Diffusion, nucleation, growth and molecular nanostructures on surfaces

Thorbjørn Erik Køppen Christensen

June 17, 2018

Part I

Diffusion nucleation and growth

1 Basic diffusion system

1.1 Random walk

The idea is that adatoms can wander freely on a surface if the thermal energy is height enough. It does so by:

$$\rangle \Delta r^2 \langle = \nu a^2 t$$

$\rangle \Delta r^2 \langle$ is the mean square displacement, ν the jump rate (generally around $10 \cdot 10^{13} \frac{1}{s}$), a the jump distance and t the time. This gives rice to the diffusion coefficient (diffusivity) or the time dependent ratio of the mean square displacement:

$$D = \frac{\rangle \Delta r^2 \langle}{zt} = \frac{\nu a^2}{z}$$

Where z is the number of possible jumps (2 is 1d, 4 is 2d square, 6 is 2d hexagonal). The frequency can be found as a function of temperature and barrier:

$$\nu = \nu_0 e^{-\frac{E_{\text{diff}}}{k_b T}}$$

D might not be equal in every direction, a 1d system could have a small chance of jumping in another direction, if this is the case the diffusion is anisotropic, it could also be caused by the unit cell not being symmetric:
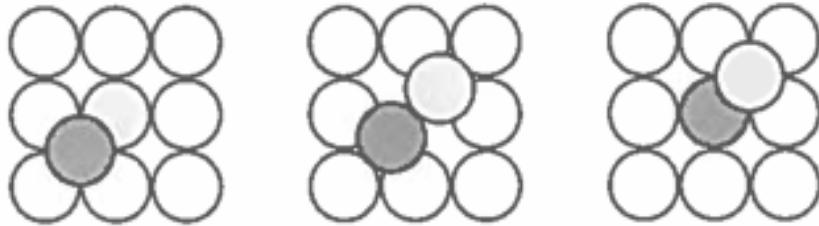
$$D(\phi) = D_x \cos^2 \phi + D_y \sin^2 \phi$$

2 Ways the atoms move

Atoms can move in different ways:

Jumping over a neighbouring atom, while this might seem simple it's not.

Exchanging: Atoms can diffuse on a surface by changing place with the atom below it, pushing it in the diffusion direction.


Fig. 13.11. Schematic representation of the atomic exc

2.1 Surface diffusion of clusters

When islands grow new forms of diffusion, these are called cluster diffusions, and the idea is that the centre of mass for the cluster changes. They are:

for individual atoms

- sequential displacement mechanism — The atoms move one by one

- Edge diffusion — Atoms move along the edge of the island

- Evaporation–condensation — An atom evaporates from the island in one place and another condensates in another place. If the island is stable the processes will be in equilibrium

- Leapfrog — An atom jumps over a series of atoms.
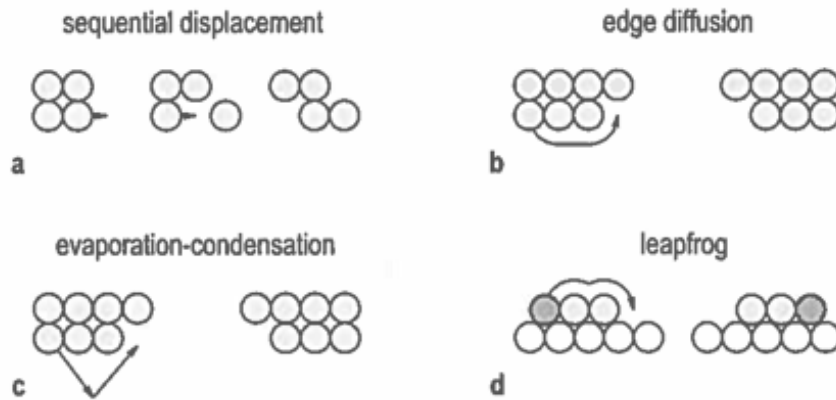
for groups

- Gliding mechanism — all atoms move simultaneously

- Shearing — A subgroup of atoms glide, but not all atoms (and not a single atom)

- Reptation — multiple shears gliding in a zigzag manner

- Dislocation — rows are seperated by a misfit, the atoms will then move through shears or individual movements to eliminate the fault
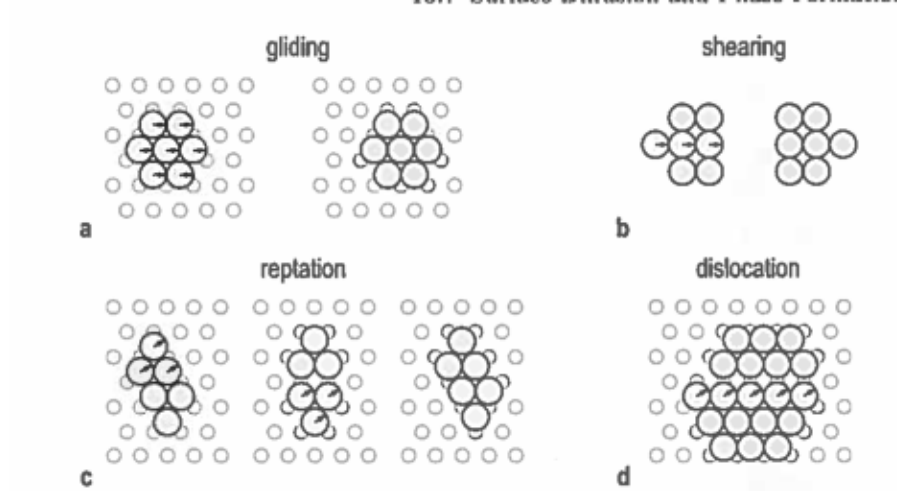
## 3 Growing islands

For a simple system with $i = 1$ one has

$$N \sim \left(\frac{R\Theta}{\nu} \right)^{\chi}$$

$$\chi = \frac{i}{i + 2}$$

3.1 modes

Islands can grow in three modes:

- *Layer-by-layer* or *Frank-van der Merve (FM)* one layer grows completely before the next one start on top. Caused by the film being stronger bound to the substrate than itself

- *Layer plus island* (*Stranski–Krastanow (SK)*) the first layer grows completely, then island can start growing in height

- *Island* (*Vollmer–Weber (VW)*) film is bound more to itself than the surface, and the islands can build height

5
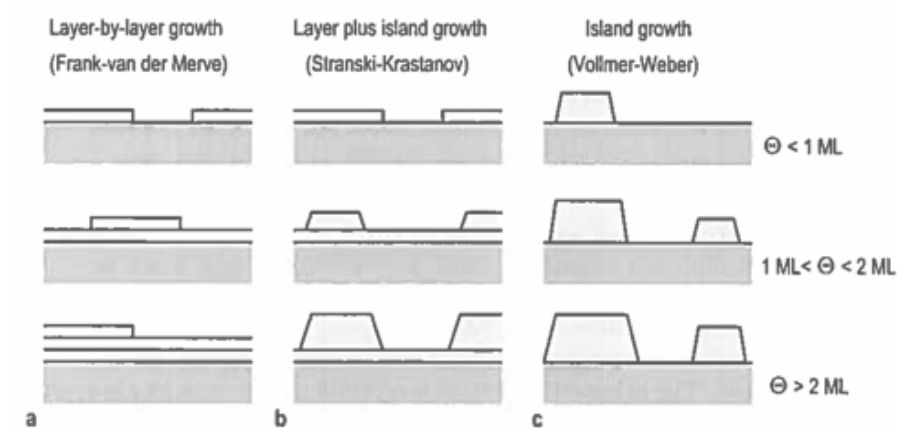
The different modes can be understood by the surface tension γ

$$\gamma_S = \gamma_{S/F} + \gamma_F \cos\phi$$

γ_S being the surface tension of the substrate, γ_F the surface tension of the film, $\gamma_{S/F}$ the film–surface tension and ϕ the contact angle. The growth mode can be found by removing the cosine factor and checking which part is larger.

3.2   Nucleation and growth

When Islands grow they have a critical surface size i, i is the size at which an island breaks. So $i + 1$ is the size at which the island is stable. There are multiple important factors for how the islands grow. some are R the rate at which atoms arrive from gas phase, E_{ads} the energy binding the adatom to the surface, putting n_1 adatoms on the surface with n_0 sites per unit area, the diffusion coeficcient

$$D = \frac{\nu}{4n_0} e^{-\frac{E_{\text{diff}}}{k_B T}}$$

The adatom can then reevaporate with the lifetime

$$\tau_{\text{ads}} = \frac{1}{\nu} e^{\frac{E_{\text{ads}}}{k_B T}}$$

Adatoms might also be captured by existing islands, they can also combine to form a new cluster
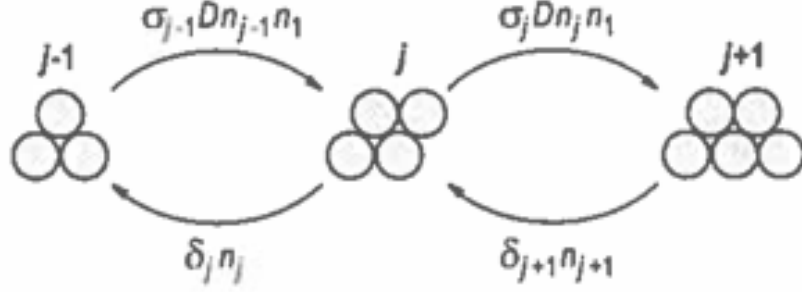
Book mathematics

For a cluster of size j there are four important processes:

- A new cluster size j is formed every time a cluster size $j-1$ get's an atom. The flux is $\sigma_{j-1}Dn_{j-1}n_1$

- The detachment of an atom from a cluster size $j+1$, the flux is $\partial_{j+1}n_{j+1}$ also creates a new group of size j

- A group of size j is lost when it losses an atom at flux $\partial_j n_j$

- A group of size j is lost when it gains an atom, flux $\sigma_j Dn_j n_1$

n_1 is the density of adatoms, D the diffusion coefficient, σ the capture number (capability of cluster to capture atom) and $\partial_{j+1} = De^{-\frac{\Delta E_j^{j+1}}{k_B T}}$ is the decay rate of an island, ΔE_j^{j+1} is the energy difference between the two island sizes. n_x is now the number density of stable islands ($j > i$)

$$\frac{dn_1}{dt} = \underbrace{R}_{\text{desposition}} - \underbrace{\frac{n_1}{\tau_{\text{ads}}}}_{\text{dissociation}} + \left(\underbrace{2\partial_2 n_2}_{\text{nucleation}} + \underbrace{\sum_{j=3}^{i}\partial_j n_j}_{} - \underbrace{2\sigma_1 Dn_1^2}_{\text{denucleation}} - \underbrace{n_1\sum_{j=2}^{i}\sigma_j Dn_j}_{\text{degrowth}} \right) - \underbrace{n_1\sigma_x Dn_x}_{\text{growth stable}}$$

where the under-bracket "growth" is under $\sum_{j=3}^{i}\partial_j n_j$.

$$\frac{dn_j}{dt} = \underbrace{n_1\sigma_{j-1}Dn_{j-1}}_{\text{growth}} - \underbrace{\partial_j n_j}_{\text{degrowth}} + \underbrace{\partial_{j+1}n_{j+1}}_{\text{degrowth}} - \underbrace{n_1\sigma_j Dn_j}_{\text{growth}}$$

$$\frac{dn_x}{dt} = \underbrace{n_1\sigma_1 Dn_1}_{\text{growth}}$$

7

This splits the system into 4 stages: "low coverage" (adatom density higher than island density), "intermediate coverage" (more islands than adatoms), "aggregation regime" (collecting the last adatoms) and the "coalescence and percolation regime" (Islands melting together). The number of island grown (normalized to sites) are:

$$\frac{n_x}{n_0} = \eta(\Theta, i)\left(\frac{R}{Dn_0^2}\right)^{\chi} e^{\frac{E_i}{(i+2)k_B T}} \qquad \text{with no reevaporation}$$

$$\frac{n_x}{n_0} = \eta(\Theta, i)\left(\frac{4R}{\nu_0 n_0}\right)^{\chi} e^{\frac{\chi\left(E_{diff}+\frac{E_i}{i}\right)}{k_B T}}$$

$$\chi_{2d} = \frac{i}{i+2}$$

$$\chi_{1d} = \frac{i}{2(i+1)}$$

Here E_i is the binding energy of the critical cluster, η an exponential factor $(10^{-2}\text{–}10^1)$. The second formulae takes temperature dependence of diffusion coefficient into account.

Trolle mathematics

!!!!OBS!!!!

Trolle did not care for adatoms leaving the surface in his 2017 lecture, also it's in general more lazy math than the one in the book

$$\frac{dN_1}{dt} = R(1-\Theta) - \frac{F_x N_1}{\tau} - (i+1)\frac{dN_x}{dt}$$

$$\frac{dN_x}{dt} = \frac{F_i N_1}{\tau}$$

$$N_x \sim \eta(\Theta, i)\left(\frac{R}{\nu}\right)^{\chi} e^{\frac{\chi\left(E_{diff}+\frac{E_i}{i}\right)}{k_B T}}$$
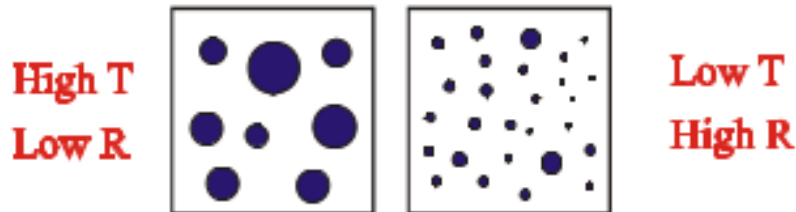
N_1: density of adatoms

N_x: density of stable islands

F_i: fraction of critical clusters

F_x: fraction of stable islands

τ average lifetime before adatom is lost to nucleation or growth.
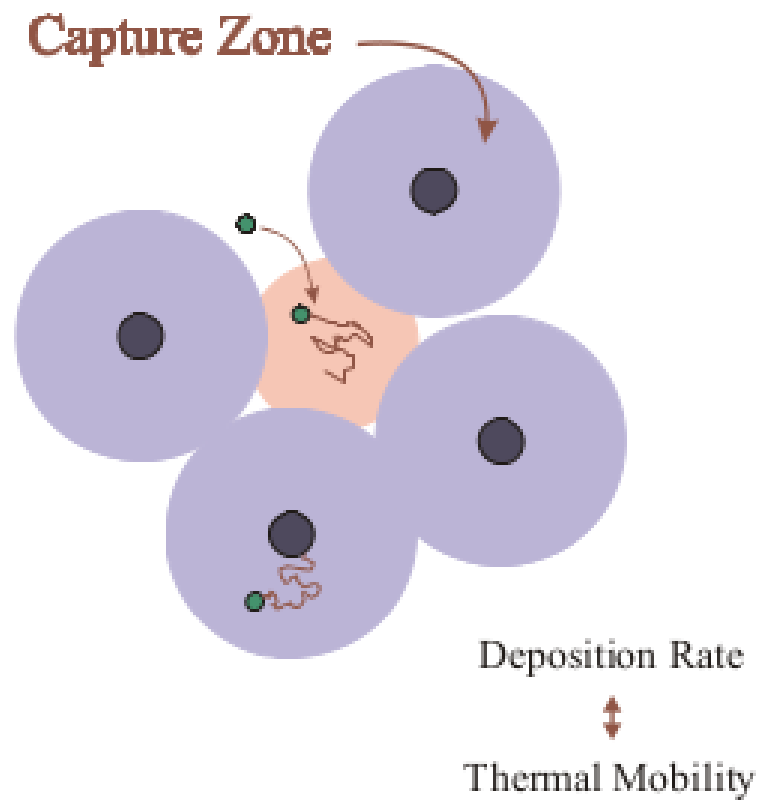
3.3   Island size distribution and coarsing phenomena

Two island shape types exist *ramified* (fractal like) (low T $\rightarrow$ low edge diffusion) and *Compact* (having straight lines for edges).
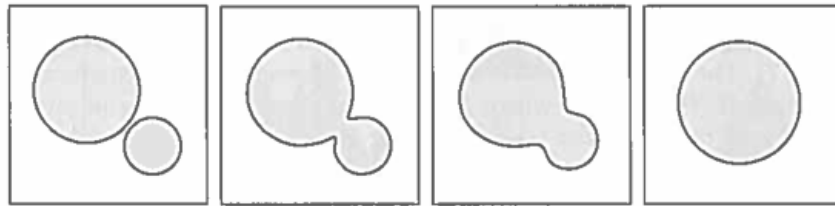
island size

$$N = \sum_{s>i} N_s \qquad \text{noncritical islands}$$

$$\Theta = \sum_{s\geq 1} sN_s$$

$$\langle s \rangle = \frac{\sum_{s>i} sN_s}{\sum_{s>i} N_s}$$

$$= \frac{\Theta - \sum_{s\leq i} SN_s}{N}$$

if i is small:

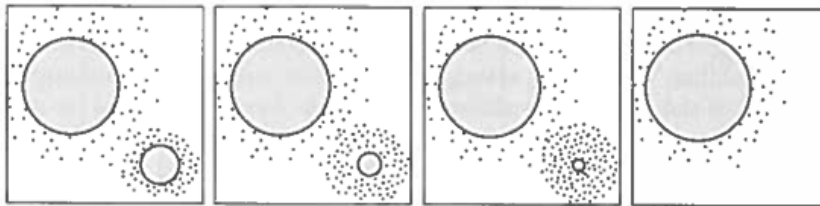$$\langle s \rangle = \frac{\Theta - N_1}{N} \approx \frac{\Theta}{N}$$

$$f_i \left(\frac{s}{\langle s \rangle} \right) = \frac{N_s (s_{av})^2}{\Theta}$$

Capture Zone

Deposition Rate
$\updownarrow$
Thermal Mobility

Ripening and coalscence

Fig. 14.15. Schematic diagram showing sequential stages of coalescence

Fig. 14.16. Schematic diagram showing sequential stages of island ripening

Part II

Molecular nanostructures on surfaces

4   Self assembly

"Molecular self-assembly is the spontanous association of molecules under equilibrium conditions into stable, structurally well defined aggregates joined by non-covalent bonds."

$$E_b > E_{\text{intermidiate}} \geq E_{\text{kin}} > E_{\text{dessorption}}$$

4.1   Covalent vs hydrogen vs metal