

# Paradoxes et apport de la DA à 1D

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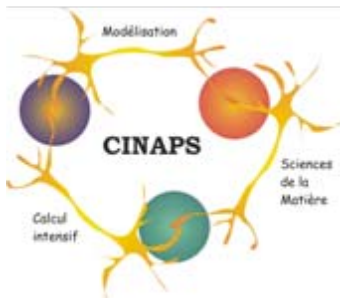


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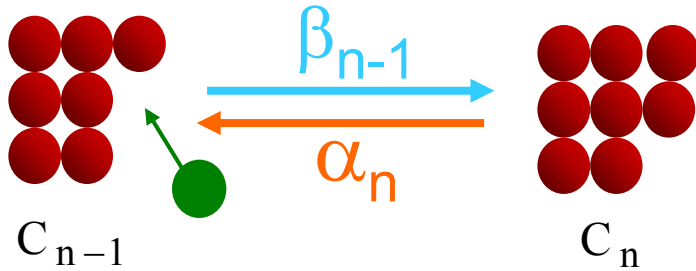
<sup>3</sup>SRMP-DMN, CEA Saclay, Gif sur Yvette Cedex, F- 91191



GDR TransDiff 16-17 Juin 2009

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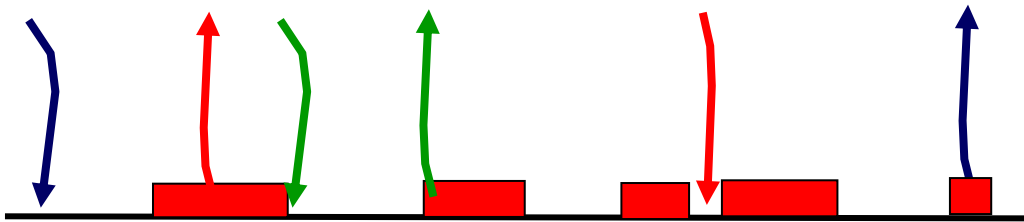
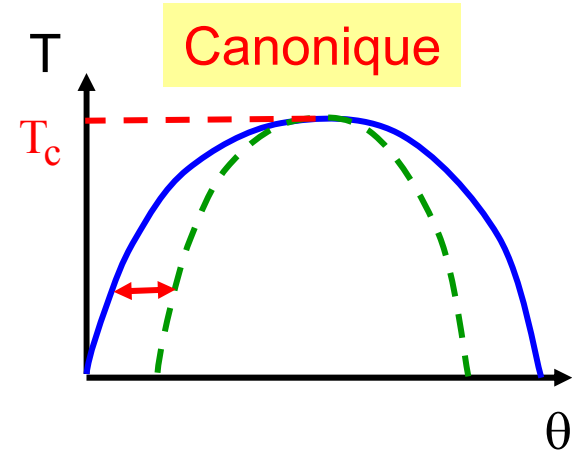
# Contexte



$$\frac{dc_n}{dt} = \beta_{n-1}c_{n-1} - (\alpha_n + \beta_n)c_n + \alpha_{n+1}c_{n+1}$$

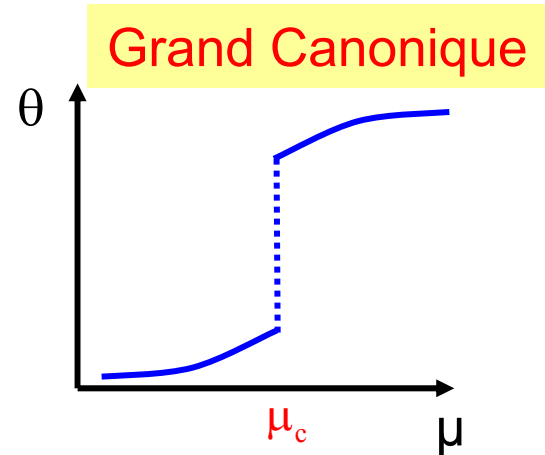
$$\beta_n = f(D, c_1) \quad \alpha_n = f(D, V_{AA})$$

diffusion, monomères



$$\beta_n = f(v, Q, V_{AA}, \mu) \quad \alpha_n = f(v, Q, V_{AA}, \mu)$$

processus local

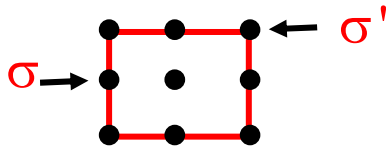


# Problèmes de la DA

## Equilibre

$$\frac{c_n}{D_n} = \exp\left(-\frac{\Delta F_n}{kT}\right)$$

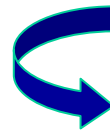
$$\Delta F_n = -n\Delta\mu + P_n\sigma + \sigma' + \tau kT \ln(n)$$



- gaz d'amas :
  - $D_n$ ,
  - Frenkel,  $D_n = 1 \forall n$

## Cinétique de diffusion

- $\beta_n$  : recouvrement de champ
- $\alpha_n$  : indépendant du milieu
- $\nabla c_1$  ou  $\nabla \theta$  ?
- au-delà du côté dilué :
  - Frenkel,
  - $D(\theta)$  ?



**1D Grand Canonique !!**

# Grand Canonique

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Pas de problèmes liés à la diffusion

- recouvrement de champ de diffusion,
- $D(\theta)$ ?

## 1D

- $T_c = 0 \Rightarrow$  DA dans l'état désordonné  $\forall \theta \in [0, 1]$
- Description analytique exacte de la distribution d'équilibre d'amas  
M.B. Yilmaz and F. Zimmermann, Phys. Rev. E **71**, 026127 (2005)

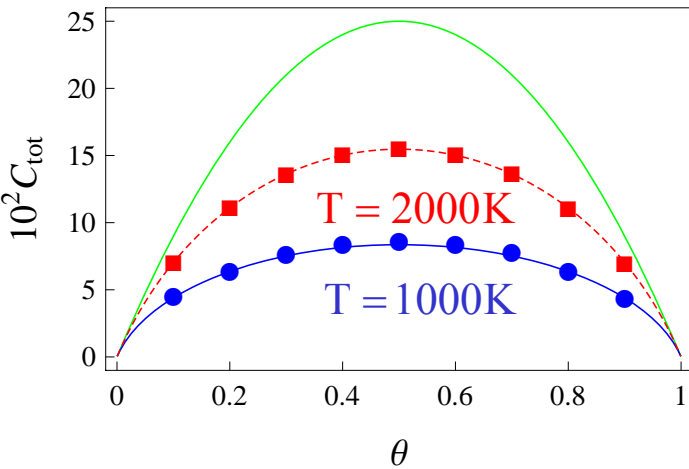


$$\theta = 0.25, T = 100 \text{ K}$$



$$\theta = 0.25, T = 3000 \text{ K}$$

# Equilibre d'amas 1D: Ising ( $V_{AA}$ , $\theta$ , $T$ )



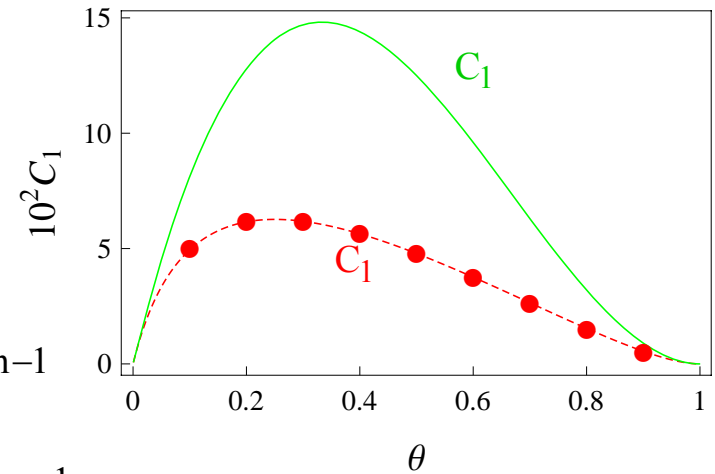
$$C_{\text{tot}} = \theta(1-\theta)$$

$$C_n = \theta^n(1-\theta)^2$$

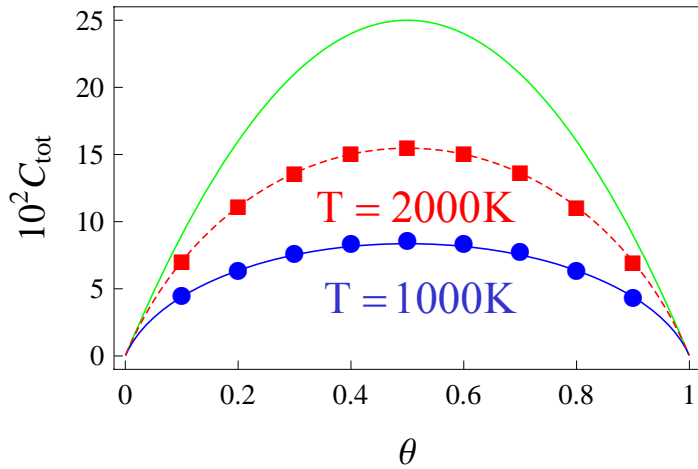
$$C_{\text{tot}} = f(\theta, V_{AA}, T)$$

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

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



# Equilibre d'amas 1D: Ising ( $V_{AA}, \theta, T$ )



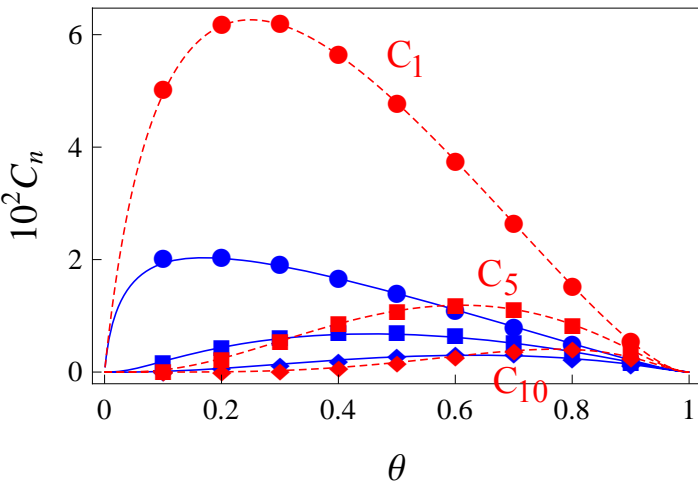
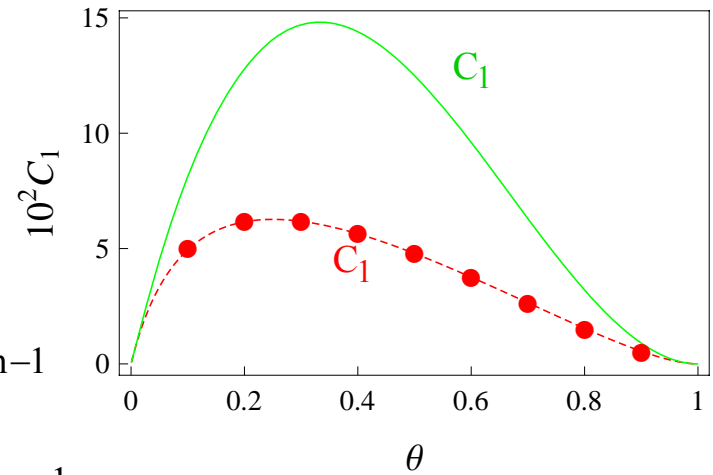
$$C_{\text{tot}} = \theta(1-\theta)$$

$$C_n = \theta^n(1-\theta)^2$$

$$C_{\text{tot}} = f(\theta, V_{AA}, T)$$

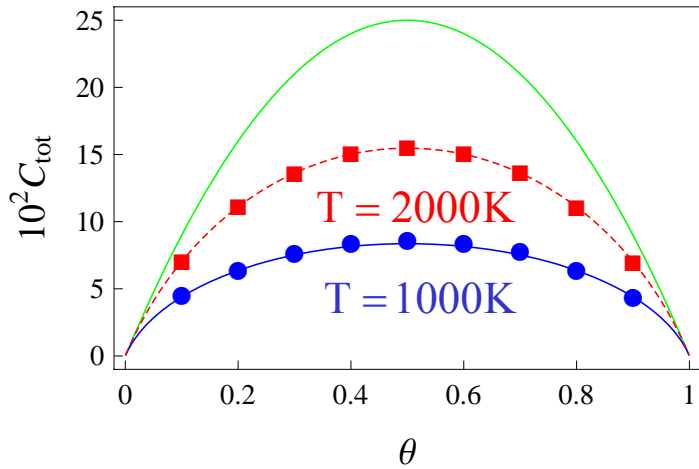
$$C_n = \frac{C_{\text{tot}}^2}{\theta} \left(1 - \frac{C_{\text{tot}}}{\theta}\right)^{n-1}$$

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



$$V_{AA} = -277\text{meV}$$

# Equilibre d'amas 1D: Ising ( $V_{AA}, \theta, T$ )



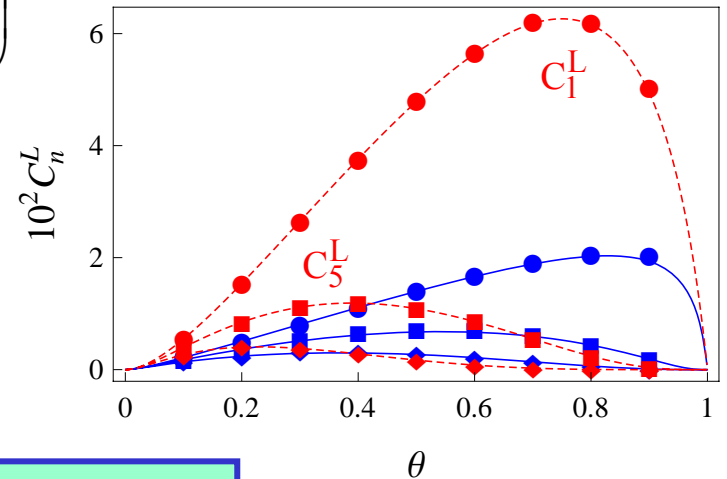
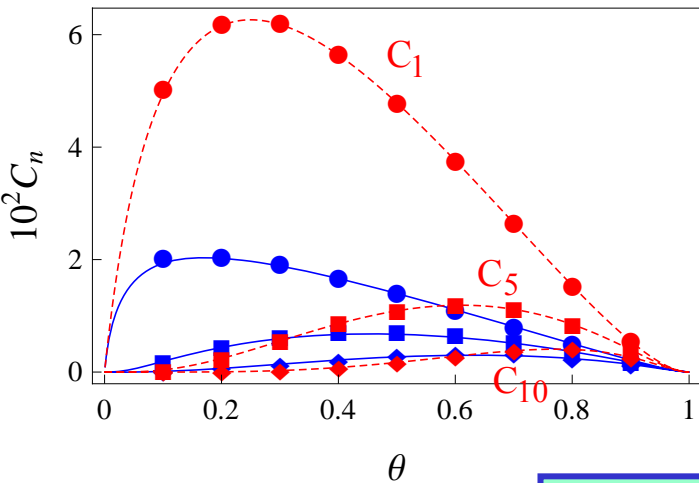
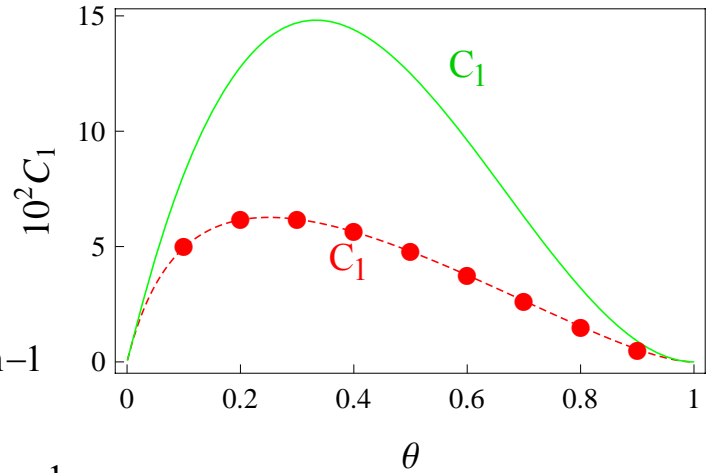
$$C_{\text{tot}} = \theta(1-\theta)$$

$$C_n = \theta^n(1-\theta)^2$$

$$C_{\text{tot}} = f(\theta, V_{AA}, T)$$

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

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

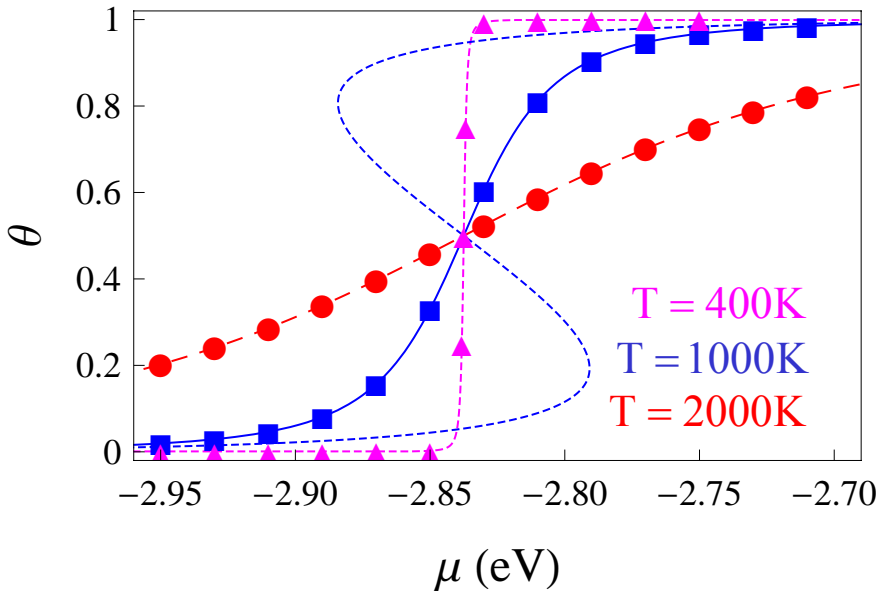


**Thermo exacte en DA :**

- $\forall \theta$
- dans l'état désordonné

$$V_{AA} = -277\text{meV}$$

# Isotherme 1D



Champ Moyen :  $\mu = E_{\text{ads}} + 2V_{\text{AA}}\theta + kT \ln\left(\frac{\theta}{1-\theta}\right)$

$$T_c = -\frac{V_{\text{AA}}}{2k} \quad \mu_c = E_{\text{ads}} + V_{\text{AA}}$$

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

**Équilibre  
Gd Canonique = Canonique**



# Distribution d'équilibre

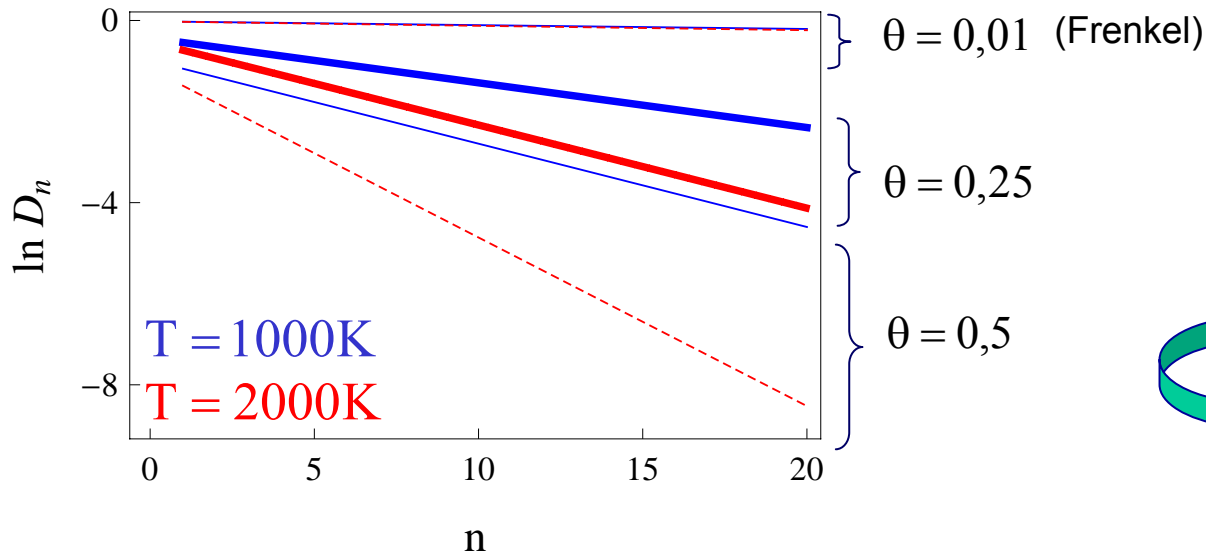
$$\left. \begin{array}{l} \text{Yilmaz : } C_n = \frac{C_{\text{tot}}^2}{\theta} \left(1 - \frac{C_{\text{tot}}}{\theta}\right)^{n-1} \\ \text{Lépinoux : } \frac{C_n}{D_n} = \exp\left(-\frac{\Delta F_n}{kT}\right) \end{array} \right\} D_n = ?$$



$$D_1 = \sum_{j>2} (j-2)C_j^L$$

$$D_n = \sum_{j>n+1} (j-(n+1))C_j^L$$

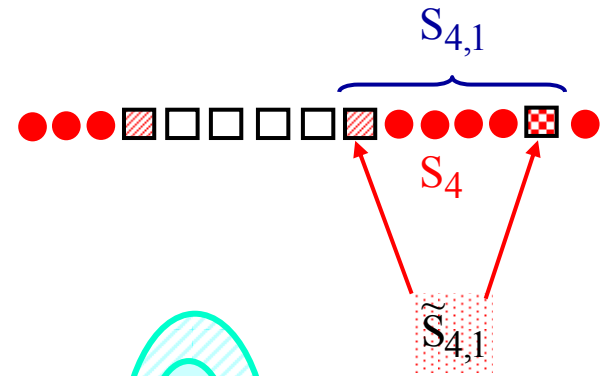
J. Lepinoux, Phil Mag **86**, 5053 (2006)



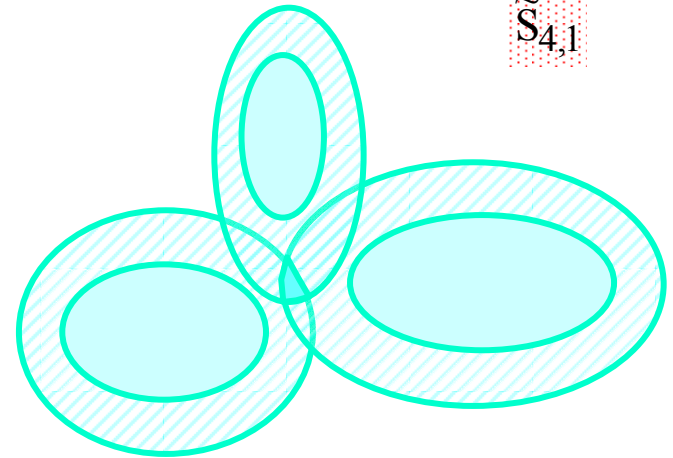
$$D_n = (1-\theta) \left(1 - \sum_k \frac{C_k}{1-\theta}\right)^{n+1}$$

# 1D, 2D, 3D et solutions concentrées : $D_n$

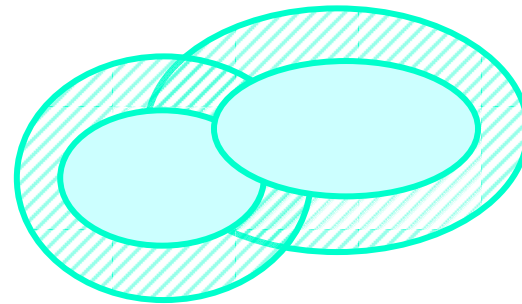
à 1D :  $D_n = (1-\theta) \left( 1 - \sum_k \frac{C_k}{1-\theta} \right)^{\tilde{S}_{k,n}}$       $\tilde{S}_{k,n} = S_{k,n} - S_k = n+1$



à 2D ou à 3D :  $D_n = (1-\theta) \prod_k \left( 1 - \frac{C_k}{1-\theta} \right)^{\tilde{S}_{k,n}}$



≠ de Lépinoux :  $D_n = \prod_{k=1} (1 - C_k)^{S_{k,n}}$

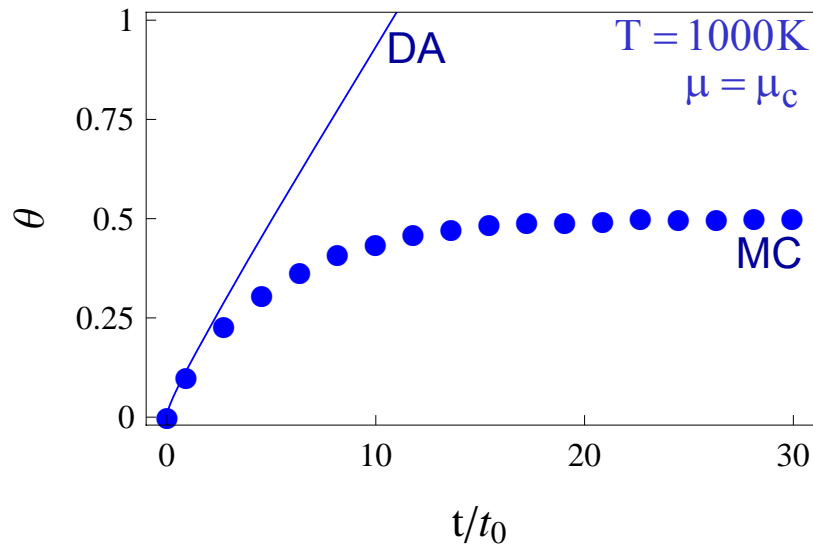


# de la DA...à la DA

$$\begin{cases} \frac{dC_1}{dt} = \beta_0 - (\alpha_0 + \beta_1)C_1 + \alpha_1C_2 \\ \frac{dC_n}{dt} = \beta_1C_{n-1} - (\alpha_1 + \beta_1)C_n + \alpha_1C_{n+1} \end{cases}$$

$$\begin{cases} \beta_i \propto \exp\left(-\frac{E_{\text{ads}} + iV_{\text{AA}} - \tilde{\mu}}{2kT}\right) \\ \alpha_i \propto \exp\left(\frac{E_{\text{ads}} + iV_{\text{AA}} - \tilde{\mu}}{2kT}\right) \end{cases}$$

$$\theta = \sum_n nC_n$$



$$i = 0,1 \text{ L}$$

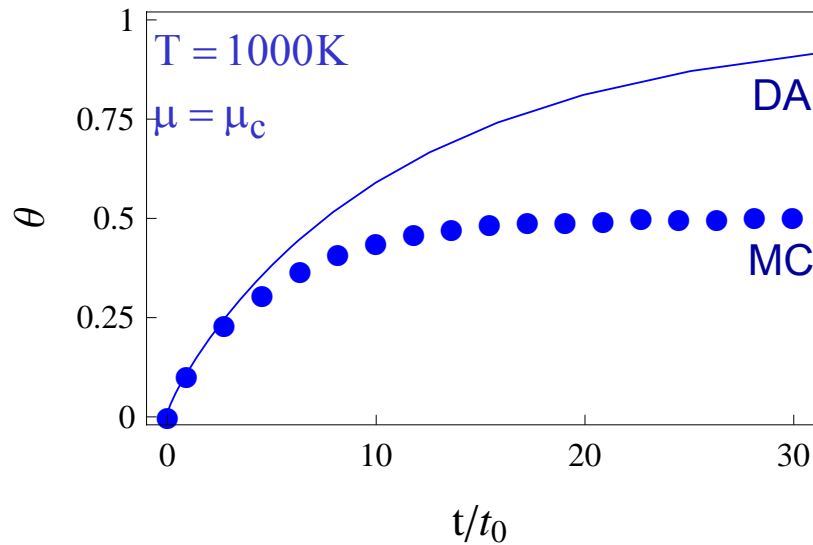
~~Bilan détaillé~~



$$t_0^{-1} = v \exp\left(-\frac{Q}{kT}\right)$$

# Place disponible pour les monomères...

$$\begin{cases} \frac{dC_1}{dt} = \beta_0 (1 - \theta) - (\alpha_0 + \beta_1)C_1 + \alpha_1 C_2 \\ \frac{dC_n}{dt} = \beta_1 C_{n-1} - (\alpha_1 + \beta_1)C_n + \alpha_1 C_{n+1} \end{cases}$$



$$i = 0, 1 L$$

~~Bilan détaillé~~



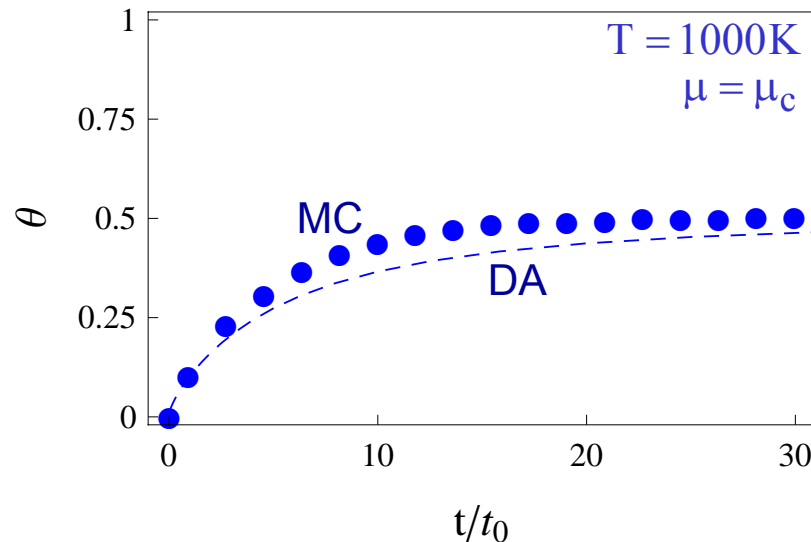
# Place disponible pour les n-mères...

$$\begin{cases} \frac{dC_1}{dt} = \beta_0 \boxed{D_1} (\alpha_0 + \beta_1 \boxed{\frac{D_2}{D_1}}) C_1 + \alpha_1 C_2 \\ \frac{dC_n}{dt} = \beta_1 \boxed{\frac{D_n}{D_{n-1}}} C_{n-1} - (\alpha_1 + \beta_1 \boxed{\frac{D_{n+1}}{D_n}}) C_n + \alpha_1 C_{n+1} \end{cases}$$

$$\begin{cases} D_1 = (1 - \theta) \left( 1 - \frac{C_{tot}}{1 - \theta} \right)^2 \\ \frac{D_{n+1}}{D_n} = \left( 1 - \frac{C_{tot}}{1 - \theta} \right) \end{cases}$$



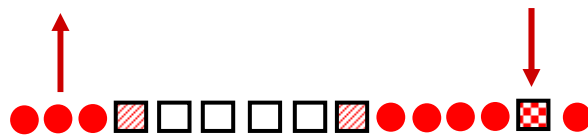
$$\theta = \sum_n n C_n \quad C_{tot} = \sum_n C_n$$



## Bilan détaillé

$$\alpha_{n+1} C_{n+1} = \beta_n \frac{D_{n+1}}{D_n} C_n$$

$$\frac{\alpha_{n+1}}{\beta_n} = \frac{C_n}{D_n} \frac{D_{n+1}}{C_{n+1}} = \exp\left(\frac{\Delta F_{n+1} - \Delta F_n}{kT}\right)$$



$$\Delta = \pm 2 L$$

# $\Delta=2 L$ : fragmentation / coagulation

## désorption 2 L

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

## adsorption 2 L

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

$$\left\{ \begin{array}{l} \beta_i \propto \exp\left(-\frac{E_{\text{ads}} + iV_{\text{AA}} - \tilde{\mu}}{2kT}\right) \\ \alpha_i \propto \exp\left(\frac{E_{\text{ads}} + iV_{\text{AA}} - \tilde{\mu}}{2kT}\right) \end{array} \right.$$

$$i = 0, 1, 2L$$



$$\left\{ \begin{array}{l} \frac{dC_1}{dt} = \beta_0 D_1 - (\alpha_0 + \beta_1 \frac{D_2}{D_1}) C_1 + \alpha_1 C_2 - \left( 2 \frac{C_1}{C_{\text{tot}}} \right) \beta_2 C_1^L + \left( 2 \sum_{j=3} C_j \right) \alpha_2 \end{array} \right.$$

$$\left\{ \begin{array}{l} \frac{dC_n}{dt} = \beta_1 \frac{D_n}{D_{n-1}} C_{n-1} - (\alpha_1 + \beta_1 \frac{D_{n+1}}{D_n}) C_n + \alpha_1 C_{n+1} \\ + \beta_2 C_1^L \left( \sum_{j=1}^{n-2} \frac{C_j C_{n-1-j}}{C_{\text{tot}}^2} - 2 \frac{C_n}{C_{\text{tot}}} \right) + \alpha_2 \left( 2 \sum_{j=n+2} C_j - (n-2) C_n \right) \end{array} \right.$$

$$C_1^L = ???$$

# Yin Yang :

## de la mono-lacune aux amas de lacunes

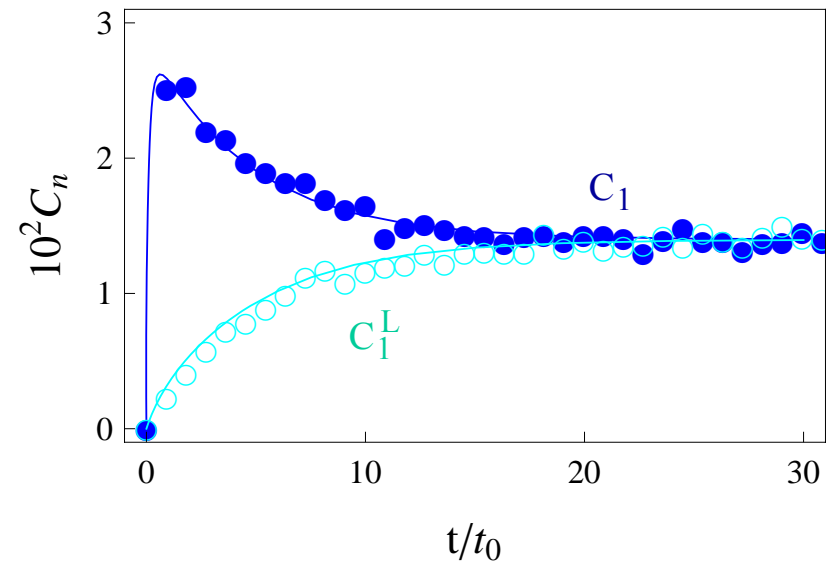
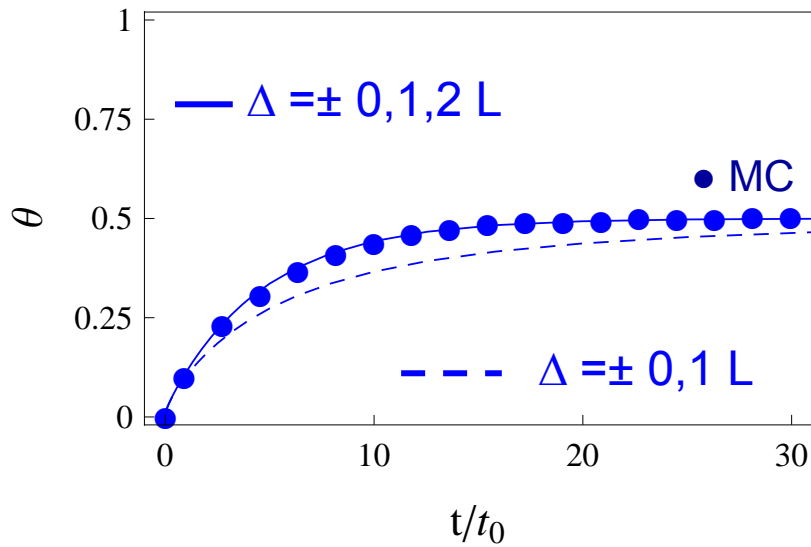
$$\left\{ \begin{aligned} \frac{dC_1}{dt} &= \beta_0 D_1 - \left( \alpha_0 + \beta_1 \frac{D_2}{D_1} \right) C_1 + \alpha_1 C_2 - \left( 2 \frac{C_1}{C_{\text{tot}}} \right) \beta_2 C_1^L + \left( 2 \sum_{j=3} C_j \right) \alpha_2 \\ \frac{dC_n}{dt} &= \beta_1 \frac{D_n}{D_{n-1}} C_{n-1} - \left( \alpha_1 + \beta_1 \frac{D_{n+1}}{D_n} \right) C_n + \alpha_1 C_{n+1} + \beta_2 C_1^L \left( \sum_{j=1}^{n-2} \frac{C_j C_{n-1-j}}{C_{\text{tot}}^2} - 2 \frac{C_n}{C_{\text{tot}}} \right) + \alpha_2 \left( 2 \sum_{j=n+2} C_j - (n-2) C_n \right) \end{aligned} \right.$$

$$\beta_i^L \propto \exp \left( \frac{E_{\text{ads}} + (2-i)V_{\text{AA}} - \tilde{\mu}}{2kT} \right) = \alpha_{2-i}$$

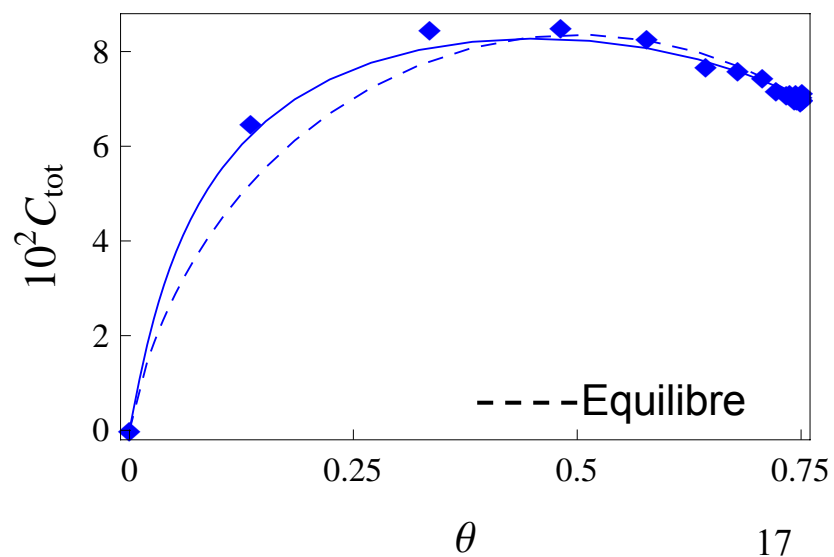
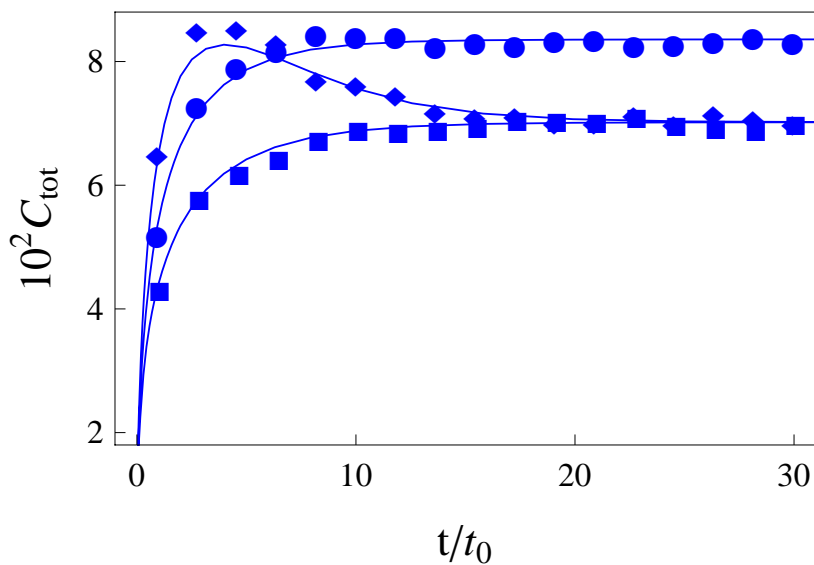
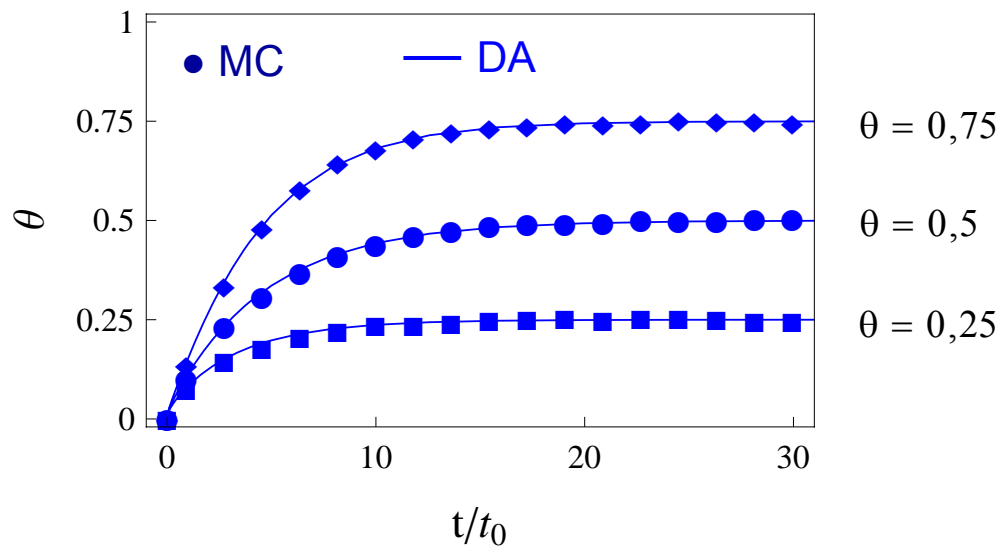
$$\alpha_i^L \propto \exp \left( - \frac{E_{\text{ads}} + (2-i)V_{\text{AA}} - \tilde{\mu}}{2kT} \right) = \beta_{2-i}$$

$$\left\{ \begin{aligned} \frac{dC_1^L}{dt} &= \beta_0^L D_1^L - \left( \alpha_0^L + \beta_1^L \frac{D_2^L}{D_1^L} \right) C_1^L + \alpha_1^L C_2^L - \left( 2 \frac{C_1^L}{C_{\text{tot}}^L} \right) \beta_2^L C_1^L + \left( 2 \sum_{j=3} C_j^L \right) \alpha_2^L \\ \frac{dC_n^L}{dt} &= \beta_1^L \frac{D_n^L}{D_{n-1}^L} C_{n-1}^L - \left( \alpha_1^L + \beta_1^L \frac{D_{n+1}^L}{D_n^L} \right) C_n^L + \alpha_1^L C_{n+1}^L + \beta_2^L C_1^L \left( \sum_{j=1}^{n-2} \frac{C_j^L C_{n-1-j}^L}{C_{\text{tot}}^L{}^2} - 2 \frac{C_n^L}{C_{\text{tot}}^L} \right) + \alpha_2^L \left( 2 \sum_{j=n+2} C_j^L - (n-2) C_n^L \right) \end{aligned} \right.$$

avec :  $\theta^L = 1 - \theta, C_{\text{tot}}^L = C_{\text{tot}}$



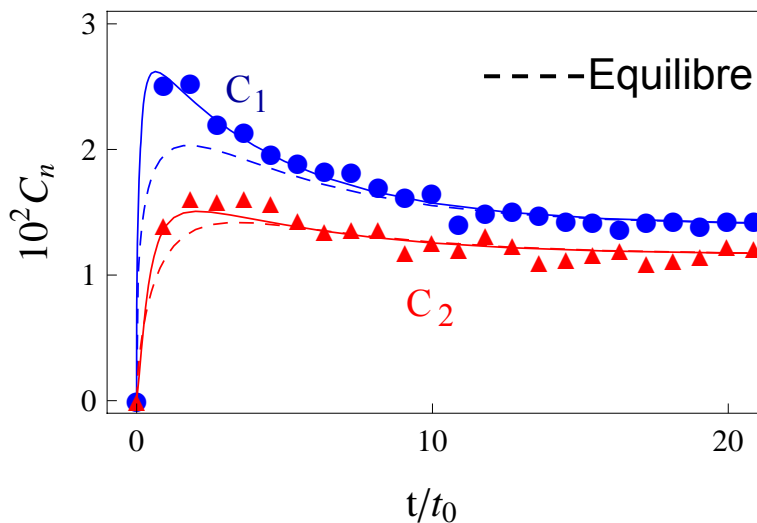
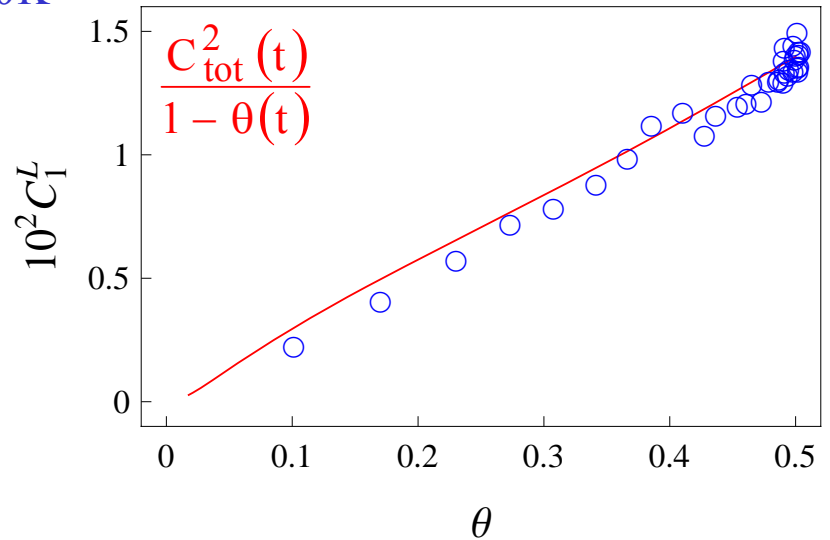
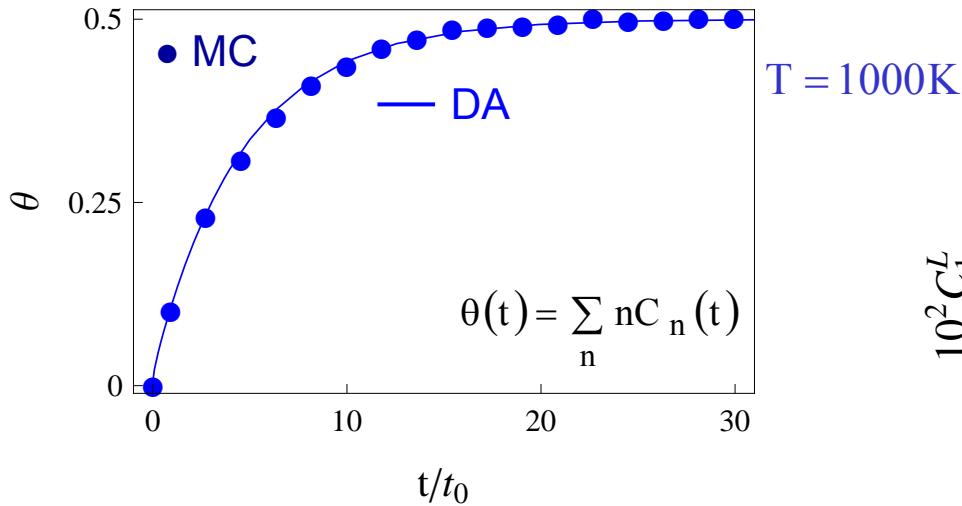




# Retour au Yin avec lacunes

Equilibre :  $C_1^L = \frac{C_{tot}^2}{1 - \theta}$

Cinétique :  $C_1^L(t) = \frac{C_{tot}^2(t)}{1 - \theta(t)}$  ???

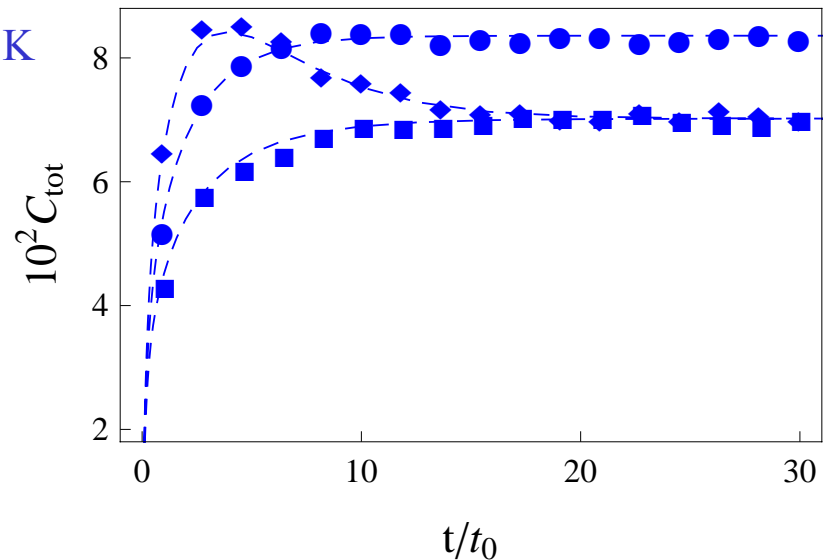
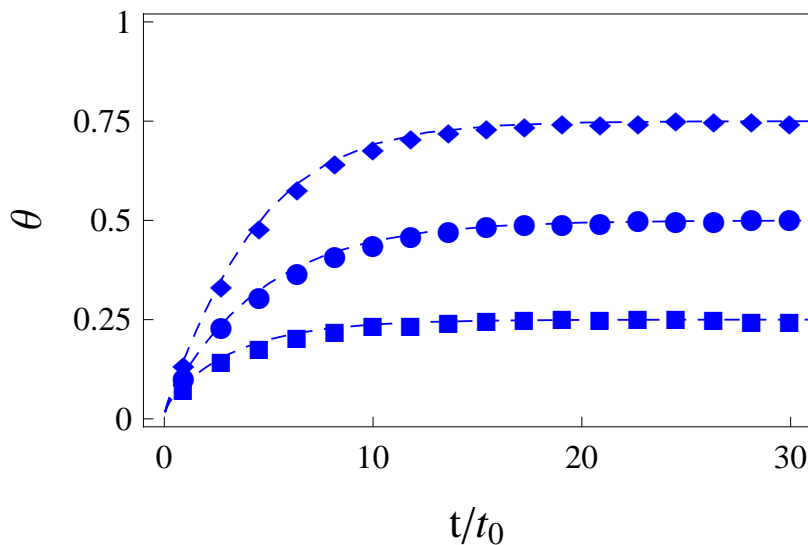


**Caractère nécessaire de 2 variables,  
... suffisant ?**

# D'où la DA à 2 variables

$$\left\{ \begin{array}{l} \frac{d\theta}{dt} = (\beta_0 D_1 - \alpha_0 C_1) + \left( \beta_1 \frac{D_{n+1}}{D_n} - \alpha_1 \frac{D_{n+1}^L}{D_n^L} \right) C_{\text{tot}} + (\beta_2 C_1^L - \alpha_2 D_1^L) \\ \frac{dC_{\text{tot}}}{dt} = (\beta_0 D_1 - \alpha_0 C_1) - (\beta_2 C_1^L - \alpha_2 D_1^L) \end{array} \right. \quad \left\{ \begin{array}{l} C_1 = \frac{C_{\text{tot}}^2}{\theta} \\ C_1^L = \frac{C_{\text{tot}}^2}{1-\theta} \end{array} \right.$$

$$D_1 = (1 - \theta) \left( 1 - \frac{C_{\text{tot}}}{1 - \theta} \right)^2 \quad D_1^L = \theta \left( 1 - \frac{C_{\text{tot}}}{\theta} \right)^2 \quad \frac{D_{n+1}}{D_n} = \left( 1 - \frac{C_{\text{tot}}}{1 - \theta} \right) \quad \frac{D_{n+1}^L}{D_n^L} = \left( 1 - \frac{C_{\text{tot}}}{\theta} \right)$$



# DA $\equiv$ SRO ?

$$P_{AA} = \theta^2 + \sigma \theta (1 - \theta)$$

$$P_{AB} = (1 - \sigma) \theta (1 - \theta)$$

$$P_{BB} = (1 - \theta)^2 + \sigma \theta (1 - \theta)$$

avec :  $P_{AB} = C_{\text{tot}}$

## Equilibre

SRO de paire

$\equiv$

DA ( $\theta$ )

$$P_A = \theta, \quad P_B = 1 - \theta$$

$$\tilde{P}_{AA} = P_{AA} / \theta, \quad \tilde{P}_{AB} = P_{AB} / \theta,$$

$$\tilde{P}_{BA} = P_{BA} / (1 - \theta), \quad \tilde{P}_{BB} = P_{BB} / (1 - \theta)$$

$$\frac{d\theta}{dt} = \left\{ \begin{array}{l} \frac{dP_A}{dt} = (\beta_0 P_B \tilde{P}_{BB}^2 - \alpha_0 P_A \tilde{P}_{AB}^2) + (\beta_2 P_B \tilde{P}_{BA}^2 - \alpha_2 P_A \tilde{P}_{AA}^2) + (\beta_2 P_B \tilde{P}_{BA}^2 - \alpha_2 P_A \tilde{P}_{AA}^2) \end{array} \right.$$

$$\frac{dC_{\text{tot}}}{dt} = \left\{ \begin{array}{l} \frac{dP_{AB}}{dt} = (\beta_0 P_B \tilde{P}_{BB}^2 - \alpha_0 P_A \tilde{P}_{AB}^2) - (\beta_2 P_B \tilde{P}_{BA}^2 - \alpha_2 P_A \tilde{P}_{AA}^2) \end{array} \right.$$

## Cinétique

PPM de paire

$\equiv$

DA ( $\theta, C_{\text{tot}}$ )

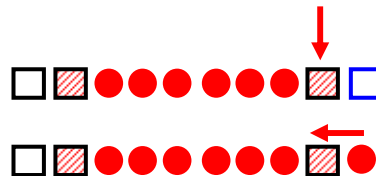
## Approximation de paire exacte à 1D

- ≡ DA ( $\theta, C_{\text{tot}}$ )
- ≡ DA (Yin+Lacunes)
- ≡ DA (Yin Yang)
- ≡ DA (fragmentation/coagulation et recouvrement)
- ≡ Monte Carlo

## Perspectives

### 1D Canonique

- diffusion  $\forall \theta \rightarrow \beta_n$  ???
- concept des  $D_n$  ???



### 2D et 3D

- $D_n$
- coagulation : utilisation des  $D_n$
- fragmentation : nb de sites conduisant à la perte de connexité

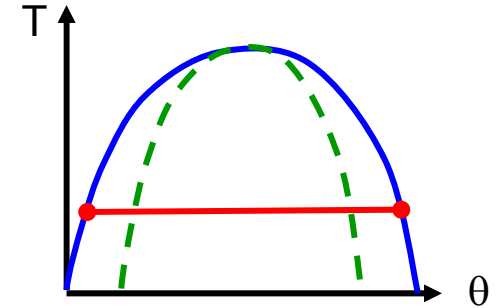
$$2D \quad \Delta F_n = -n\Delta\mu + 4\sqrt{n}\sigma + \sigma'$$

$$\Delta\mu = \mu - \mu_c, \mu_c = ZV_{AA} / 2$$

$$1D \quad \Delta F_n = -n\Delta\mu + \sigma' \quad \sigma' = -V_{AA}$$

$$2D \quad \frac{\alpha_{n+1}}{\beta_n} = \frac{C_n}{D_n} \frac{D_{n+1}}{C_{n+1}} = \exp\left(\frac{\Delta F_{n+1} - \Delta F_n}{kT}\right)$$

$$\frac{\alpha_{n+1}}{\beta_n} = \exp\left(\frac{4(\sqrt{n+1} - \sqrt{n})\sigma}{kT}\right) \exp\left(-\frac{\Delta\mu}{kT}\right)$$



$$1D \quad \frac{\alpha_{n+1}}{\beta_n} = \frac{C_n}{D_n} \frac{D_{n+1}}{C_{n+1}} = \exp\left(\frac{\Delta F_{n+1} - \Delta F_n}{kT}\right)$$

$$\frac{\alpha_{n+1}}{\beta_n} = \exp\left(-\frac{\Delta\mu}{kT}\right)$$

$$\left. \begin{array}{l} \beta_n \propto \exp\left(-\frac{V_{AA} - \mu}{2kT}\right) \\ \alpha_n \propto \exp\left(\frac{V_{AA} - \mu}{2kT}\right) \end{array} \right\} \frac{\alpha_{n+1}}{\beta_n} = \exp\left(-\frac{\mu - V_{AA}}{kT}\right) = \exp\left(-\frac{\Delta\mu}{kT}\right)$$