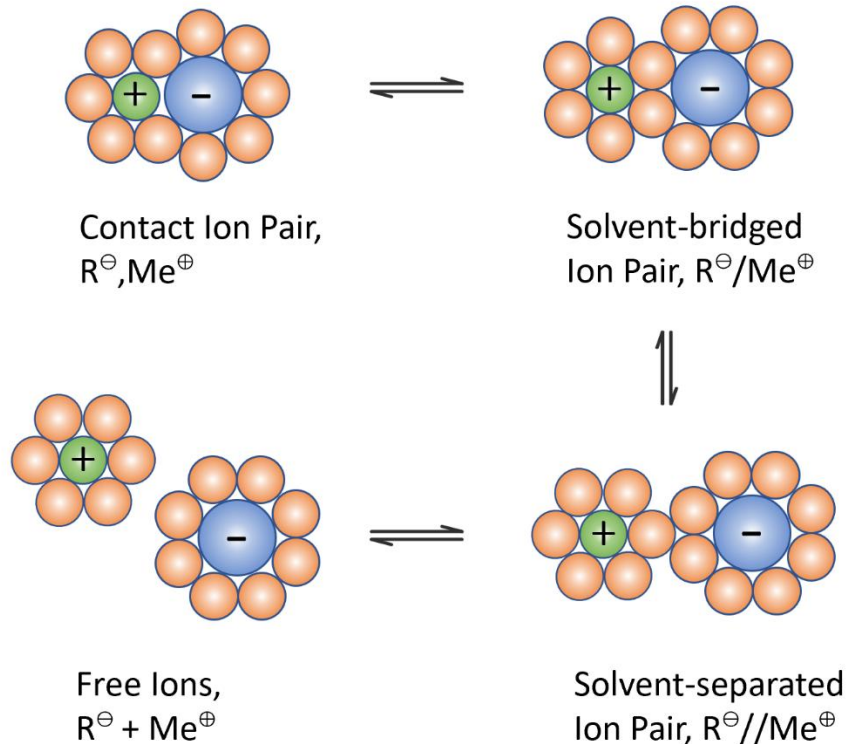


# 4 – Atomistic aspects of electrocrystallization

# I) Solvation of ions

## 1) Dissolution of a metal salt in polar solvents



Solvent dipoles screen the electrical charge of the ions

Electrical neutrality of the electrolyte is preserved:  $\sum_{\alpha} q_{\alpha} \rho_{\alpha} = 0$

with  $q$  the charge and  $\rho$  the number density

# 1) Solvation of ions

## 2) Ion solvation

3 types of interactions:

Ion-ion: 
$$U_{i,j} = \frac{2\pi}{\sum_{\alpha} \rho_{\alpha}} \sum_{i,j} q_i q_j \rho_i \rho_j \int_0^{\infty} g_{i,j}(r) r dr$$

Ion-dipole: 
$$U_{i,\mu} = -\frac{4\pi N \rho_{\mu} \mu}{3 \sum_{\alpha} \rho_{\alpha}} \sum_i q_i \rho_i \int_0^{\infty} g_{i,\mu}(r) dr$$

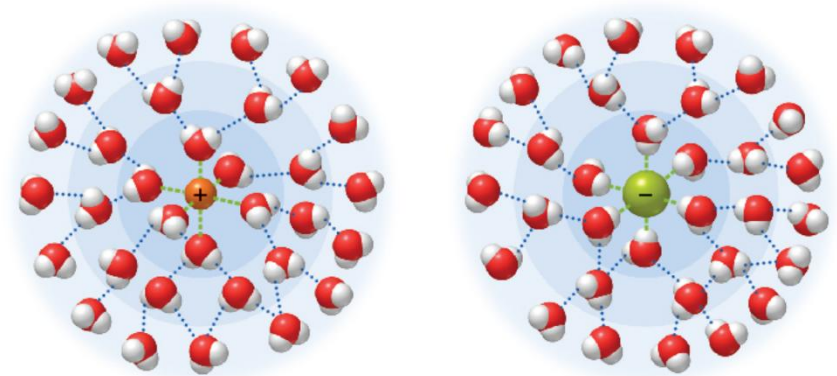
with  $g(r)$  the radial distribution function

Dipole-dipole: 
$$U_{i,\mu} = -\frac{4\pi N \rho_{\mu}^2 \mu^2}{3 \sum_{\alpha} \rho_{\alpha}} \int_0^{\infty} \frac{g_{\mu,\mu}(r)}{r} dr$$

A hard solvation sphere is formed

→ Metal cations are hydrated

→ Hydration number depends on the Pauling's ionic radius



■ Inner sphere of hydration  
■ Outer sphere of hydration  
■ Bulk water

--- Ion-dipole interaction  
..... Dipole-dipole interaction

**Octahedral solvation sphere !**

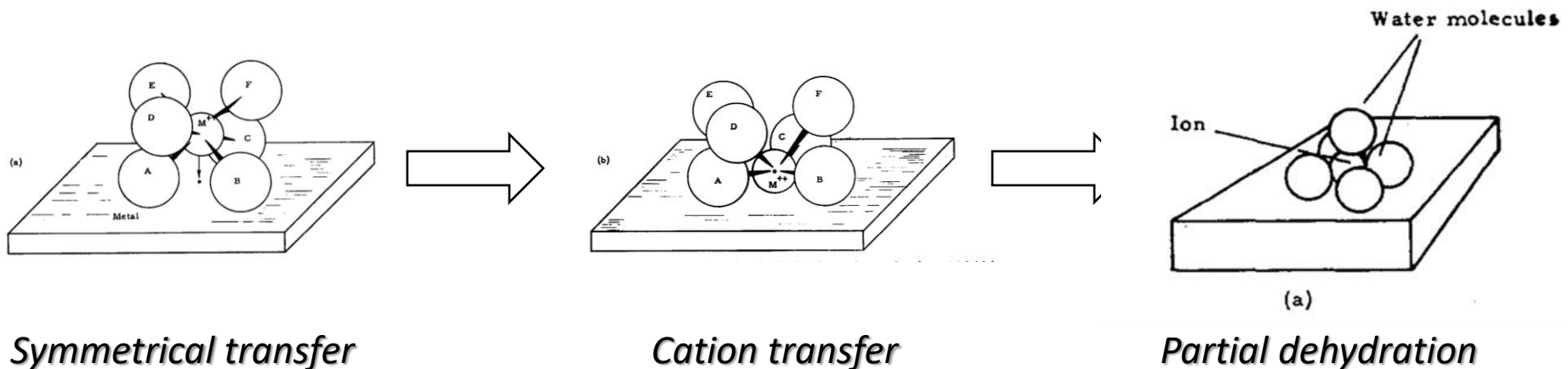
## II) Cation-surface interaction

### 1) Adsorption on a planar surface

A negative potential is imposed to the substrate

Interaction cathode (-) — cations (+)

Displacement of the hydration shell and transfer of the cation to the surface



Symmetrical transfer: only the outer solvation shell is displaced  
Need to disrupt the inner shell to transfer the cation to the surface  
Loss of one water molecule

## II) Cation-surface interaction

### 2) Real surfaces

Real surfaces are not ideal surfaces

Density of metal surface atoms  $10^{15} \text{ cm}^{-2}$

Density of dislocations  $10^4 - 10^8 \text{ cm}^{-2}$

Perfect flat face, terrace

Emerging screw dislocation

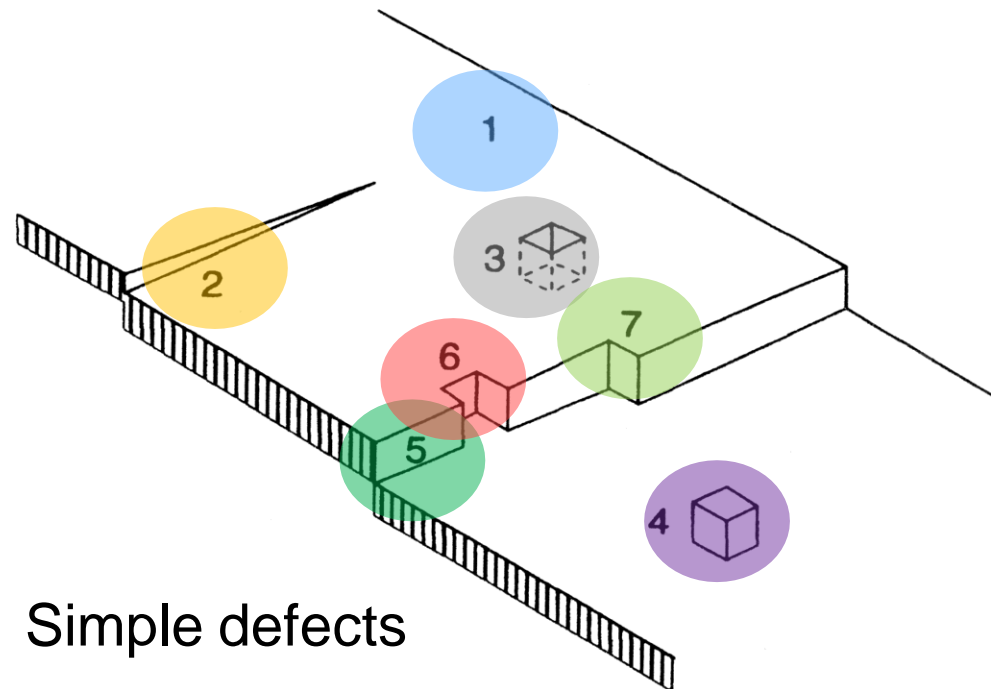
A ledge: monoatomic step

Vacancy in the ledge

Kink: a ledge in the ledge

Vacancy in the terrace

Atom on the terrace

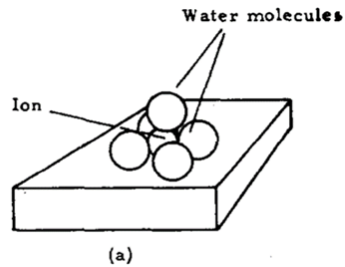


Simple defects

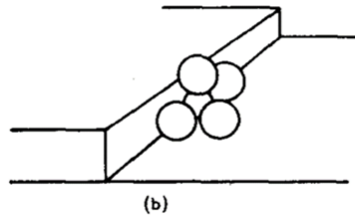
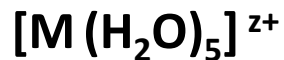
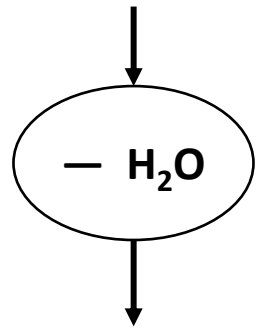
## II) Cation-surface interaction

### 3) Different adsorption sites

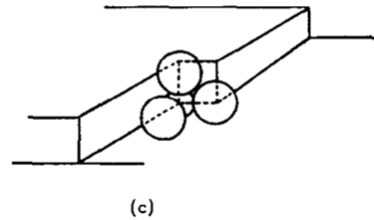
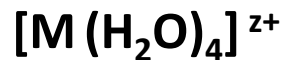
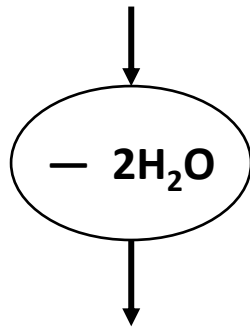
Let us consider the initial state  $[M(H_2O)_6]^{z+}$  an octahedral metal hydrate



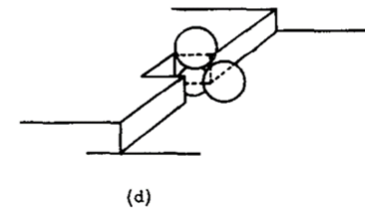
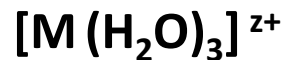
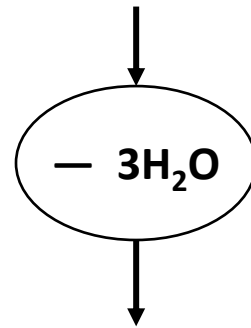
Plane



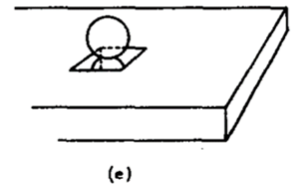
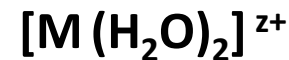
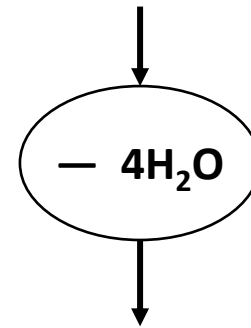
Ledge



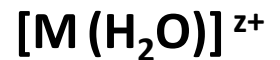
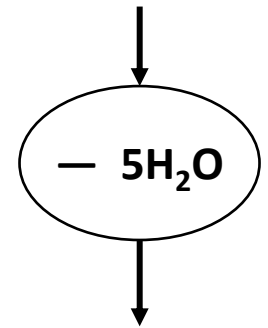
Ledge kink



Ledge vacancy

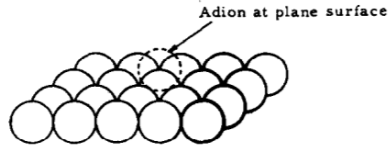


Plane vacancy

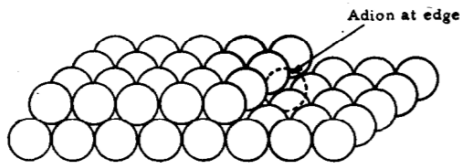


## II) Cation-surface interaction

### 4) Coordination number = neighbouring metal atoms

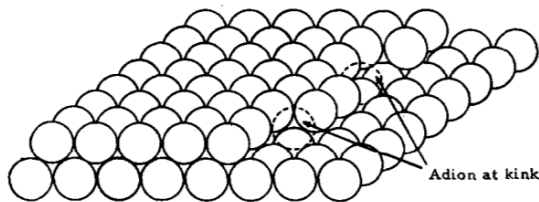


Adion at a plane surface site: C.N. = 3



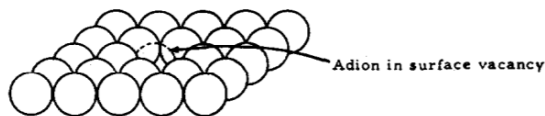
Adion at a monoatomic ledge site: C.N. = 5

Adion at a polyatomic ledge site: C.N. = 6



Adion at kink sites: C.N. = 5 or 6

Adion at edge vacancy sites: C.N. = 7 or 8



Adion at a surface vacancy: C.N. = 9

## II) Cation-surface interaction

### 5) Consequence on the electrical activation energy

The electrical activation energy depends on surface site

$$\Delta G_{e,3}^* < \Delta G_{e,6}^* < \Delta G_{e,7}^* \approx \Delta G_{e,5}^* \approx \Delta G_{e,2}^* < \Delta G_{e,4}^* < \Delta G_{e,1}^*$$

$$C.N.: 9 > 8 - 7 > 6 - 5 \geq 6 - 5 \geq 5 > 4 > 3$$

Perfect flat face, terrace

Emerging screw dislocation

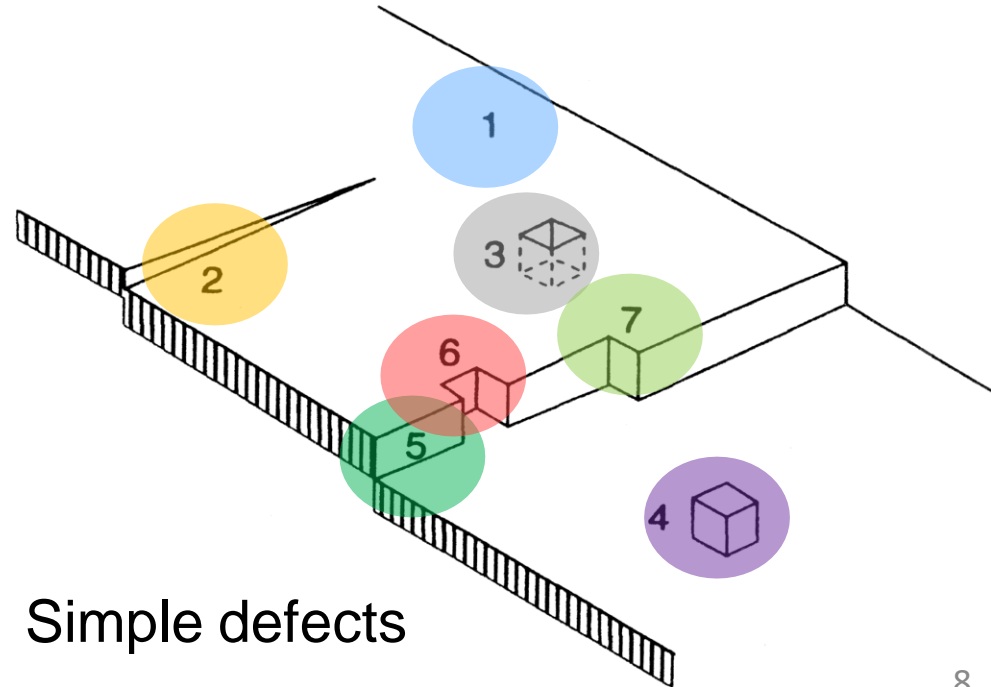
Vacancy in the terrace

Adatom in the terrace

A ledge: monoatomic step

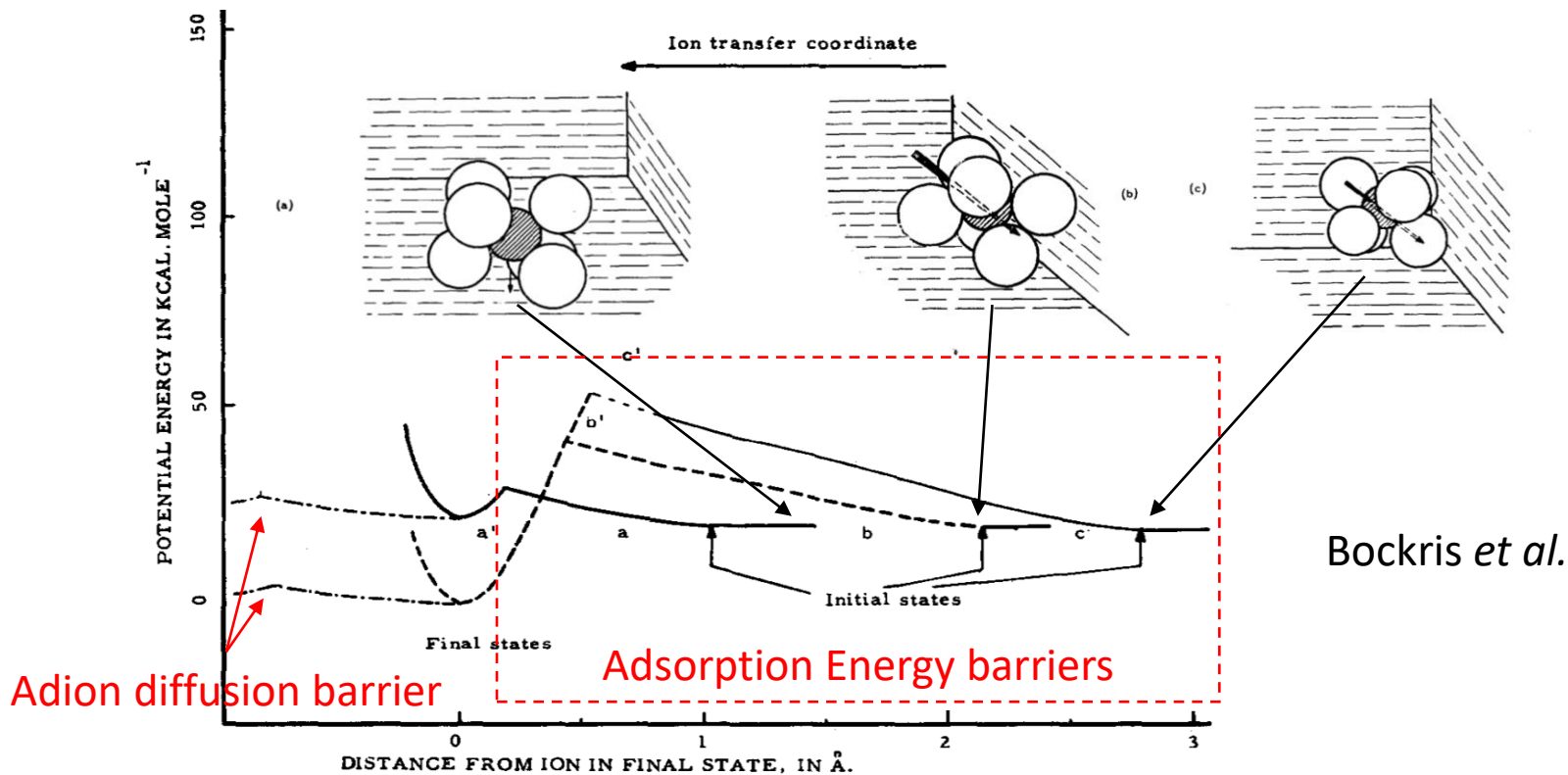
Vacancy in the ledge

Kink: a ledge in the ledge



## II) Cation-surface interaction

### 6) Potential energy considerations

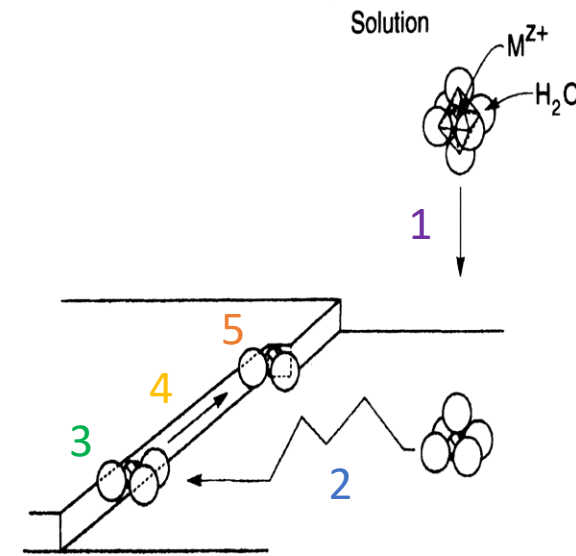
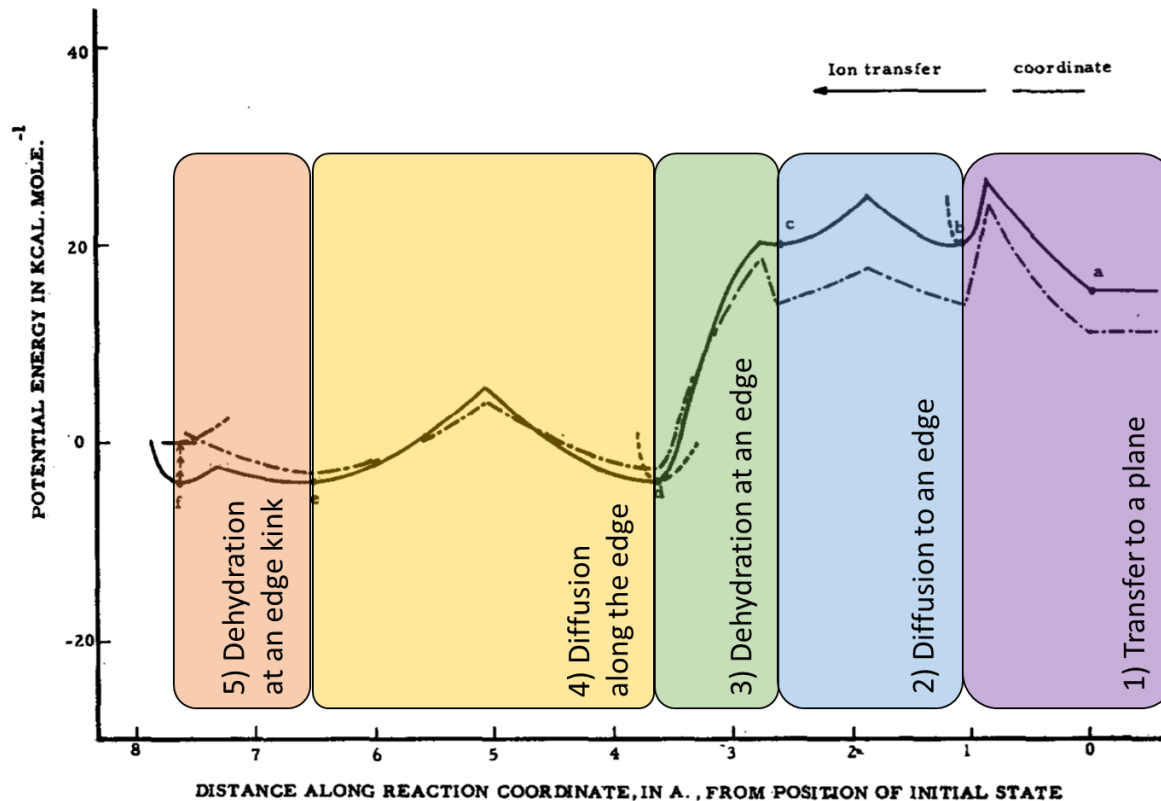


Energy barrier lowest for adsorption on planar surface

Final state most stable at a ledge

## II) Cation-surface interaction

### 7) Most probable pathway



Dashed line = Free energy profile

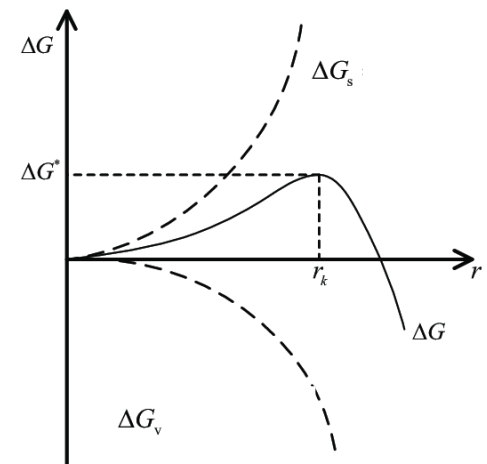
### III) Nucleation and growth process

## 1) Homogeneous nucleation: spherical nucleus

Formation of a monoatomic cluster  $c_\alpha$  followed by the progressive addition of  $N$  atoms to the cluster:  $c_\alpha = c_{\alpha+N}$

Free energy variation during nucleus formation is a function of the number of atoms:

$$\Delta G = \Delta G_{surface} - \Delta G_{volume}$$



### III) Nucleation and growth process

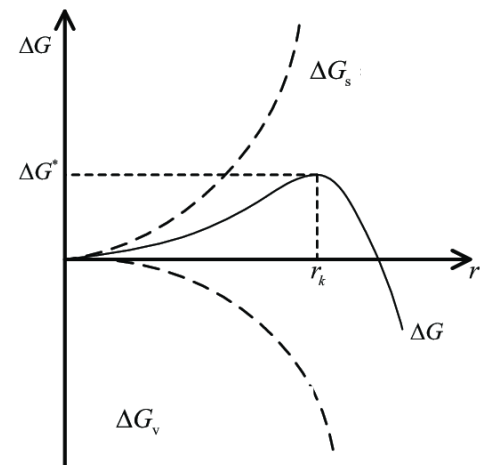
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Free energy variation during nucleus formation is a function of the number of atoms:

$$\Delta G = \Delta G_{surface} - \Delta G_{volume} = \sigma_s S - \Delta\mu \frac{V}{V_m} = f(\eta)$$

$\sigma_s$  the surface energy, S the surface,  $\Delta\mu$  the chemical potential, V and  $V_m$  the volume and molar volume



# III) Nucleation and growth process

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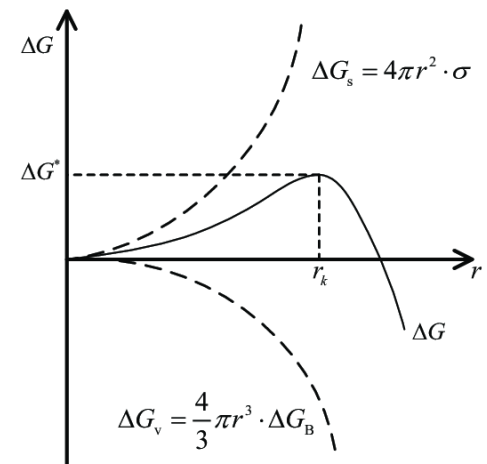
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---

For a spherical nucleus  $\Delta G = 4\pi r^2 \sigma_s - \frac{4\pi}{3} r^3 \frac{\Delta\mu}{V_m}$



# III) Nucleation and growth process

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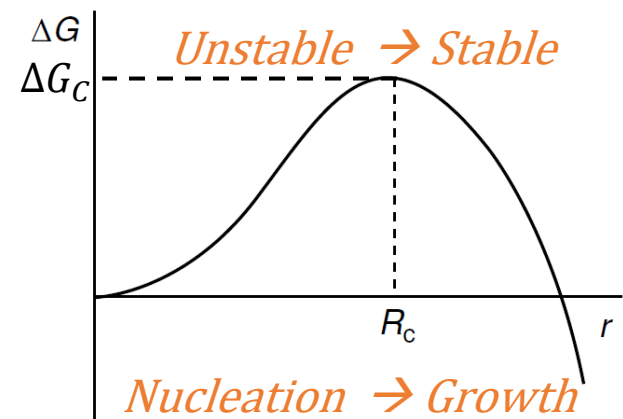
$$\Delta G = \Delta G_{surface} - \Delta G_{volume} = S\sigma_s - V \frac{\Delta\mu}{V_m} \neq f(\eta)$$

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For a spherical nucleus  $\Delta G = 4\pi r^2 \sigma_s - \frac{4\pi}{3} r^3 \frac{\Delta\mu}{V_m}$

**Critical nucleus** size  $R_c$  and  $V_c$ :  $\Delta G$  is maximum,  $\frac{\partial \Delta G}{\partial r} = 0$

➤ Differentiation:  $\frac{\partial \Delta G}{\partial r} = 8\pi r \sigma_s - 4\pi r^2 \frac{\Delta\mu}{V_m}$



# III) Nucleation and growth process

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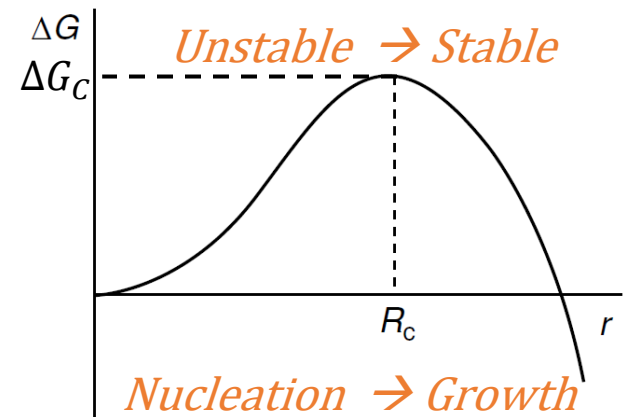
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For a spherical nucleus  $\Delta G = 4\pi r^2 \sigma_s - \frac{4\pi}{3} r^3 \frac{\Delta\mu}{V_m}$

**Critical nucleus** size  $R_c$  and  $V_c$ :  $\Delta G$  is maximum,  $\frac{\partial \Delta G}{\partial r} = 0$

$$\frac{\partial \Delta G}{\partial r} = 8\pi R_c \sigma_s - 4\pi R_c^2 \frac{\Delta\mu}{V_m} = 0 \Rightarrow R_c = 2\sigma_s \frac{V_m}{\Delta\mu}$$



# III) Nucleation and growth process

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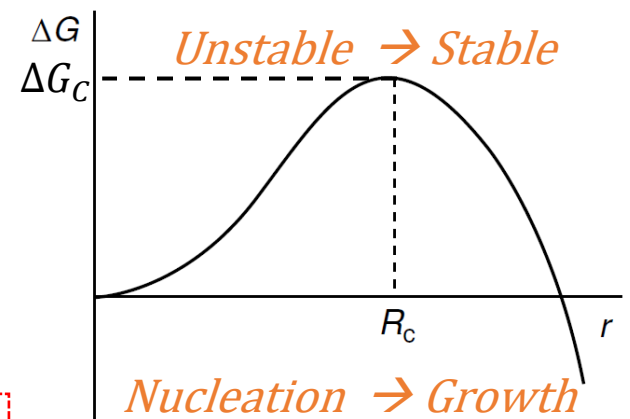
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$$\frac{\partial \Delta G}{\partial r} = 8\pi R_c \sigma_s - 4\pi R_c^2 \frac{\Delta\mu}{V_m} = 0 \Rightarrow R_c = 2\sigma_s \frac{V_m}{\Delta\mu}$$

$$\text{hence } V_c = \frac{32\pi}{3} \left( \sigma_s \frac{V_m}{\Delta\mu} \right)^3 \text{ and } \Delta G_c = \frac{16\pi}{3} \sigma_s^3 \left( \frac{V_m}{\Delta\mu} \right)^2 = \frac{V_c \Delta\mu}{2 V_m}$$



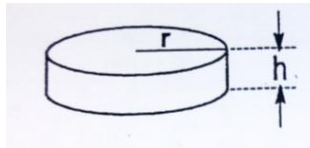
Free energy variation vs nucleus radius

### III) Nucleation and growth process

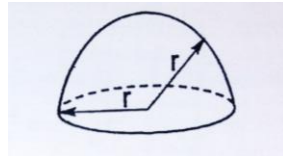
## 2) Homogeneous nucleation: real nuclei

Expression of the critical volume still holds:  $V_c = \Gamma \left( \sigma_s \frac{V_m}{\Delta\mu} \right)^3$

with  $\Gamma$  the shape factor ( $\Gamma_{sphere} = \frac{32\pi}{3}$ ,  $\Gamma_{cube} = 64$ )



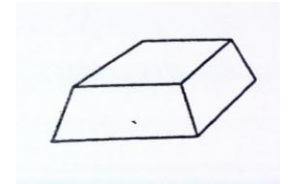
Cylindrical



Hemispherical



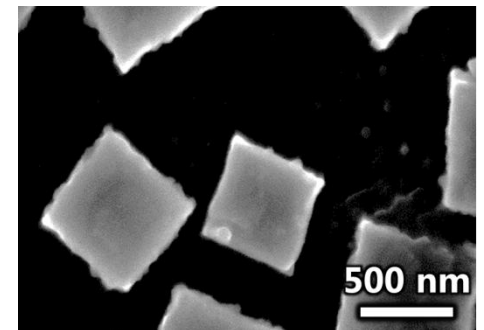
Conical



Facetted



Anisotropy of the crystal properties  
Growth on high surface energy crystal plane is favored

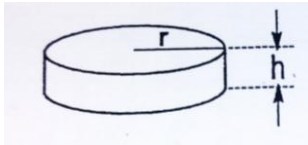


### III) Nucleation and growth process

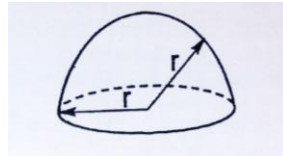
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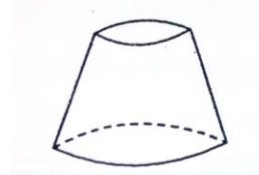
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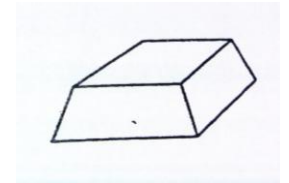
Cylindrical



Hemispherical



Conical



Facetted

More convenient to determine the critical number of atoms  $n_C$  than  $R_C$

Let us consider  $v = \frac{V_m}{\mathcal{N}_A}$  the volume occupied by an atom

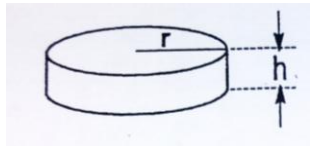
$$n_C = \frac{V_C}{v} = \Gamma \left( \frac{\sigma_s \mathcal{N}_A}{\Delta\mu} \right)^3 v^2 \quad \text{and} \quad \Delta G_C = \frac{V_C \Delta\mu}{2 V_m} = \frac{\Delta\mu}{2 \mathcal{N}_A} n_C$$

### III) Nucleation and growth process

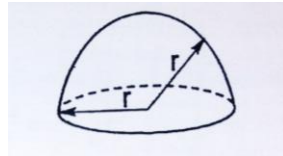
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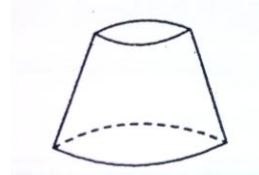
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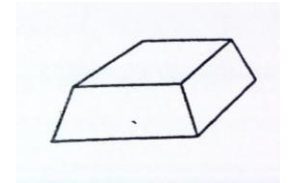
Cylindrical



Hemispherical



Conical



Facetted

More convenient to determine the critical number of atoms  $n_C$  than  $R_C$

Let us consider  $v = \frac{V_m}{\mathcal{N}_A}$  the volume occupied by an atom

$\Delta\mu$  is related to the overpotential:  $\Delta\mu = zF|\eta| = ze\mathcal{N}_A|\eta|$

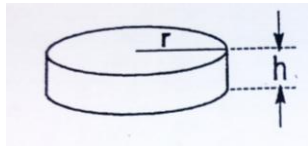
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### III) Nucleation and growth process

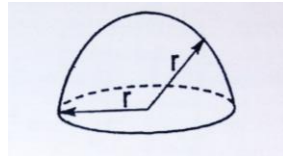
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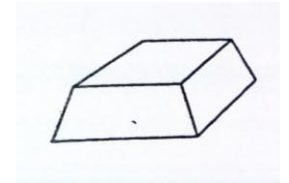
Cylindrical



Hemispherical



Conical



Facetted

More convenient to determine the critical number of atoms  $n_C$  than  $R_C$

Let us consider  $\nu = \frac{V_m}{\mathcal{N}_A}$  the volume occupied by an atom

$\Delta\mu$  is related to the overpotential:  $\Delta\mu = zF|\eta| = ze\mathcal{N}_A|\eta|$

$$n_C = \frac{V_C}{\nu} = \Gamma \left( \frac{\sigma_s}{ze|\eta|} \right)^3 \nu^2 \quad \text{and} \quad \Delta G_C = \frac{V_C}{2} \frac{\Delta\mu}{V_m} = \frac{ze|\eta|}{2} n_C$$

**Increasing the overpotential decreases the critical size of nuclei !!!**

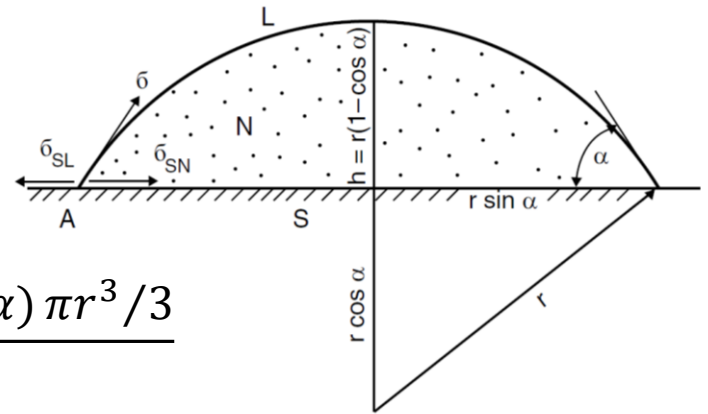
# III) Nucleation and growth process

## 3) Heterogeneous 3D nucleation:

Nucleation occurs on a foreign substrate:

$$\Delta G_C^{het} = \Delta G_C^{hom} \cdot \Theta$$

$$\Theta = \frac{\text{Volume of the shell}}{\text{Volume of the sphere}} = \frac{(2 - 3 \cos \alpha + \cos^3 \alpha) \pi r^3 / 3}{4\pi r^3 / 3}$$



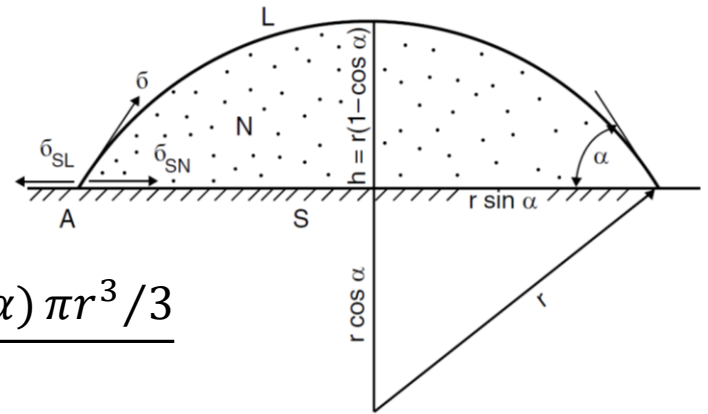
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#### 3) Heterogeneous 3D nucleation:

Nucleation occurs on a foreign substrate:

$$\Delta G_C^{het} = \Delta G_C^{hom} \cdot \Theta$$

$$\Theta = \frac{\text{Volume of the shell}}{\text{Volume of the sphere}} = \frac{(2 - 3 \cos \alpha + \cos^3 \alpha) \pi r^3 / 3}{4\pi r^3 / 3}$$



The contact angle is related to the surface energies via the Young equation:

$$\Theta = \frac{\overset{\text{Surface}}{2\sigma_s} - \overset{\text{Adhesion}}{\sigma_{Ad}}}{2\sigma_s} = \frac{\Delta\sigma}{2\sigma_s} < 1$$

$$n_C = \frac{V_C}{v} = \frac{16\pi}{3} \frac{\sigma_s^2 \Delta\sigma}{(ze|\eta|)^3} v^2 \quad \text{and} \quad \Delta G_C^{3D} = \frac{ze|\eta|}{2} n_C$$

**Stronger adhesion decreases the critical size of nuclei !!!**

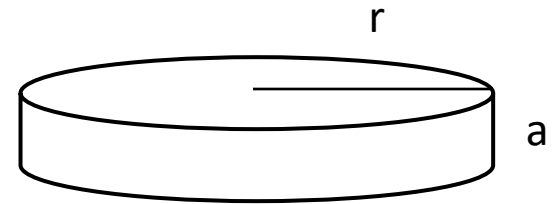
### III) Nucleation and growth process

#### 4) Heterogeneous 2D nucleation:

Nucleation occurs on a foreign substrate (only a few atoms thick):

$$\Delta G = \sigma_s S - \Delta\mu \frac{V}{V_m}$$

$$\Delta G = \{\pi r^2 \Delta\sigma + 2\pi r a \sigma_s\} - \left\{ zF\eta \frac{\pi r^2 a}{V_m} \right\}$$



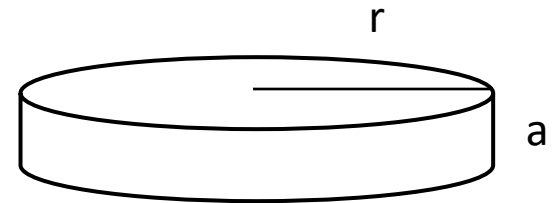
### III) Nucleation and growth process

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$$r_c = \frac{V_m a \sigma_s}{zF|\eta|a - V_m \Delta\sigma} \text{ and } \Delta G_C^{2D} = \frac{\pi \sigma_s^2 v a^2}{ze|\eta|a - v \Delta\sigma}$$

**The critical size of nuclei decreases for higher overpotential and stronger adhesion !!!**

### III) Nucleation and growth process

#### 5) Nucleation mechanism:

Weak adhesion:  $\Delta\sigma > 0$        $\sigma_{Ad} < 2\sigma_s$

$$\Delta G_C^{2D} = \Delta G_C^{3D} \Leftrightarrow \frac{\pi\sigma_s^2\nu a^2}{ze\eta a - \nu\Delta\sigma} = \frac{8\pi\sigma_s^2\Delta\sigma}{3(z\eta)^2}\nu^2$$

$$\eta_{3D\rightarrow 2D} = \frac{2\Delta\sigma}{azF}$$

# III) Nucleation and growth process

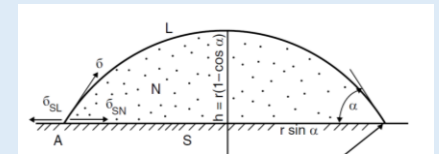
## 5) Nucleation mechanism:

Weak adhesion:  $\Delta\sigma > 0$

$$\sigma_{Ad} < 2\sigma_s$$

$\Rightarrow 0 < \eta < \frac{2\Delta\sigma}{azF} \Rightarrow$  3D nucleation process

$\Rightarrow \eta \geq \frac{2\Delta\sigma}{azF} \Rightarrow$  2D nucleation process



# III) Nucleation and growth process

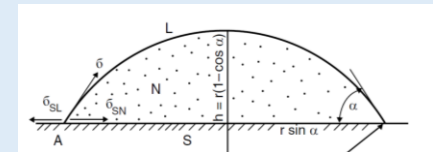
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Strong adhesion:  $\Delta\sigma < 0$

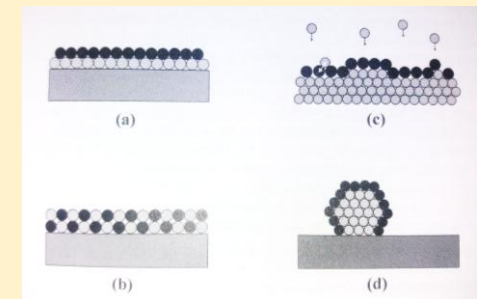
$$\sigma_{Ad} > 2\sigma_s$$

$\Rightarrow \frac{\Delta\sigma}{azF} < \eta < 0 \Rightarrow$  2D nucleation can occur above  $E_{eq}$

Underpotential Deposition (UPD)

Limited to 1 or 2 monolayers

Enables electrochemical atomic layer epitaxy (ECALE)



### III) Nucleation and growth process

#### 6) Growth of single nucleus

The growth rate normal to a surface  $R(t) = \frac{iV_m t}{zF}$  (from Faraday law)

##### Hemispherical 3D cluster

*Show that  $I(t) = f(t^2)$*

##### Cylindrical 2D cluster

*Show that  $I(t) = f(t)$*

### III) Nucleation and growth process

#### 6) Growth of single nucleus

The growth rate normal to a surface  $R(t) = \frac{iV_m t}{zF}$

##### Hemispherical 3D cluster

$$I(t) = 2\pi R(t)^2 i$$

with the hemisphere radius:  $R(t) = \frac{iV_m t}{zF}$

$$\text{thus } I(t) = 2\pi \left(\frac{V_m t}{zF}\right)^2 i^3 = f(t^2)$$

##### Cylindrical 2D cluster

$$I(t) = 2\pi a R(t) i$$

with the cylinder radius:  $R(t) = \frac{iV_m t}{zF}$

$$\text{thus } I(t) = 2\pi \frac{V_m t}{zF} i^2 = f(t)$$

### III) Nucleation and growth process

#### 7) Nucleation kinetics

##### Nucleation law:

There exists a uniform probability that a surface site is converted into a nucleus

A surface has only a limited number of available nucleation sites  $N_0$

The number of sites  $N(t)$  occupied at time  $t$  follows a linear kinetics:

$$N(t) = N_0(1 - \exp^{-k_n t})$$

where  $k_n$  is the nucleation constant

### III) Nucleation and growth process

#### 7) Nucleation kinetics

##### Nucleation law:

There exist a uniform probability that a surface site is converted into a nucleus  
A surface has only a limited number of available nucleation sites  $N_0$

The number of sites  $N(t)$  occupied at time  $t$  follows a linear kinetics:

$$N(t) = N_0(1 - \exp^{-k_n t})$$

where the nucleation constant  $k_n$  strongly depends on  $i/\eta$

*$k_n$  is large  $\Rightarrow$  fast nucleation  $\Rightarrow N(t = \tau) = N_0$*

**Instantaneous nucleation**: all sites are occupied in a short induction time  $\tau$

*$k_n$  is small  $\Rightarrow$  slow nucleation  $\Rightarrow N(t) = N_0 k_n t$*

**Progressive nucleation**: site occupation is linear with time

### III) Nucleation and growth process

## 8) Nucleation models

$$N(t = \tau) = N_0$$

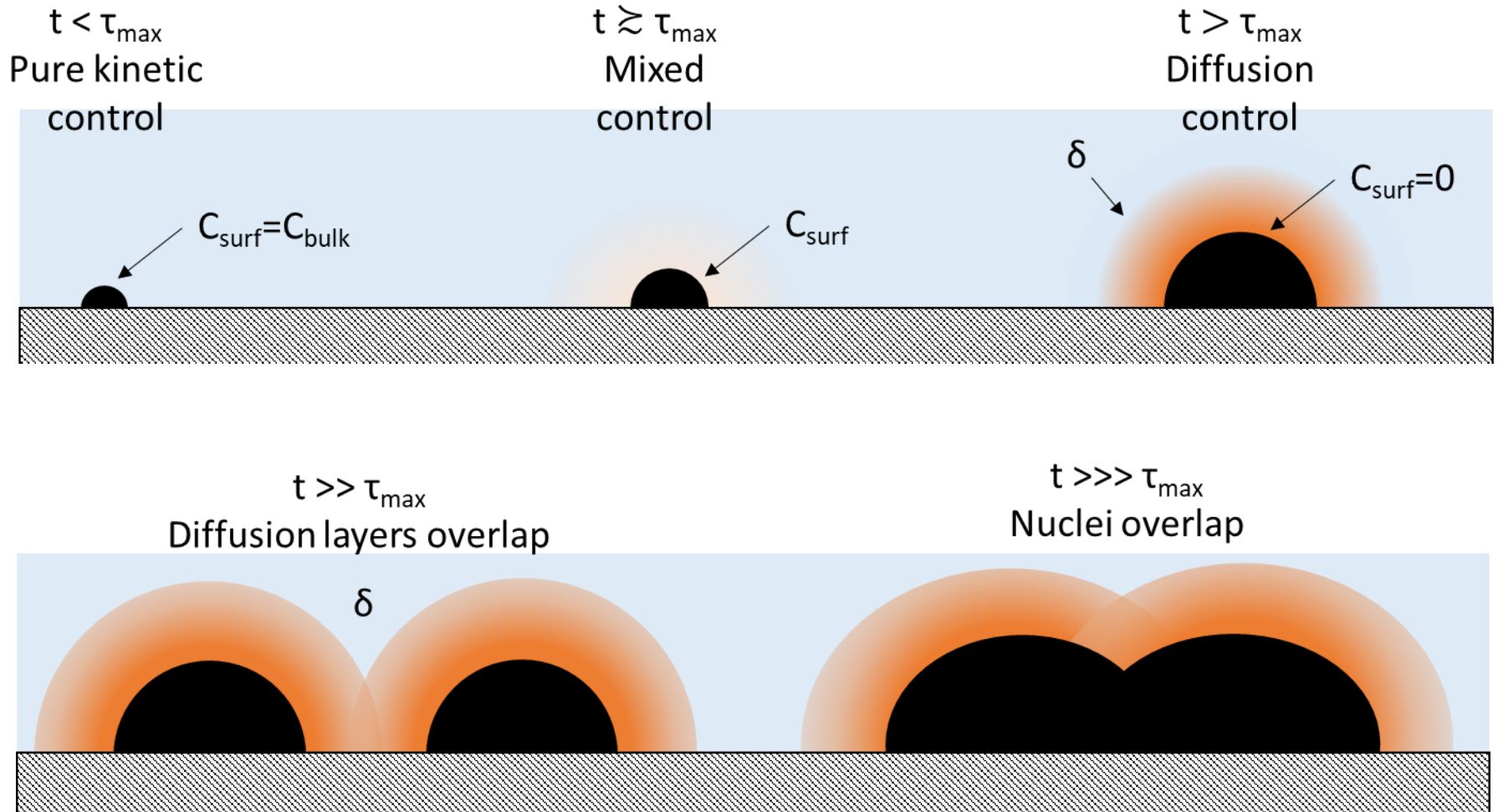
$$N(t) = N_0 k_n t$$

	Instantaneous	Progressive
3D	$i(t) = 2\pi N_0 \left(\frac{V_m}{zF}\right)^2 i^3 \cdot t^2$	$i(t) = 2\pi N_0 k_n \left(\frac{V_m}{zF}\right)^2 i^3 \cdot t^3$
2D	$i(t) = 2\pi N_0 \frac{V_m}{zF} i^2 \cdot t$	$i(t) = 2\pi N_0 k_n \frac{V_m}{zF} i^2 \cdot t^2$

$t < t_{\max}$ : no mass transfer limitation, no overlapping

# III) Nucleation and growth process

## 9) Nucleation and growth models



### III) Nucleation and growth process

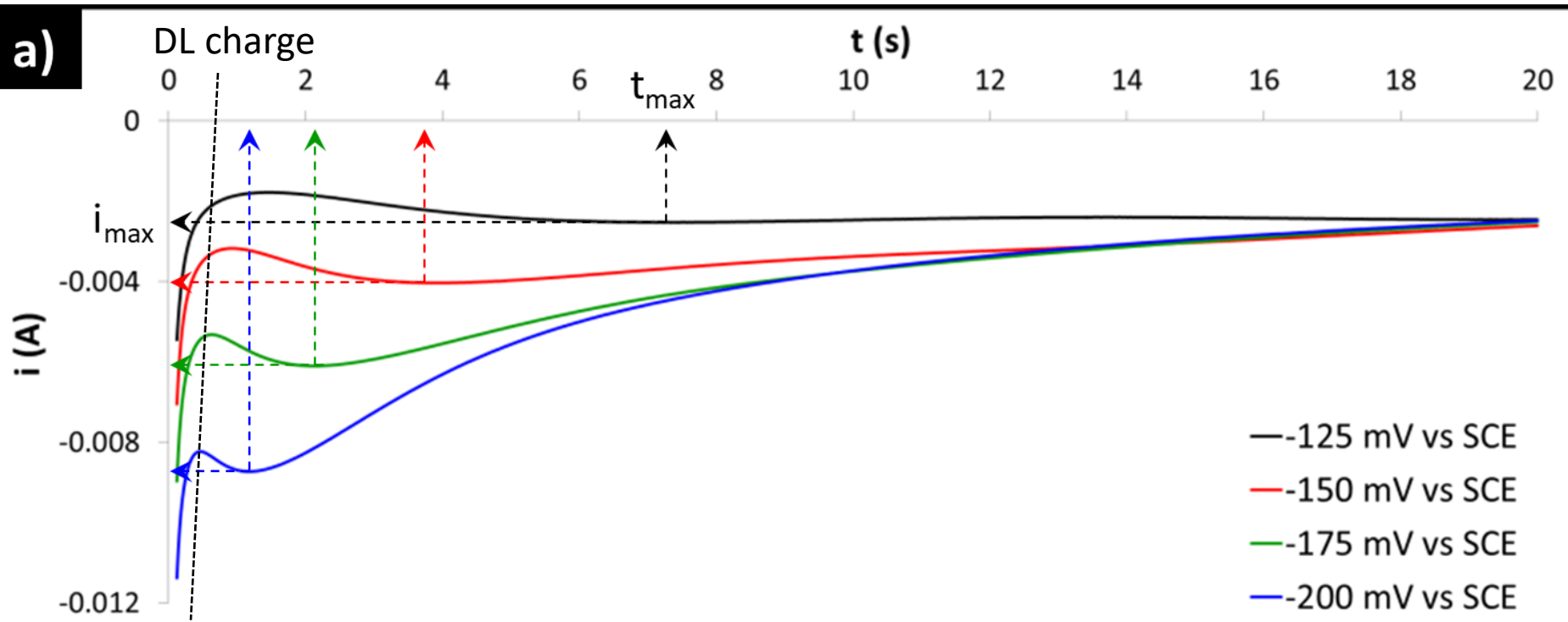
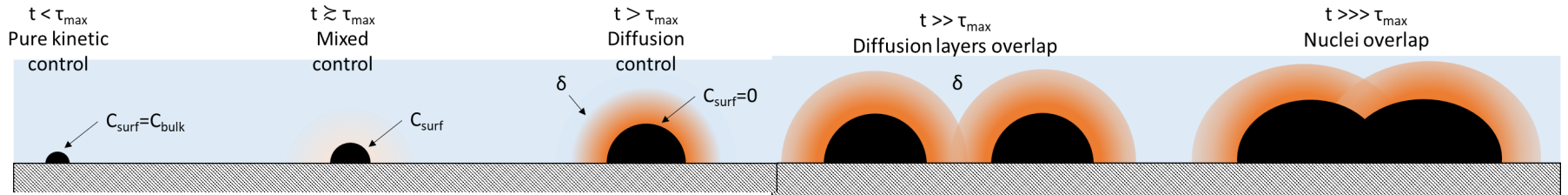
## 9) Nucleation and growth models

Accounting for overlapping: *Bewick, Scharifker and Hills (1962, 1983)*

	Instantaneous	Progressive
3D	$i(t) = 2\pi N_0 \left(\frac{V_m}{zF}\right)^2 i^3 \cdot t^2 \cdot \exp^{-\pi V_m^2 N_0 k_n^2 t^2}$	$i(t) = 2\pi N_0 k_n \left(\frac{V_m}{zF}\right)^2 i^3 \cdot t^3 \cdot \exp\frac{-\pi V_m^2 N_0 k_n^2 t^3}{3}$
2D	$i(t) = 2\pi N_0 \frac{V_m}{zF} i^2 \cdot t \cdot \exp^{-\pi V_m^2 N_0 k_n^2 t^2}$	$i(t) = 2\pi N_0 k_n \frac{V_m}{zF} i^2 \cdot t^2 \cdot \exp\frac{-\pi V_m^2 N_0 k_n^2 t^3}{3}$

# III) Nucleation and growth process

## 9) Nucleation and growth models



### III) Nucleation and growth process

## 9) Nucleation and growth models

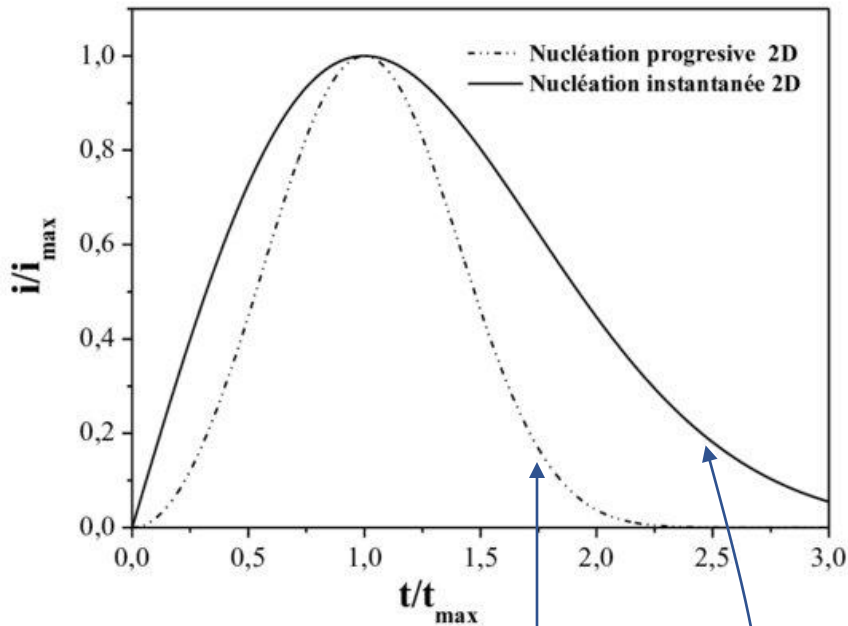
Accounting for overlapping: *Bewick, Scharifker and Hills (1962, 1983)*

	Instantaneous	Progressive
3D	$\left(\frac{i}{i_{\max}}\right)^2 = 1.9542 \left(\frac{t_{\max}}{t}\right) \left[1 - \exp^{-1.2564\left(\frac{t}{t_{\max}}\right)}\right]^2$	$\left(\frac{i}{i_{\max}}\right)^2 = 1.2254 \left(\frac{t_{\max}}{t}\right) \left[1 - \exp^{-2.3367\left(\frac{t}{t_{\max}}\right)^2}\right]^2$
2D	$\left(\frac{i}{i_{\max}}\right) = \left(\frac{t}{t_{\max}}\right) e^{\left[\frac{1}{2} - \frac{1}{2}\left(\frac{t}{t_{\max}}\right)^2\right]}$	$\left(\frac{i}{i_{\max}}\right) = \left(\frac{t}{t_{\max}}\right)^2 e^{\left[\frac{2}{3} - \frac{2}{3}\left(\frac{t}{t_{\max}}\right)^3\right]}$

# III) Nucleation and growth process

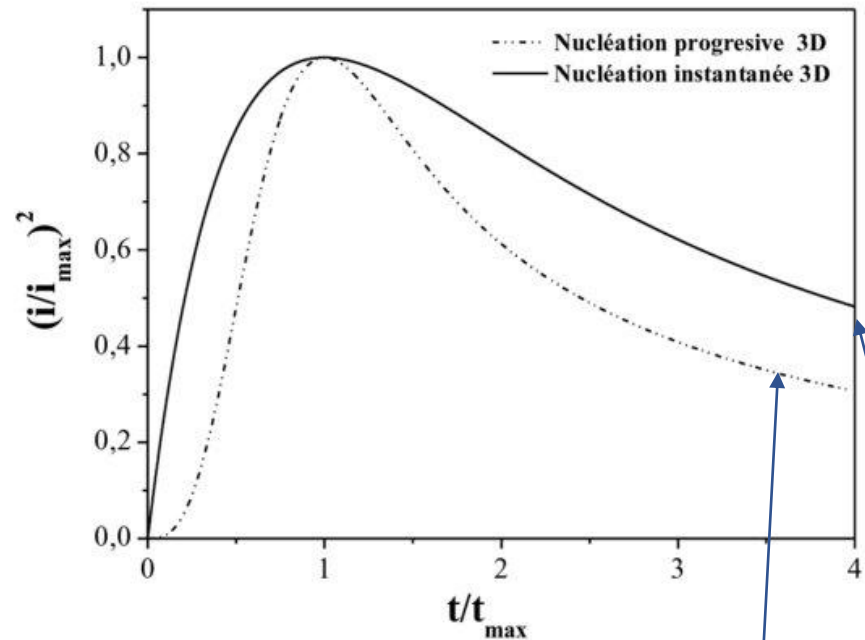
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$$\left(\frac{i}{i_{\max}}\right) = \left(\frac{t}{t_{\max}}\right)^2 e^{\left[\frac{2}{3} - \frac{2}{3}\left(\frac{t}{t_{\max}}\right)^3\right]}$$

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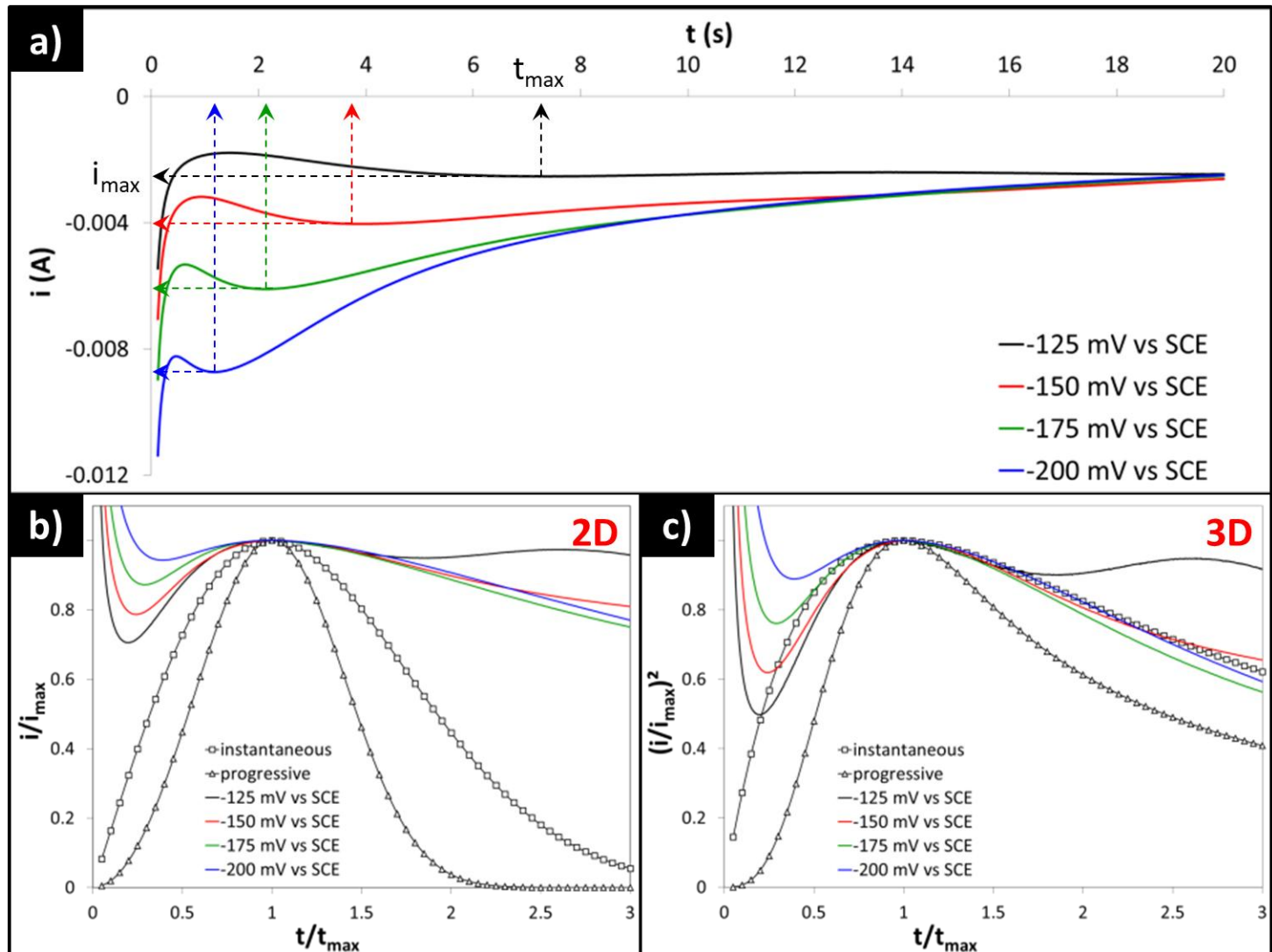


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# III) Nucleation and growth process

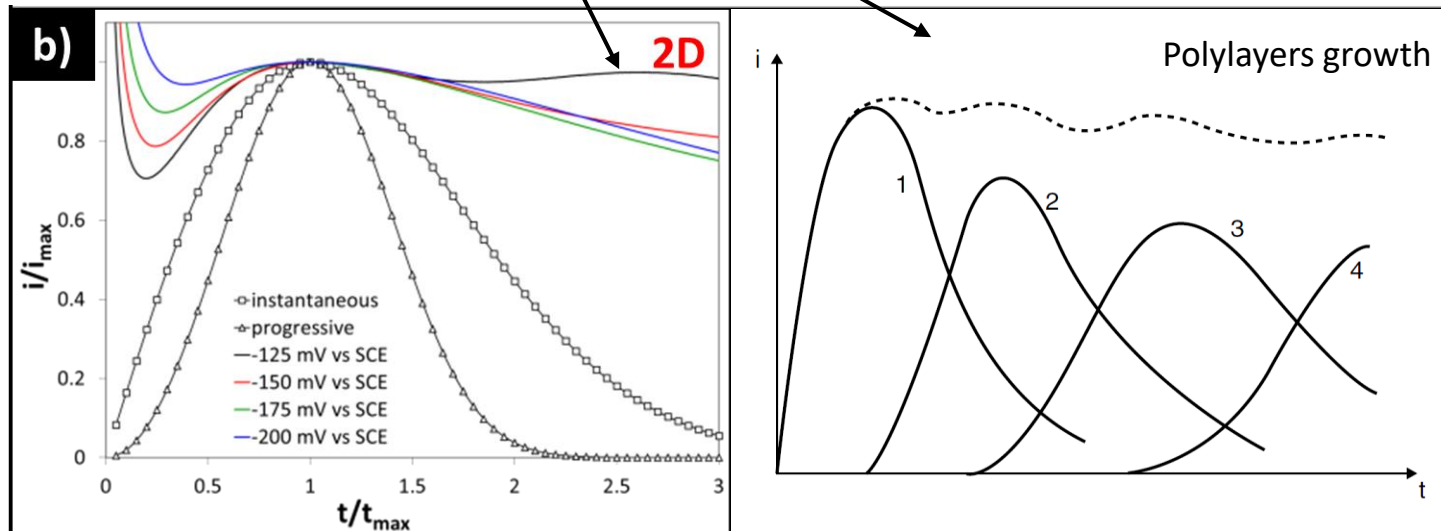
## 9) Nucleation and growth models



# III) Nucleation and growth process

## 9) Nucleation and growth models

Successive nucleation and overlapping of 2D layers



# IV) Electrodeposit characteristics

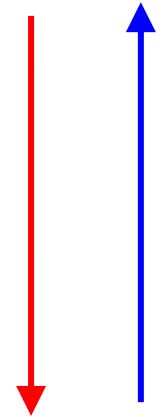
## Microstructure and morphology

### Microstructure:

Atoms are arranged in 3 dimensions with a certain periodicity degree

- Monocrystalline: periodicity extends on the whole solid
- Polycrystalline: periodicity is interrupted at grain boundaries
- Nanocrystalline: periodicity extends over a few nanometers
- Amorphous: periodicity breaks at short distance (lattice parameter)

Ductility ↗



Hardness ↗

Brightness ↗

Brittleness ↗

Resistivity ↗

# IV) Electrodeposit characteristics

## Microstructure and morphology

Morphology:

