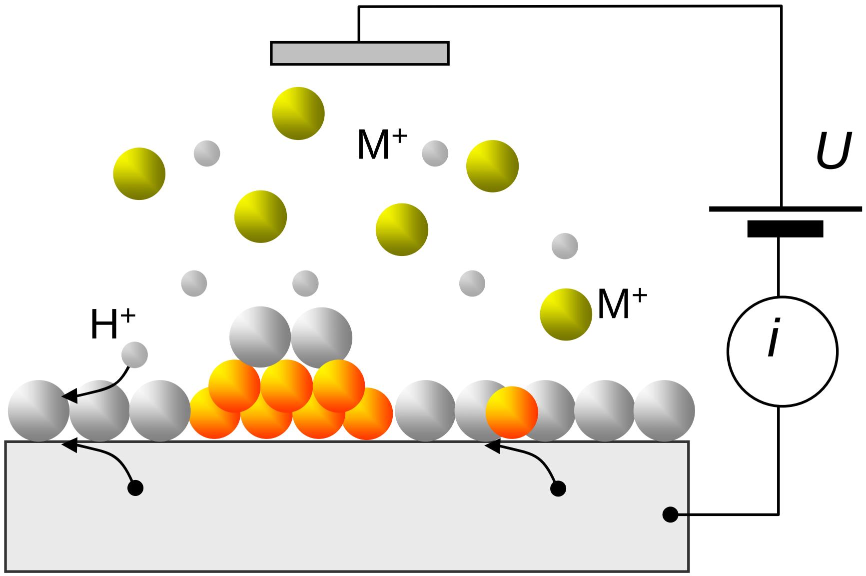
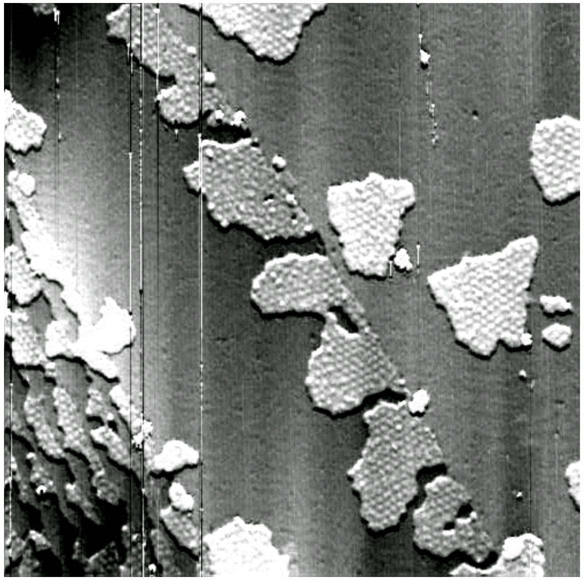
Cinétiques multiéchelles de dépôt 1D

Émile, Isabelle, Fabienne, Bernard





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Problématique

- ✓ Thermodynamique d'amas

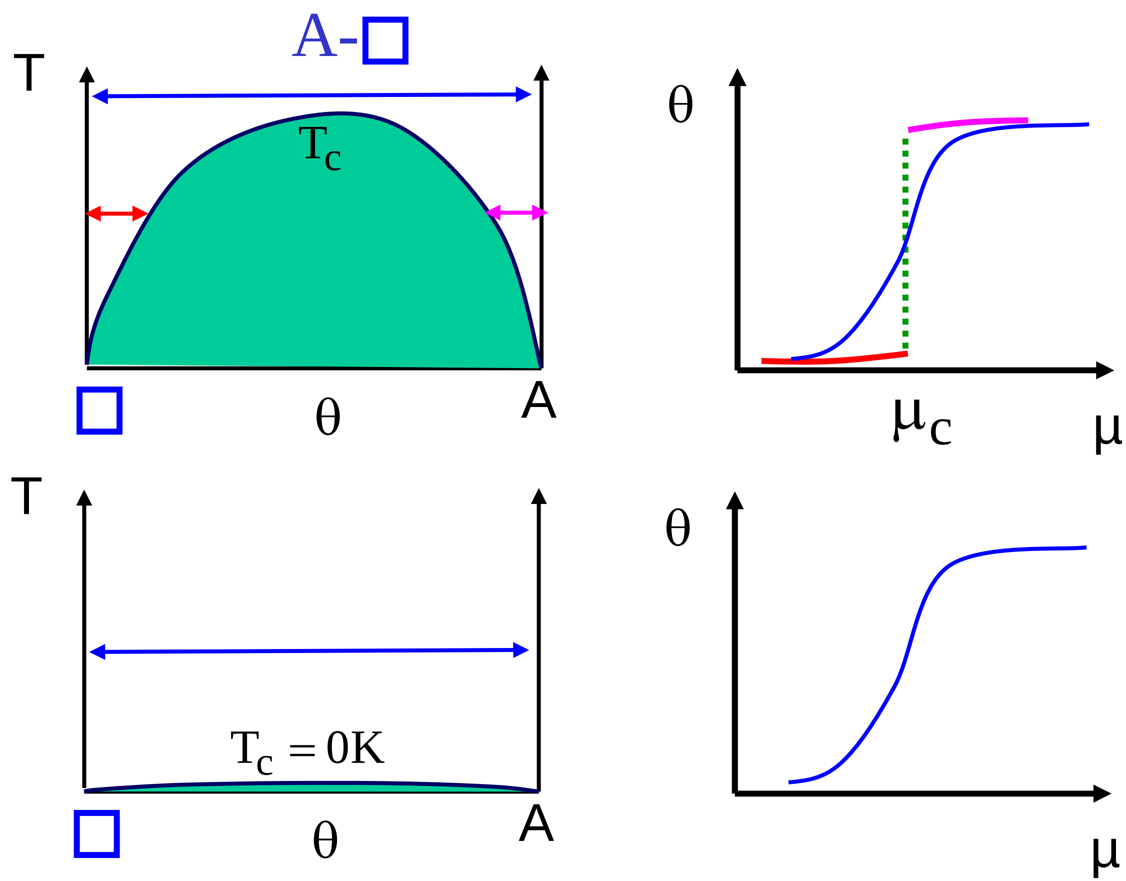
- ✓ Cinétique de croissance :
Simulations Monte Carlo / modélisation mésoscopique

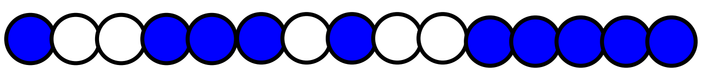
- ✓ De la croissance au vieillissement

Diagrammes de phases

2 D

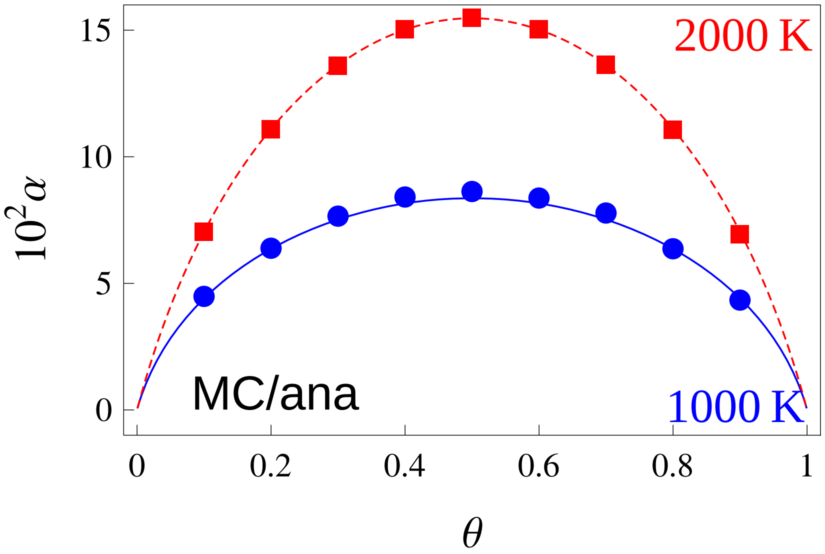
1 D

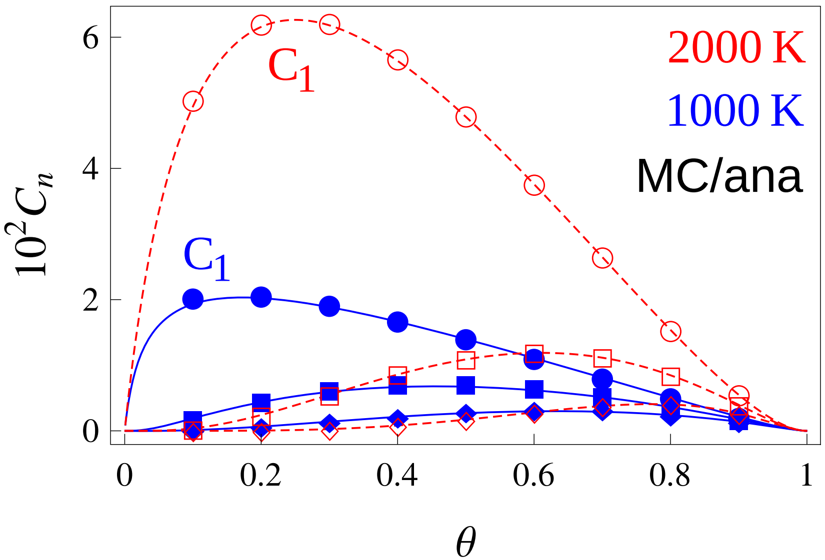




$$N_s \qquad C_n = \frac{N_n}{N_s} \qquad C_n^{lac} = \frac{N_n^{lac}}{N_s} \qquad \alpha = \sum_{n=1} C_n = \sum_{n=1} C_n^{lac} \qquad \theta = \sum_{n=1} nC_n$$

Thermodynamique 1 D





Ensemble canonique

$$a = \exp\left(-\frac{V_{AA}}{kT}\right) - 1$$

$$C_{tot} = \frac{\sqrt{1 + 4a(1-\theta)\theta} - 1}{2a}$$

$$C_n = \frac{C_{tot}^2}{\theta}\left(1 - \frac{C_{tot}}{\theta}\right)^{n-1}$$

$$C_n^{lac} = \frac{C_{tot}^2}{(1-\theta)}\left(1 - \frac{C_{tot}}{(1-\theta)}\right)^{n-1}$$

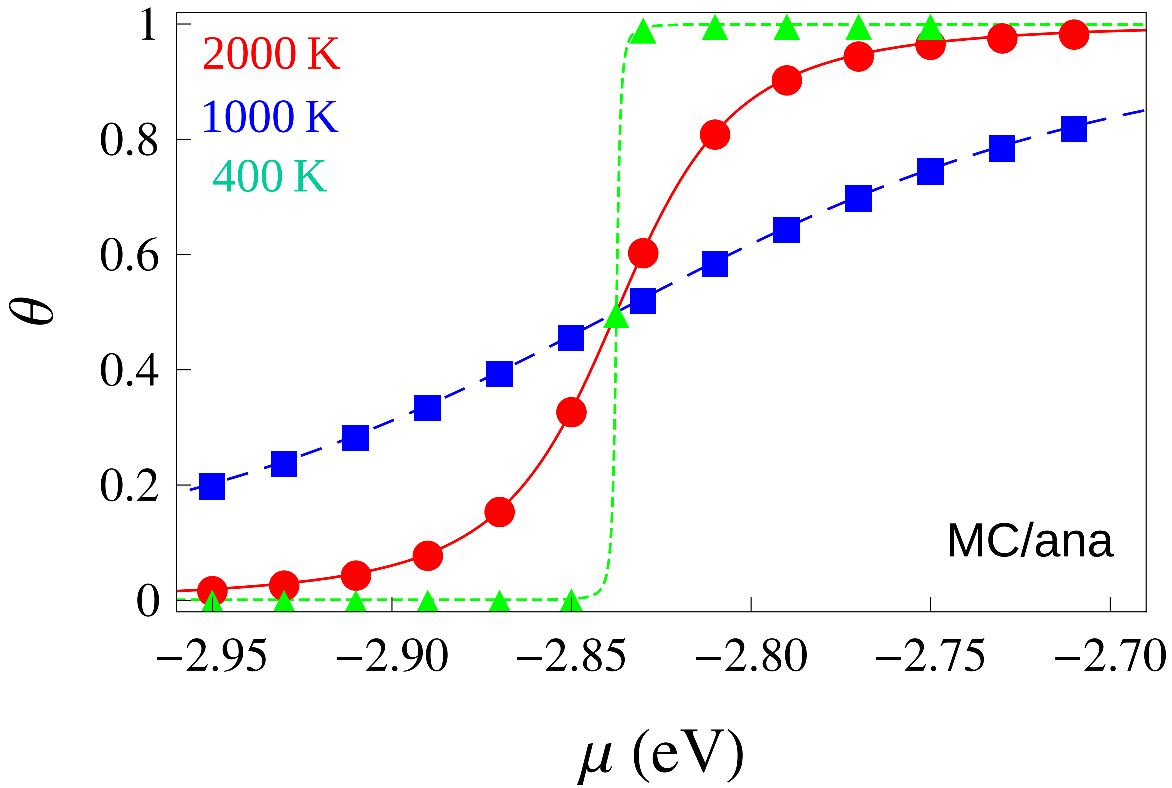
M.B. Yilmaz and F. Zimmermann, Phys. Rev. E 71, 026127 (2005)

Ensemble grand-canonique

$$\mu = \underbrace{E_{ads} + V_{AA}}_{\mu_c} + kT \ln\left(\frac{1 - C_{tot}/\theta}{1 - C_{tot}/(1-\theta)}\right)$$

$E_{ads} = -2.56\,\text{eV},$

$V_{AA} = -0.28\,\text{eV}$



Distribution d'amas

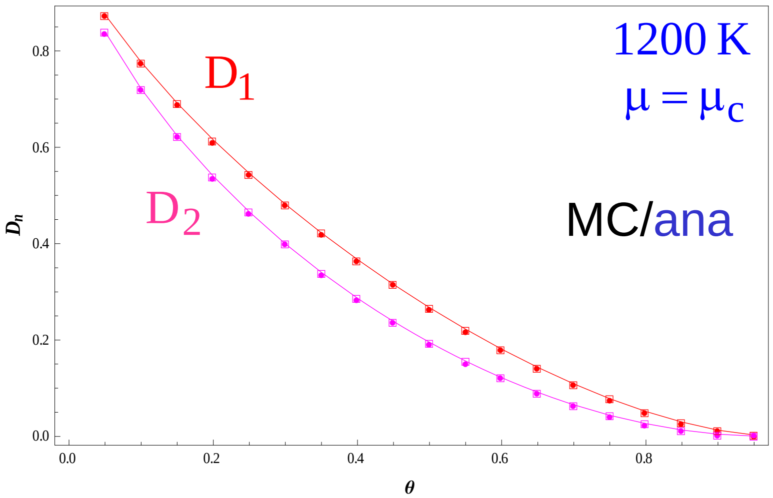
J. Lepinoux, Phil Mag 86, 5053 (2006) :

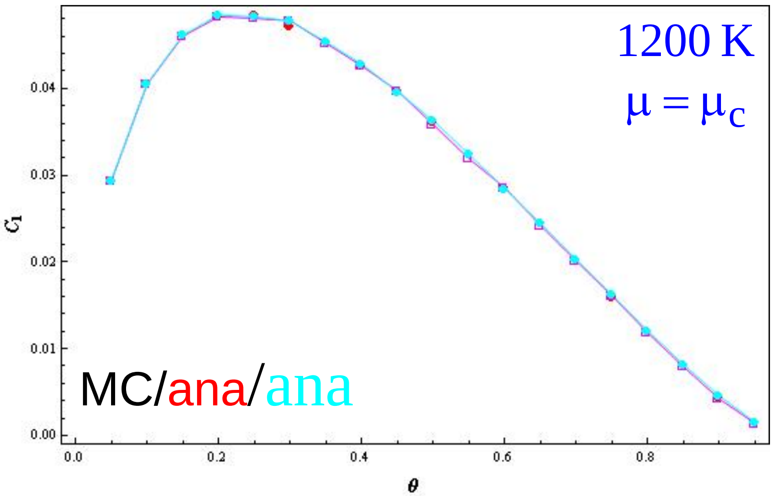
$$C_n = \frac{C_{tot}^2}{\theta}\left(1 - \frac{C_{tot}}{\theta}\right)^{n-1}$$

$$C_n = D_n \exp\frac{(-\Delta F_n)}{kT}$$

$$\begin{cases} \Delta F_n = nE_{ads} - (n-1)V_{AA} - n\mu \\ D_n = ??? \end{cases}$$

$$D_n = \sum_{j=n} \left(j - (n-1)\right) C_j^{lac}$$

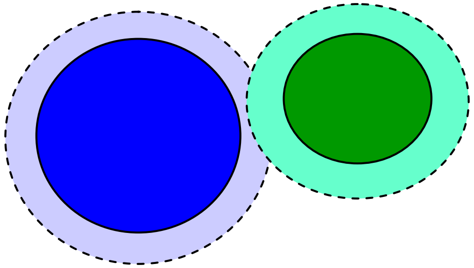




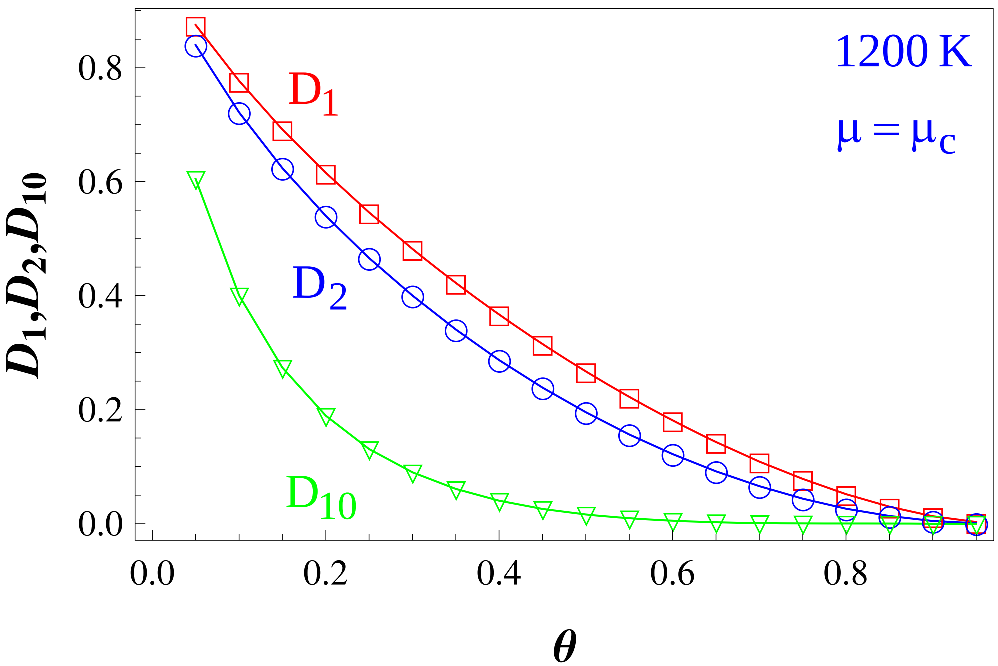
Validation de la formule : $C_n = D_n \exp\frac{(-\Delta F_n)}{kT} \; \forall n$

$D_n(C_{tot}, \theta)$

$$D_n = (1-\theta)\prod_k\left(1-\frac{c_k}{1-\theta}\right)^{\tilde{s}_{k,n}}$$



$$D_n = (1-\theta)\left(1-\sum_k\frac{c_k}{1-\theta}\right)^{n+1} = (1-\theta)\left(1-\frac{C_{tot}}{1-\theta}\right)^{n+1}$$



$$D_n = (1-\theta)\left(1-\frac{C_{tot}}{1-\theta}\right)^{n+1}$$ □ ○ ▽

$$D_n = \sum_{j=n}(j-(n-1))C_j^{lac}$$ **Traits**

Validation de la formule

$$D_n = (1-\theta)\left(1-\frac{C_{tot}}{1-\theta}\right)^{n+1}$$

De l'équilibre à la cinétique de dépôt

$$\frac{dC_1(t)}{dt} = \beta_0 D_1 - \left(\alpha_0 + \beta_1 \frac{D_2}{D_1} \right) C_1(t) + \alpha_1 C_2(t)$$

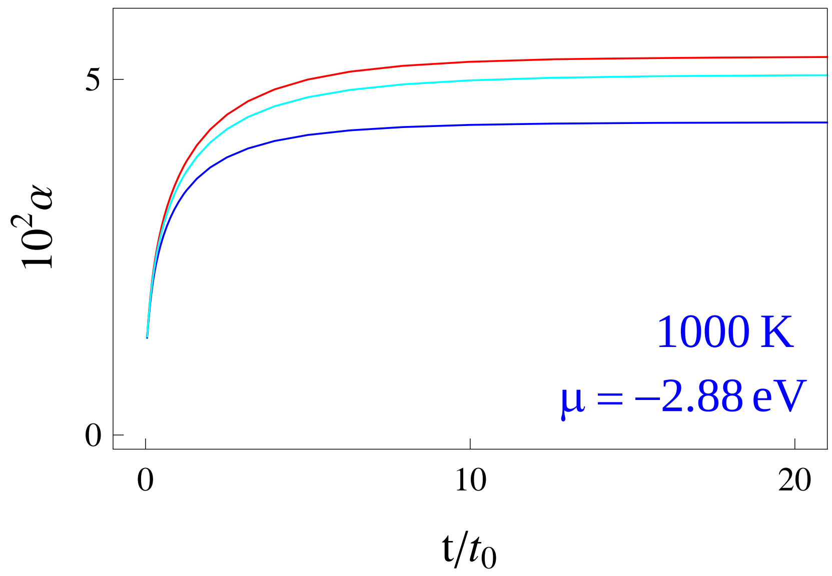
$$\frac{dC_n(t)}{dt} = \beta_1 \frac{D_n}{D_{n-1}} C_{n-1}(t) - \left(\alpha_1 + \beta_1 \frac{D_{n+1}}{D_n} \right) C_n(t) + \alpha_1 C_{n+1}(t)$$

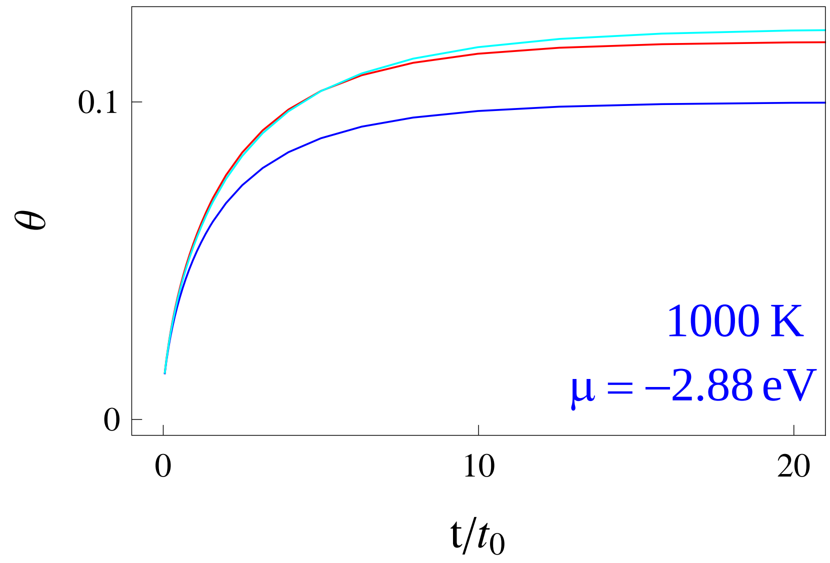
$n \leftrightarrow n+1$

$$\beta_0 = \exp\left(-\frac{E_{ads} - \mu}{2kT} \right) \qquad \alpha_0 = \exp\left(\frac{E_{ads} - \mu}{2kT} \right)$$

$$\beta_1 = 2\exp\left(-\frac{E_{ads} + V_{AA} - \mu}{2kT} \right) \qquad \alpha_1 = 2\exp\left(\frac{E_{ads} + V_{AA} - \mu}{2kT} \right)$$

Influence des zones d'exclusion





$$D_n = (1-\theta)\left(1-\frac{C_t}{1-\theta}\right)^{n+1}$$

$$D_n = 1$$

$$D_n = (1-\theta)$$

Coagulation/fragmentation

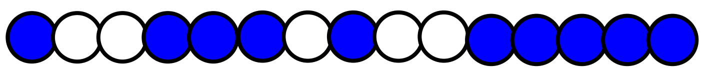
désorption 2 L

- création d'une lacune + amas i + amas j (avec i + j + 1 = n)
- perte d'un amas de taille n

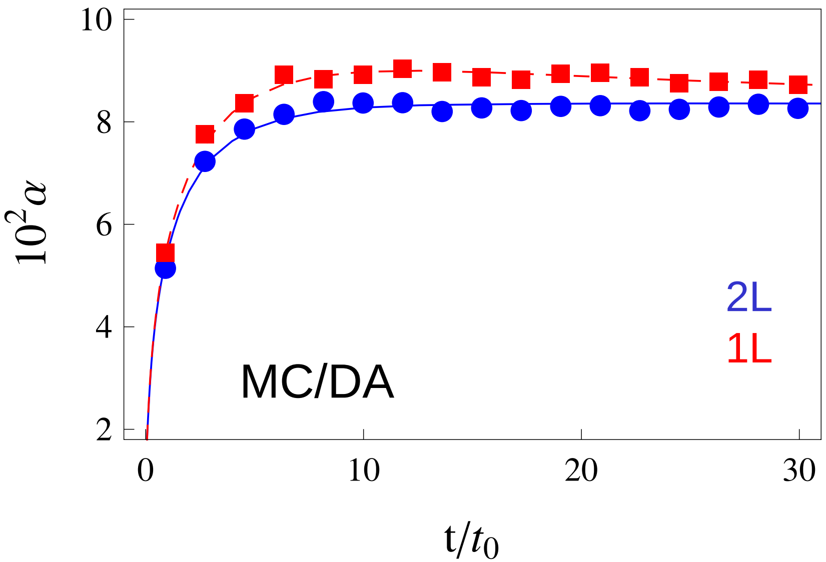
$n \leftrightarrow m$

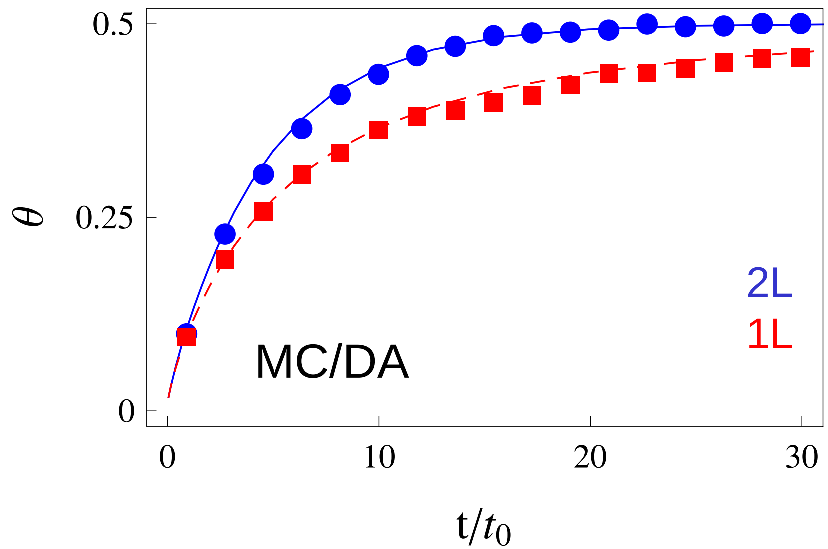
adsorption 2 L

- perte d'une lacune + amas i + amas j (avec i + j + 1 = n)
- création d'un amas de taille n



$$C_1^{lac} = \frac{C_{tot}^{\;2}}{(1-\theta)}$$





bilan

✓ validation de la formule donnant la distribution des amas

✓modélisation mésoscopique :

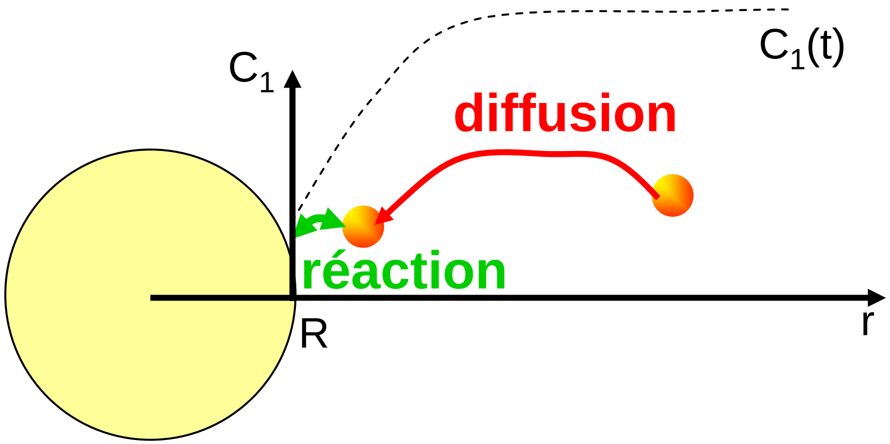
zones d'exclusion

coagulation/fragmentation

Cinétiques de vieillissement

$$\frac{dC_n(t)}{dt} = \beta_{n-1}\frac{D_n}{D_{n-1}}C_{n-1}(t) - \left(\alpha_n D_1 + \beta_n \frac{D_{n+1}}{D_n}\right)C_n(t) + \alpha_{n+1}D_1 C_{n+1}(t)$$

$$\beta_n, \alpha_n = ?$$



$$C_I = 0$$

$$\beta_n = \frac{dn}{dt} = 2\pi R\left|-D(\nabla C_1)_R\right|$$

Cinétique limitée par la diffusion

$$C_I = C_1$$

$$\frac{dn}{dt} = \beta_n C_I - \alpha_n(1 - C_I)$$

Cinétique limitée par la réaction

De l'électrochimie au vieillissement

$$v_n = \frac{dn}{dt} = -J = m\left(C_1 - C_I\right) \qquad v_n = K_n^+ C_I - K_n^- \left(1 - C_I\right)$$

$$\Longrightarrow \quad m\left(C_1 - C_I\right) = K_n^+ C_I - K_n^- \left(1 - C_I\right)$$

$$C_I = \frac{mC_1 + K_n^-}{m + K_n^+ + K_n^-}$$

$$v_n = \underbrace{\frac{K_n^+}{1 + \left(K_n^+ + K_n^-\right)/m}}_{\beta_n} C_1 - \underbrace{\frac{K_n^-}{1 + \left(K_n^+ + K_n^-\right)/m}}_{\alpha_n} \left(1 - C_1\right)$$

Du 1D au 2D

Emile !

Et du mono au bimétallique…

Isabelle !