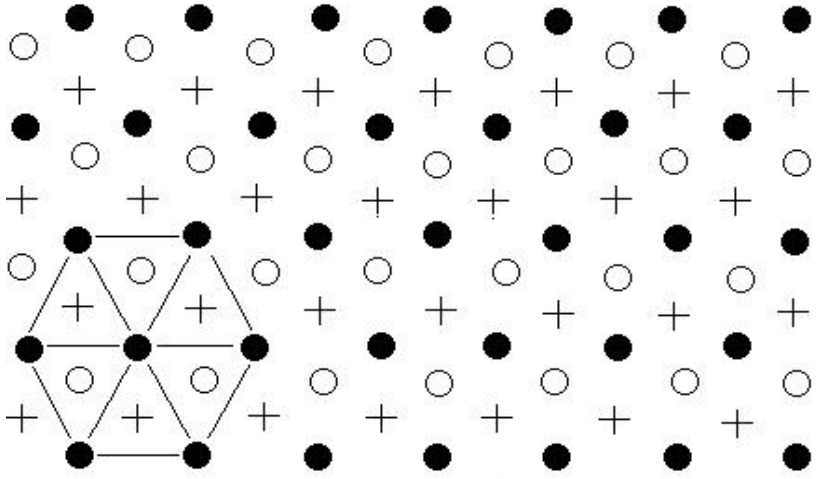
1. Introducing a second (buffer) layer for a realistic 3D simulation. Particles can be deposited, can diffuse and can jump on this layer (providing that the first layer is occupied).

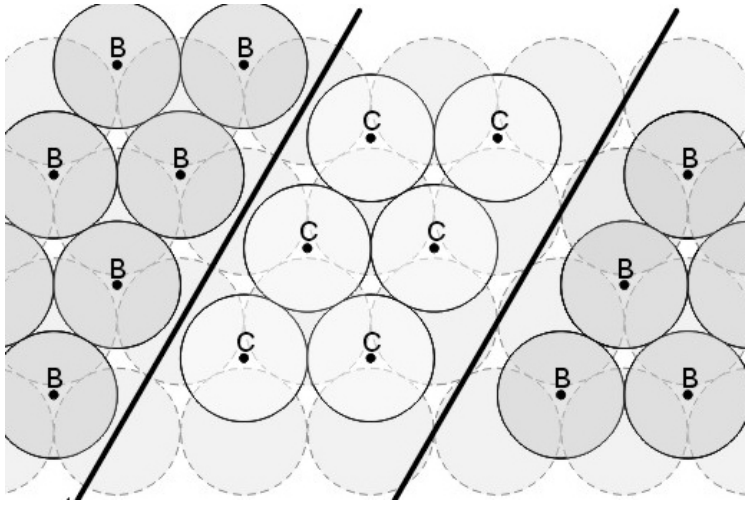
   in case the geometry allows, vacancy mechanism and lattice defects should be allowed in the system (case of triangular lattice, where on the top of the substrate atoms on two equivalent triangular layers can be deposited → possibilities of stacking faults

2. The energy barrier should be calculated from

   - realistic type pair-potentials

   - should depend also on the energy difference between the binding energy in the final and initial state (not only the binding energy in the initial state)





The energy barrier for the hopping process

$$U_{XY}(r) = K_{XY}\left(\left(\frac{\sigma_{XY}}{r}\right)^{12} - \left(\frac{\sigma_{XY}}{r}\right)^{6}\right)$$

-the pair potential is derived from a Lenard-Jones type interaction potential (*X, Y= A or B*)

$$\frac{dU_{XY}}{dr}(1) = 0 \qquad U_{XY}(1) = -E_{XY}$$

-the binding energy at one sight should be calculated from the pair-potentials with the neighbours

$$U_X(\vec{r}) = \sum_{|\vec{R}-\vec{r}|<s} \sum_{Y} U_{XY}(|\vec{R}-\vec{r}|)$$

s: characterizes the considered interaction range (usually up to 3 lattice sites)

-The energy barrier ($E^X_{I\to F}$) for an atom of species *X* for a jump from an *I* initial site to an *F* final site should depend both on the energy of the initial state (U^I_X) and the difference between the final and initial states (U^F_X-U^I_X)

$$E^X_{I\to F} = -\alpha U^I_X + (1-\alpha)(U^F_X - U^I_X)$$

α: a parameter governing the balance between U^I_X and (U^F_X-U^I_X) (for getting the barrier >0 usually α>0.3).

Simulation details

-Simulation on triangular lattice with periodic boundary conditions (L up to 300 lattice sites)

- The following microscopic processes are taken into account:

1. deposition of particles (*A* and *B* type) with fluxes $F_A = F_B$
2. diffusion of particles on two layers (and two different lattice sites)
3. de-cohesion of particles

$$R^X_{dep} = F_X \cdot (L\times L)$$

$$R^X_{diff} = k_0 \exp\left(-\frac{E^X_{I\to F}}{kT}\right)$$

$$R^X_{dec} = k_0 \exp\left(-\frac{U^I_X}{kT}\right)$$

Fixed parameters: α=0.6; E_{AA}=0.1 eV; E_{BB}=0.01 eV; k_0=10^{13} Hz

Other parameters: E_{AB}=0.01 – 0.07 eV; T= 300 – 500 K;

F_A=F_B=0.0001 – 0.1 ML/s

Results

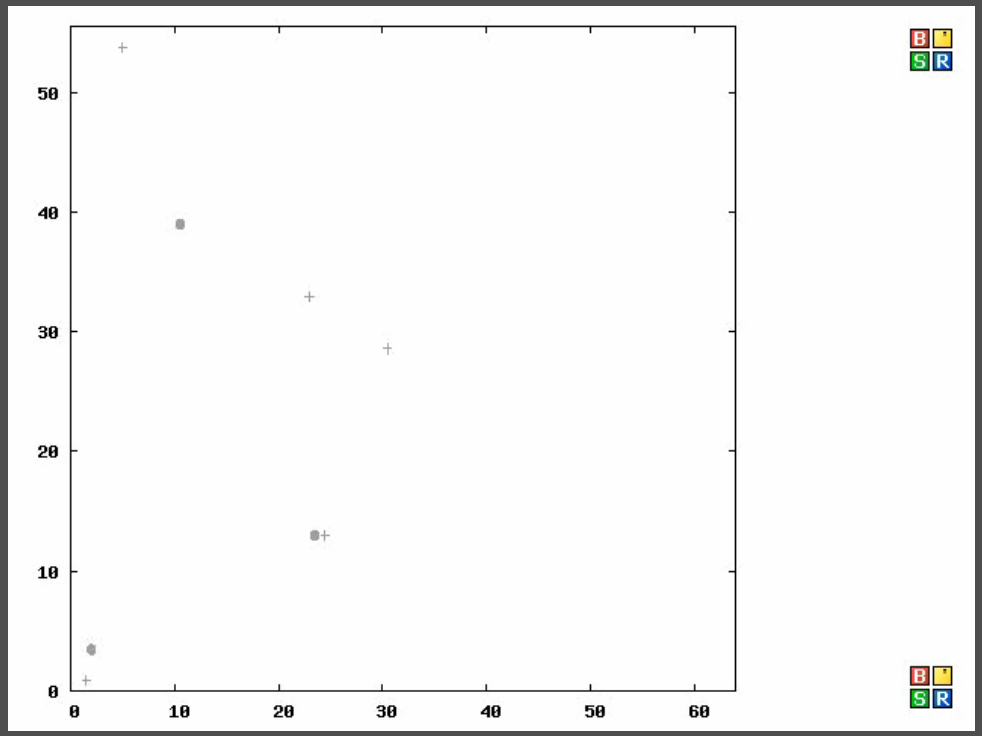
-Deposition of one single type of atoms (A)

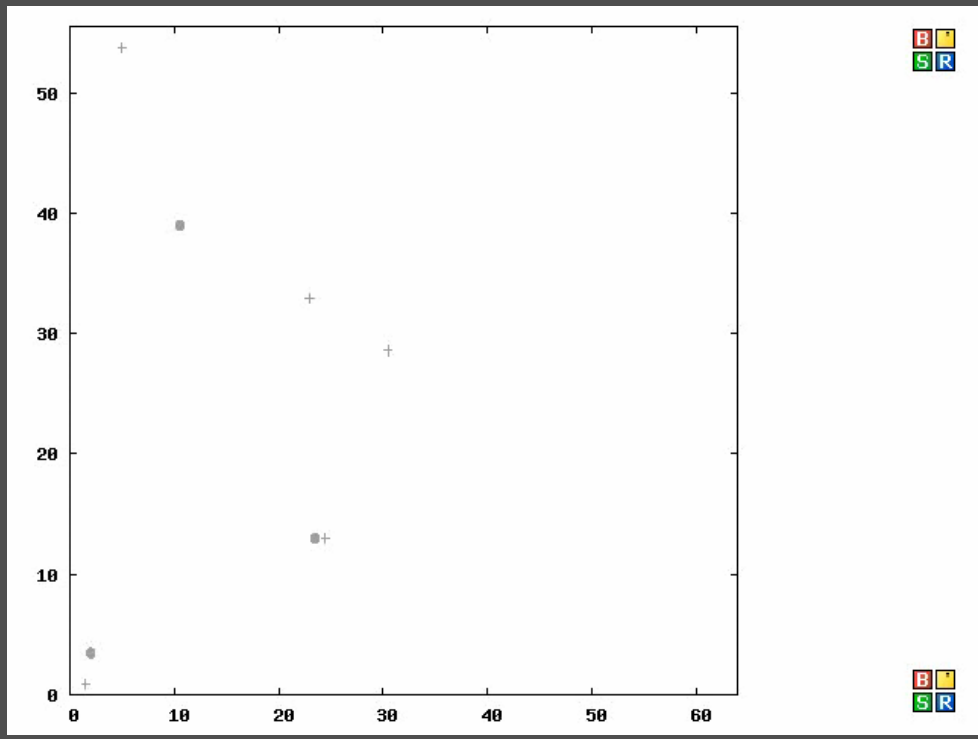
motion of a stacking fault ⟶

-For the two-species deposition decorated islands were found in a broad range of the parameter values

E_{AB}=[0.03 → 0.06] eV; T=[300→500] K;

F=[0.0001→0.1] ML/s

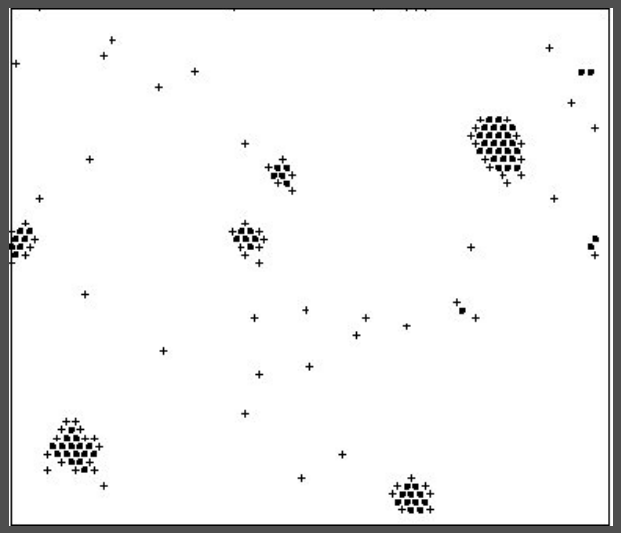




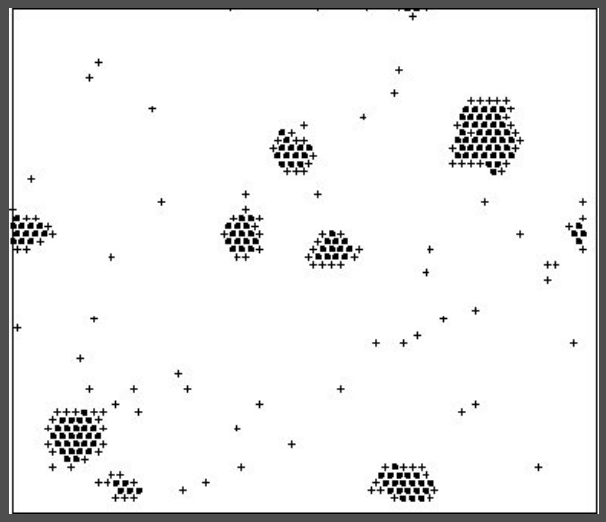
formation of decorated islands (E_{AB}= 0.04 eV, T=400 K , F=0.001 ML/s…..)

a characteristic time-evolution

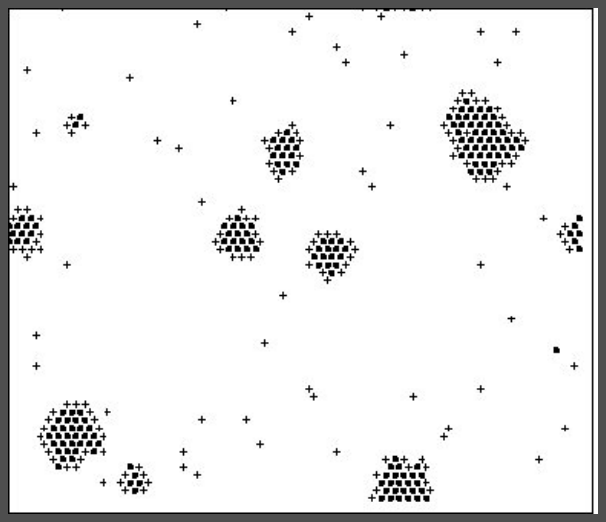
E_{AB}=0.05 eV; F= 0.0001 ML/s; T=350 K



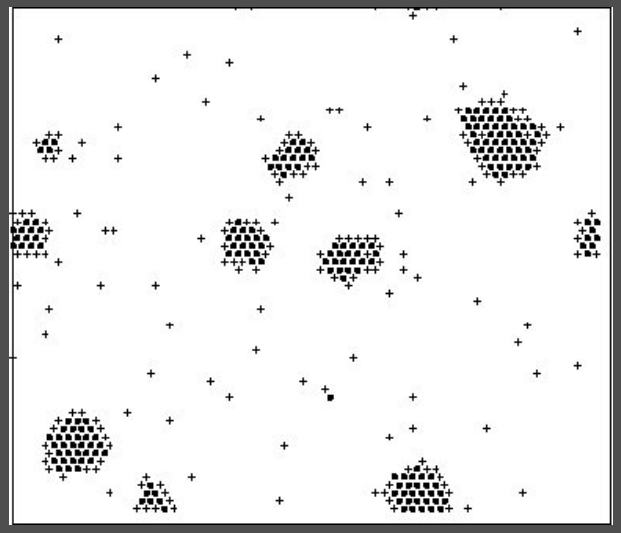
t=500



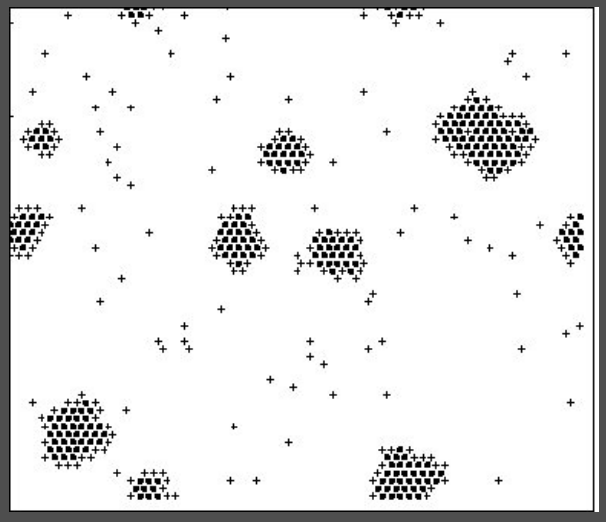
t=1500



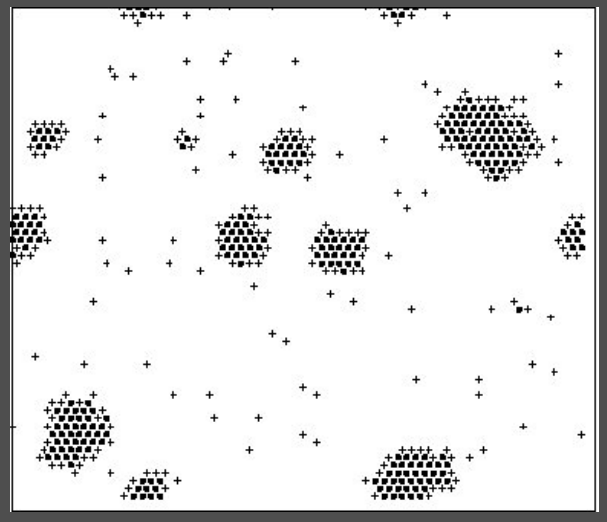
t=2000



t=2500



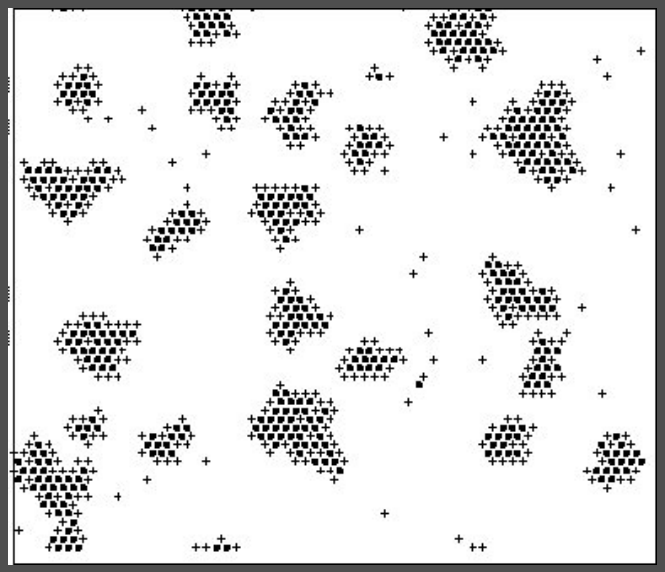
t=3500



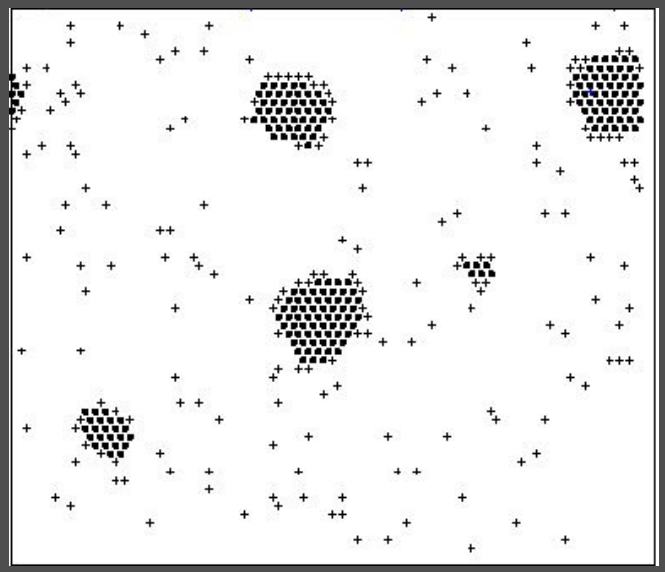
t=4000

Influence of the E_{AB} interparticle interaction energy

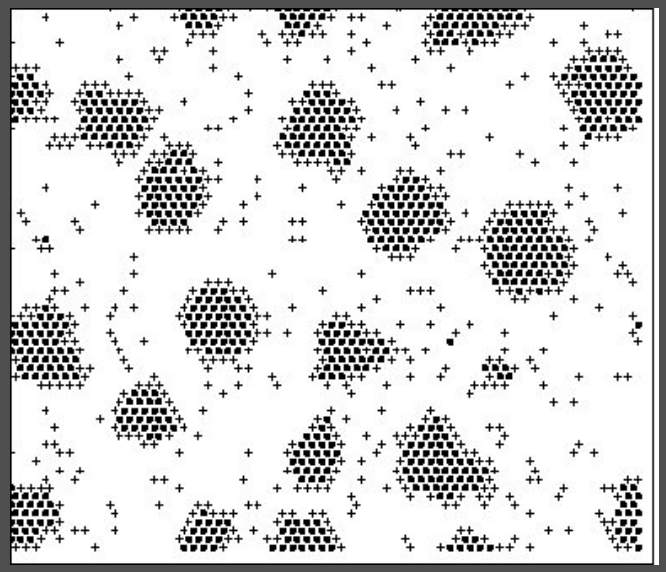
T=400 K; *F*= 0.001 ML/s



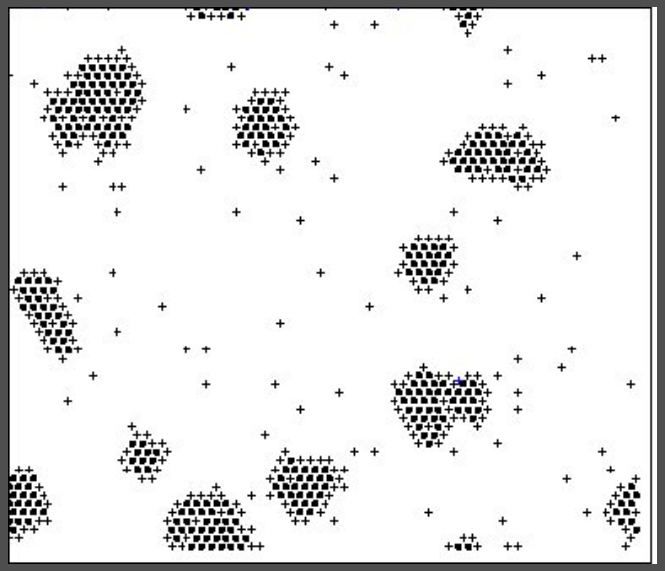
E_{AB}=0.01 eV



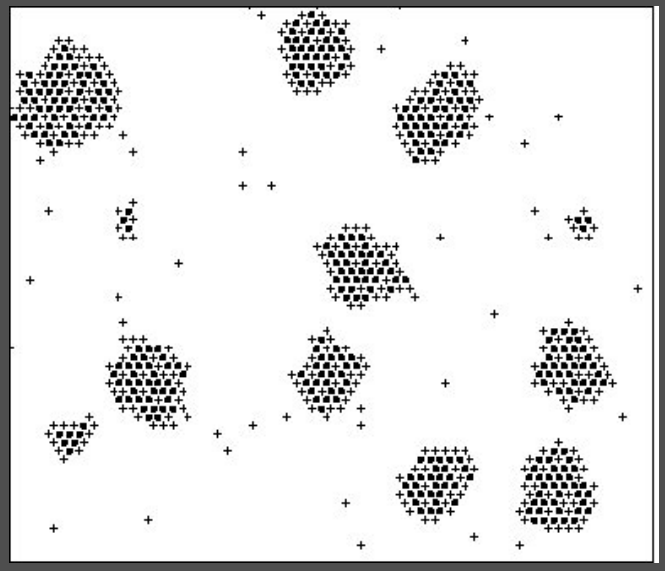
E_{AB}=0.03 eV



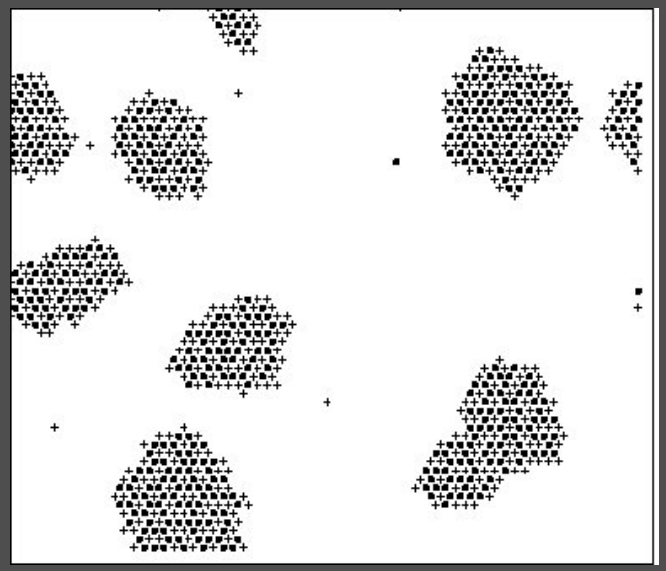
E_{AB}=0.04 eV



E_{AB}=0.06 eV



E_{AB}=0.07 eV



E_{AB}=0.1 eV

Conclusions

-The simultaneous deposition and pattern formation of two species of atoms can be modelled successfully and efficiently with lattice KMC without using a direct exchange mechanism

For this:

1. less restricted geometries that permit more freedom for the diffusion of the particles is necessary (more possibilities that can permit particle exchange)
2. more realistic barrier energies for the diffusion process are necessary