Paradoxes et apport de la DA à 1D

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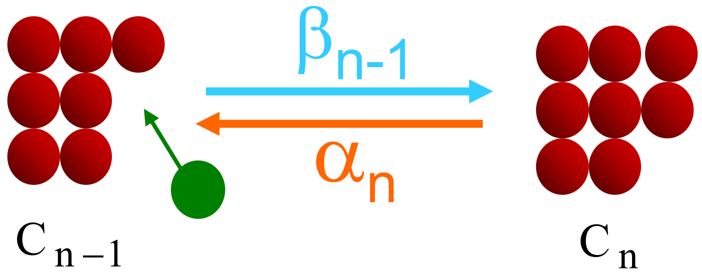
GDR TransDiff 16-17 Juin 2009

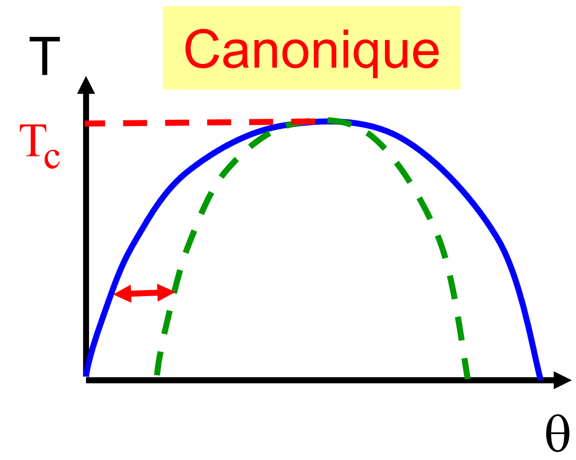
Contexte

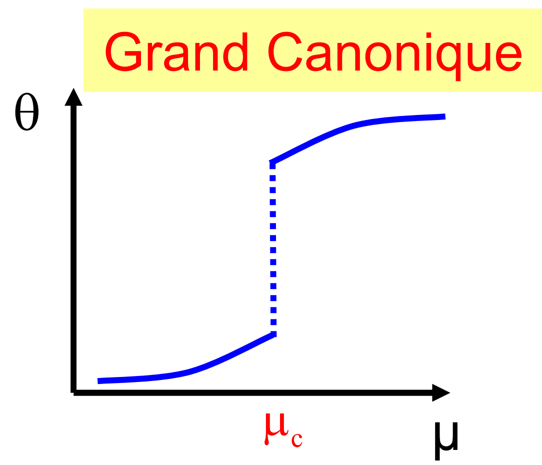


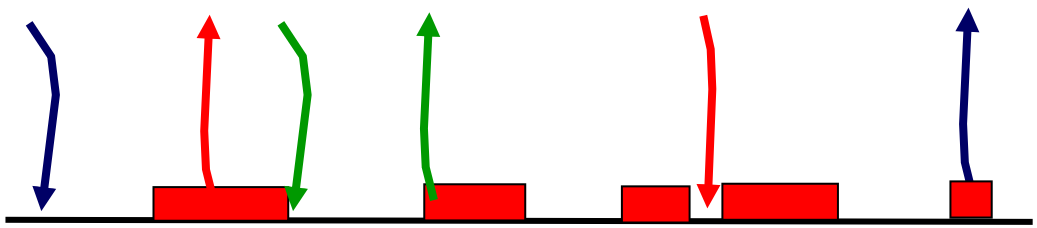
$$\frac{dc_n}{dt} = \beta_{n-1}c_{n-1} - (\alpha_n + \beta_n)c_n + \alpha_{n+1}c_{n+1}$$

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

diffusion, monomères







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

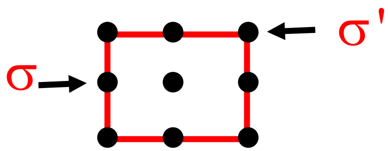
processus local

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

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

1D Grand Canonique !!

Grand Canonique

Pas de problèmes liés à la diffusion

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

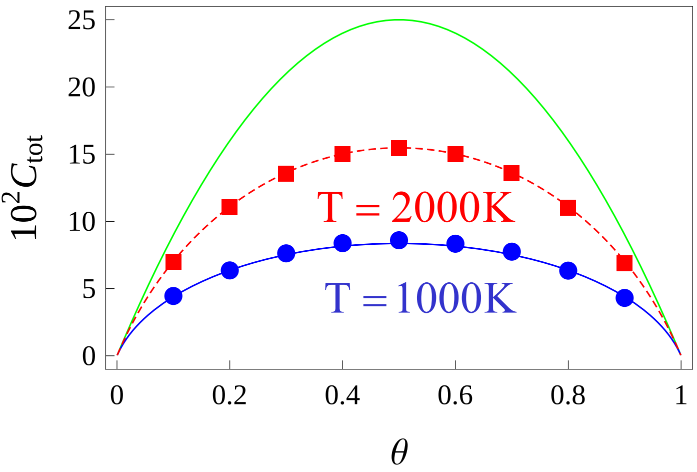
1D

- $T_c = 0 \Rightarrow$ 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)

$\theta = 0.25, T = 100$ K

$\theta = 0.25, T = 3000$ K

Equilibre d'amas 1D: Ising (V_{AA}, θ, T)



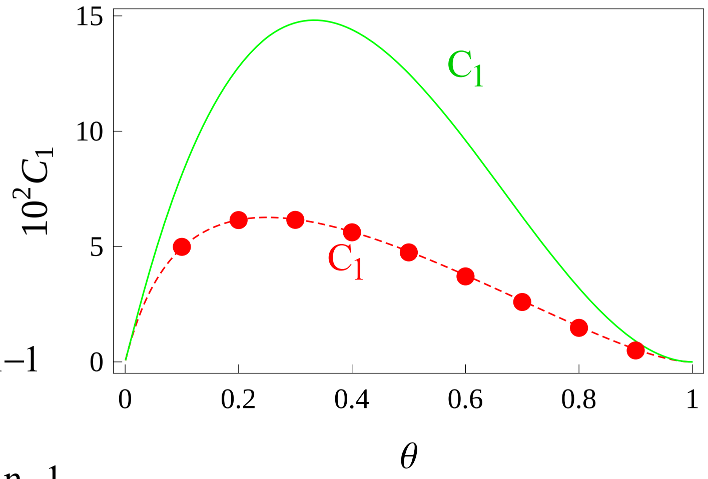
$$C_{tot} = \theta(1-\theta)$$

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

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

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

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

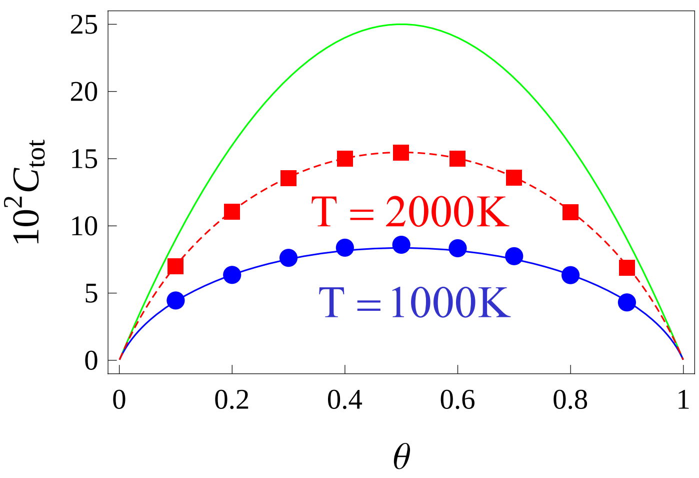


■■■ MC

—— Yilmaz

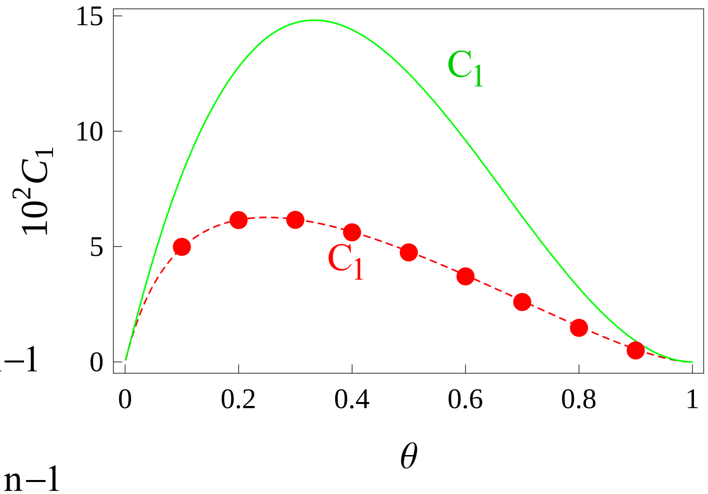
$V_{AA} = -277 \text{meV}$

Equilibre d'amas 1D: Ising (V_{AA}, θ, T)



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

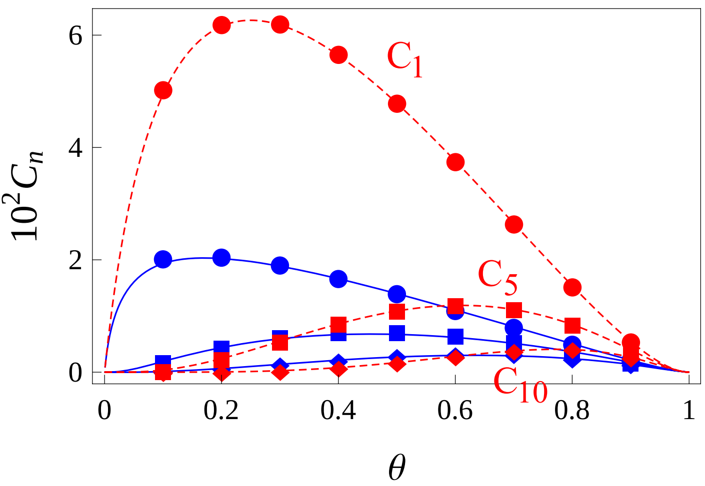
$$C_n = \theta^n (1-\theta)^2$$



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

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

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



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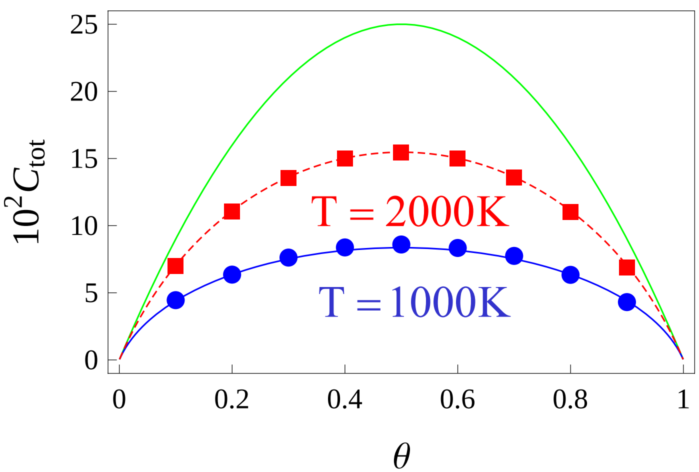
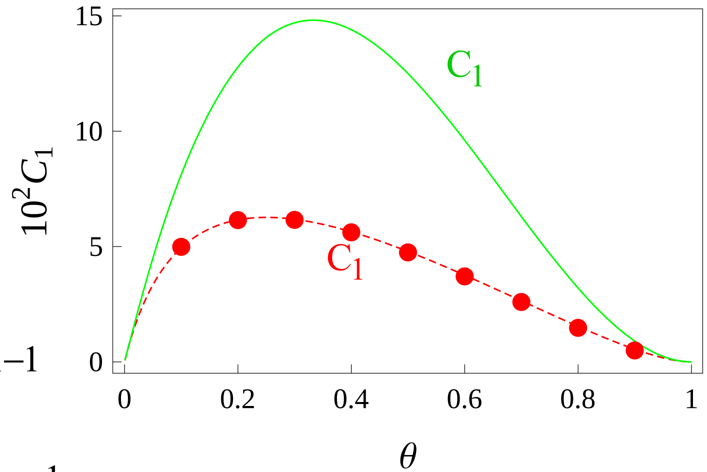
Equilibre d'amas 1D: Ising (V_{AA}, θ, T)



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

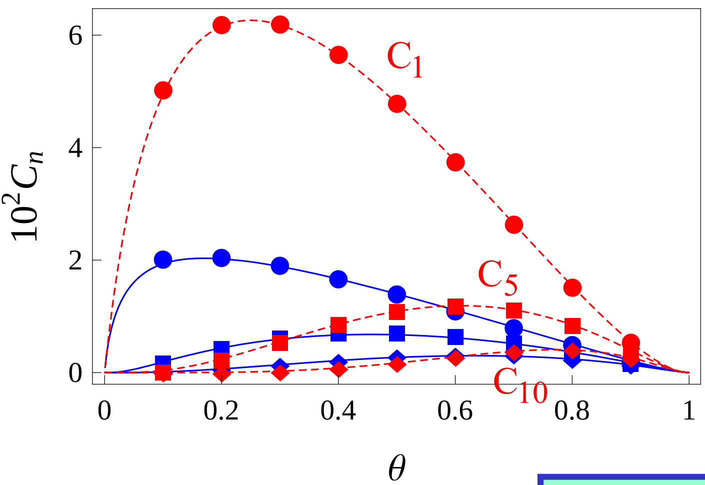
$$C_n = \theta^n (1-\theta)^2$$



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

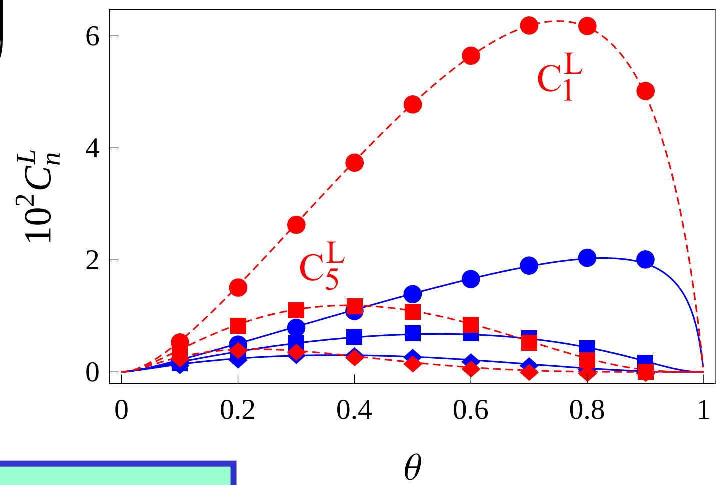
$$C_n = \frac{C_{tot}^2}{\theta}\left(1-\frac{C_{tot}}{\theta}\right)^{n-1}$$

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



■■■ MC

—— Yilmaz

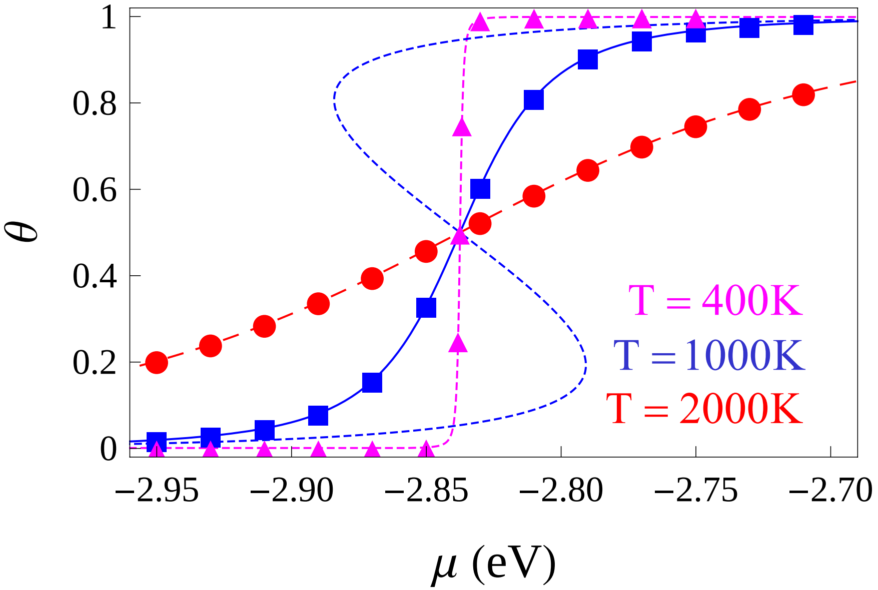


$V_{AA} = -277 \text{meV}$

Thermo exacte en DA :

- **∀ θ**
- **dans l'état désordonné**

Isotherme 1D



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

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

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

Équilibre
Gd Canonique = Canonique

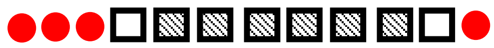
Distribution d'équilibre

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

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

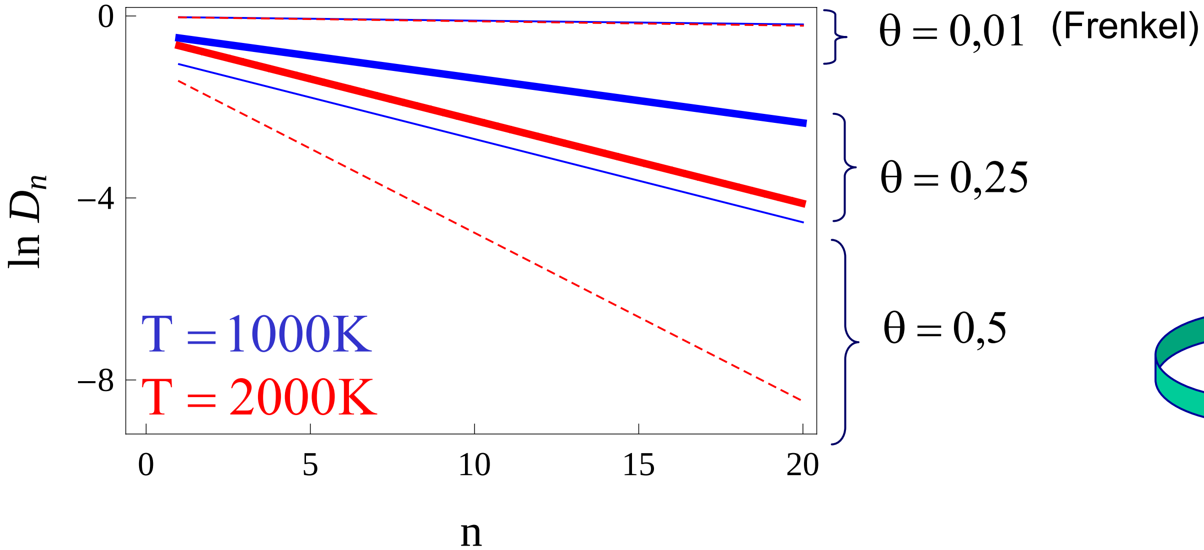
$D_n = ?$

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



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

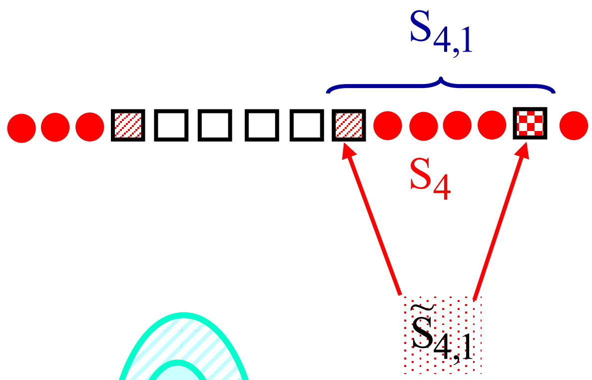
$$D_n = \sum_{j>n+1} (j-(n+1)) C_j^L$$



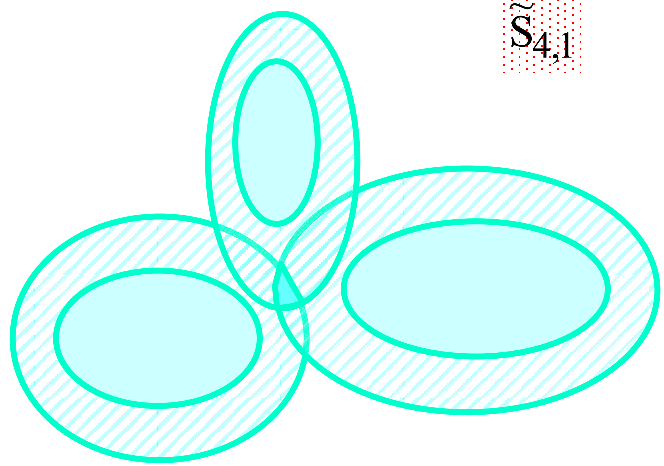
$$D_n = (1-\theta)\left(1 - \sum_k \frac{C_k}{1-\theta}\right)^{n+1}$$

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

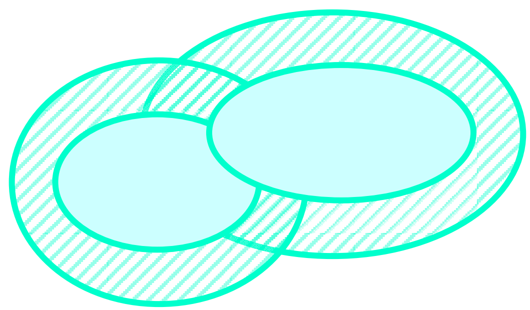
à 1D : $D_n = (1-\theta)\left(1-\sum_k \frac{C_k}{1-\theta}\right)^{\tilde{S}_{k,n}}$ $\tilde{S}_{k,n} = S_{k,n} - S_k = n+1$



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

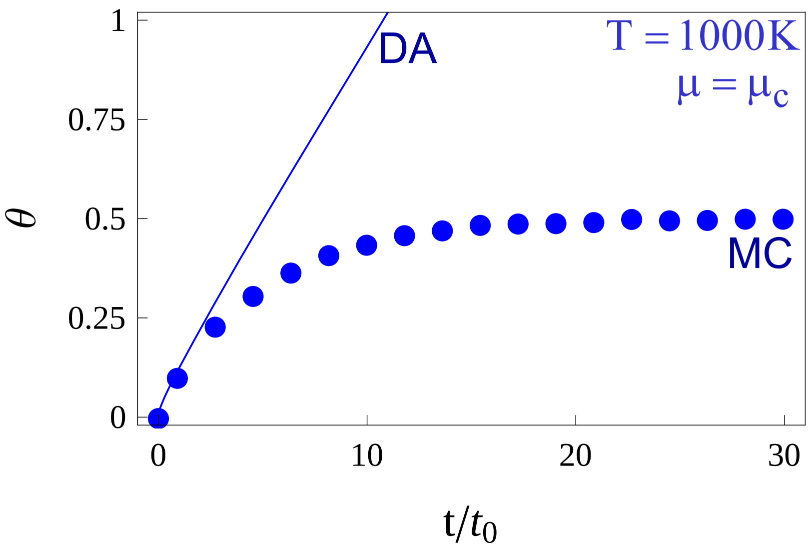


de la DA…à la DA

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

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

$$\theta = \sum_n nC_n$$



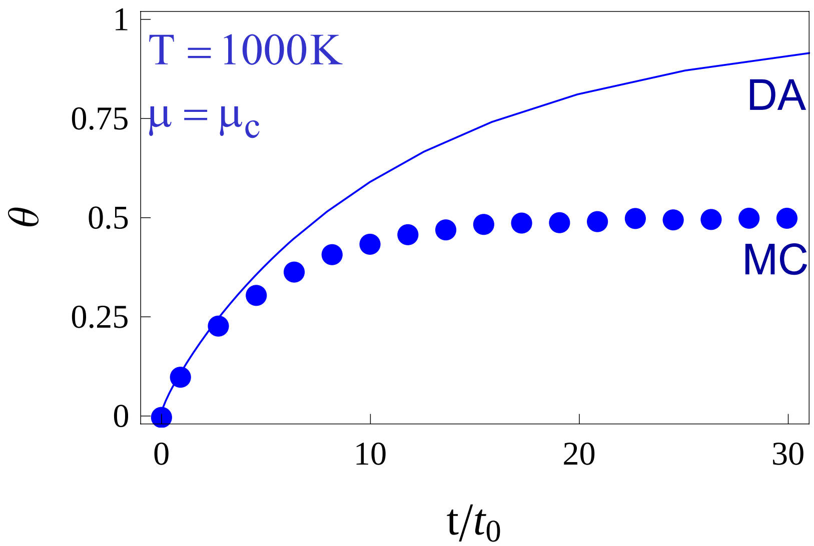
$i = 0{,}1$ L

~~Bilan détaillé~~

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

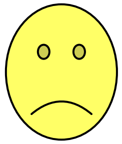
Place disponible pour les monomères…

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



$i = 0{,}1\ L$

~~Bilan détaillé~~

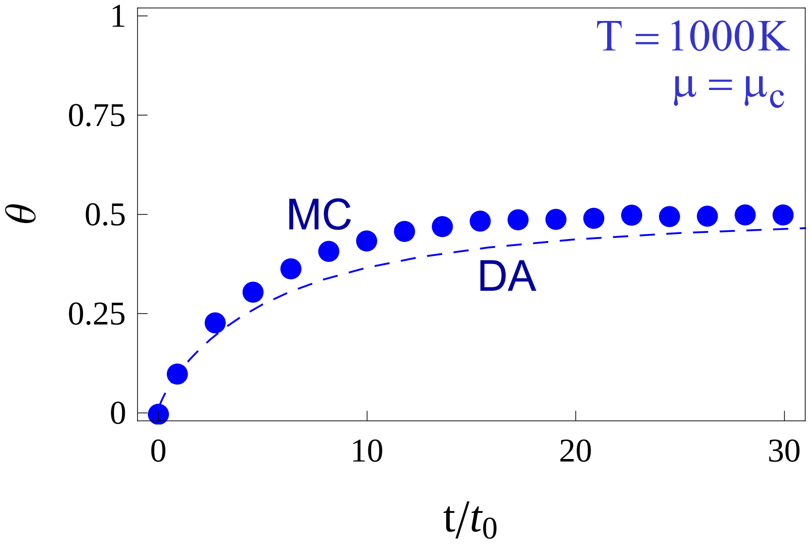


Place disponible pour les n-mères…

$$\begin{cases} \dfrac{dC_1}{dt} = \beta_0 \boxed{D_1} - \left(\alpha_0 + \beta_1 \boxed{\dfrac{D_2}{D_1}}\right) C_1 + \alpha_1 C_2 \\[2ex] \dfrac{dC_n}{dt} = \beta_1 \boxed{\dfrac{D_n}{D_{n-1}}} C_{n-1} - \left(\alpha_1 + \beta_1 \boxed{\dfrac{D_{n+1}}{D_n}}\right) C_n + \alpha_1 C_{n+1} \end{cases}$$

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

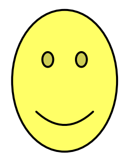
$$\theta = \sum_n n C_n \qquad C_{tot} = \sum_n C_n$$

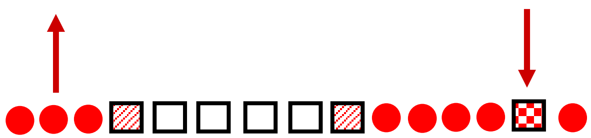


Bilan détaillé

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

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





$\Delta = \pm 2$ L

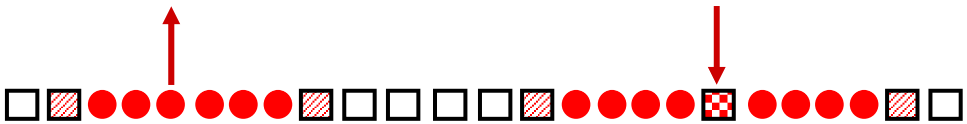
Δ=2 L : fragmentation / coagulation

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

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

$i = 0,1,2\ L$



$$\begin{cases} \dfrac{dC_1}{dt} = \beta_0 D_1 - (\alpha_0 + \beta_1 \dfrac{D_2}{D_1})C_1 + \alpha_1 C_2 - \left(2\dfrac{C_1}{C_{tot}}\right)\beta_2 C_1^L + \left(2\sum_{j=3} C_j\right)\alpha_2 \\[3ex] \dfrac{dC_n}{dt} = \beta_1 \dfrac{D_n}{D_{n-1}} C_{n-1} - (\alpha_1 + \beta_1 \dfrac{D_{n+1}}{D_n})C_n + \alpha_1 C_{n+1} \\ \qquad + \beta_2 C_1^L \left(\sum_{j=1}^{n-2} \dfrac{C_j C_{n-1-j}}{C_{tot}^2} - 2\dfrac{C_n}{C_{tot}}\right) + \alpha_2 \left(2\sum_{j=n+2} C_j - (n-2)C_n\right) \end{cases}$$

$C_1^L = ???$

Yin Yang : de la mono-lacune aux amas de lacunes

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

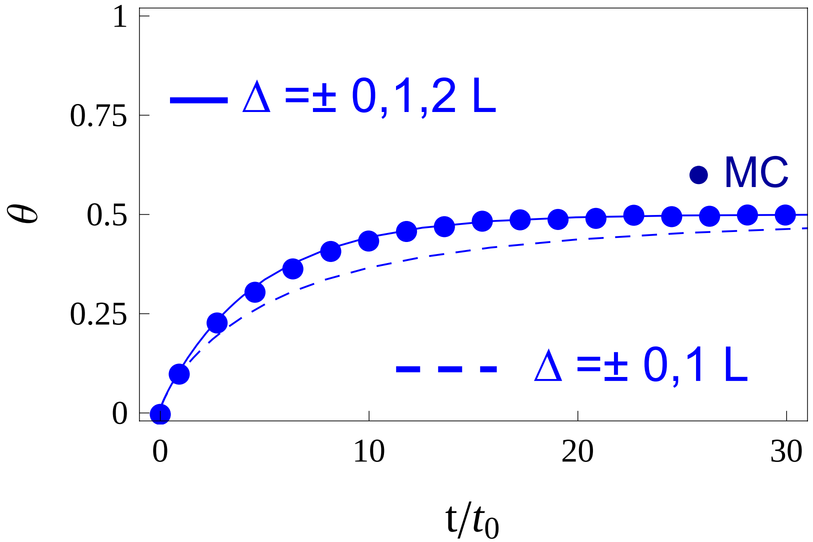
$$\beta_i^L \propto \exp\left(\frac{E_{ads} + (2-i)V_{AA} - \tilde{\mu}}{2kT}\right) = \alpha_{2-i} \qquad \alpha_i^L \propto \exp\left(-\frac{E_{ads} + (2-i)V_{AA} - \tilde{\mu}}{2kT}\right) = \beta_{2-i}$$

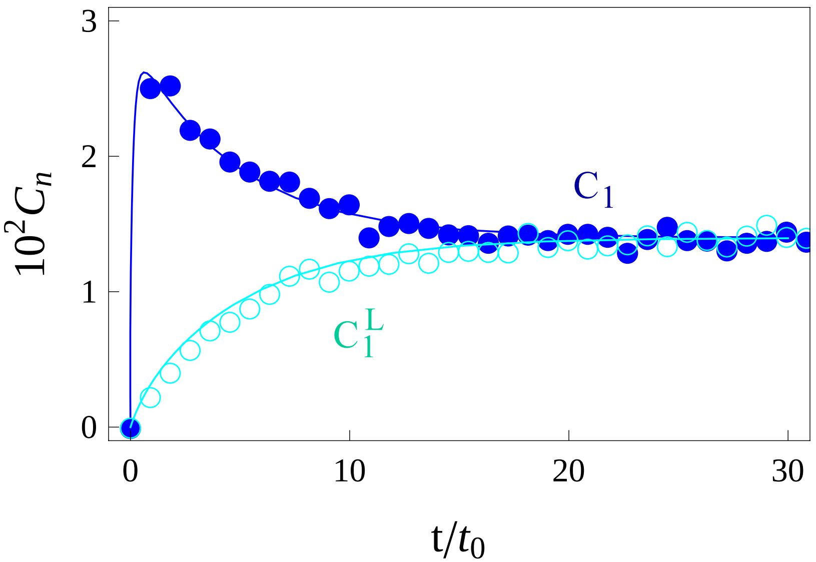
$$\begin{cases} \dfrac{dC_1^L}{dt} = \beta_0^L D_1^L - (\alpha_0^L + \beta_1^L \dfrac{D_2^L}{D_1^L})C_1^L + \alpha_1^L C_2^L - \left(2\dfrac{C_1^L}{C_{tot}^L}\right)\beta_2^L C_1 + \left(2\sum_{j=3} C_j^L\right)\alpha_2^L \\ \dfrac{dC_n^L}{dt} = \beta_1^L \dfrac{D_n^L}{D_{n-1}^L} C_{n-1}^L - (\alpha_1^L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

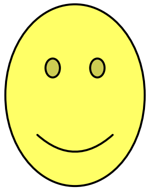
avec : $\theta^L = 1 - \theta, C_{tot}^L = C_{tot}$

DA avec D_n, condensation et fragmentation

$T = 1000K$

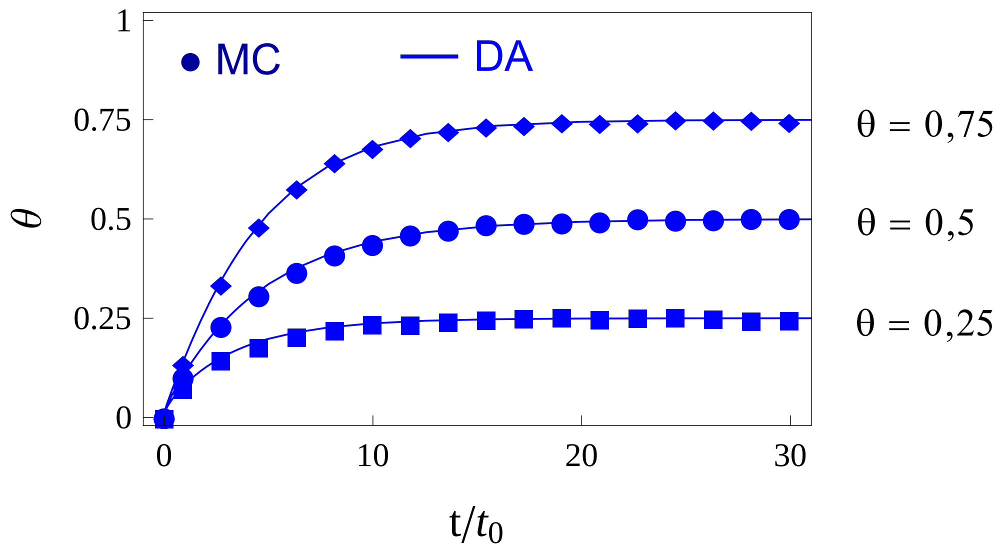


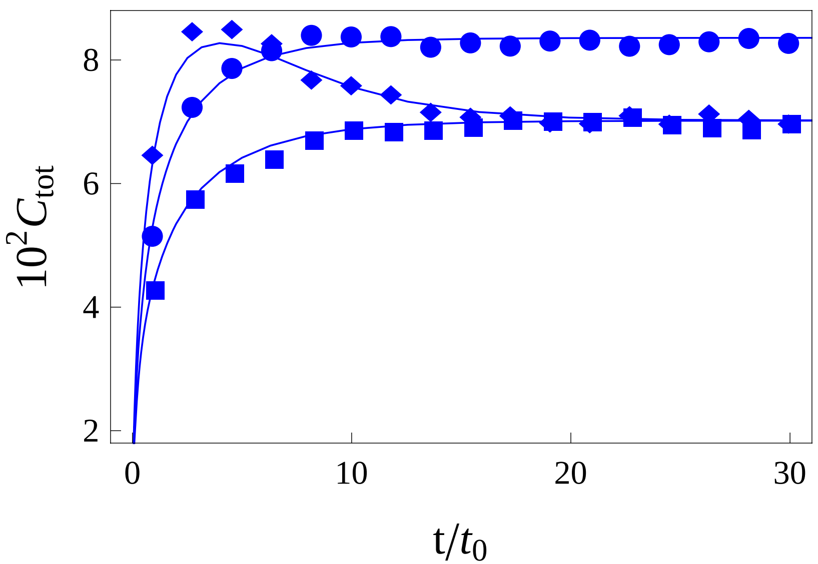


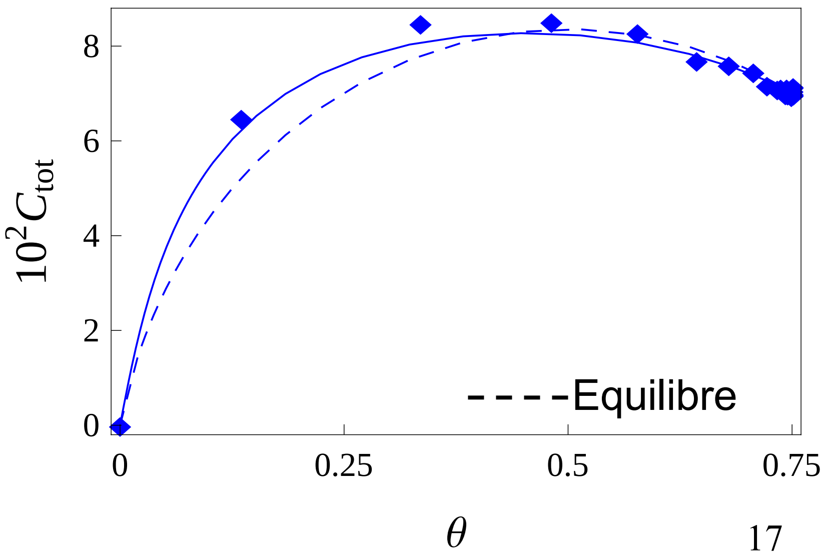


DA avec D_n, condensation et fragmentation

T = 1000K



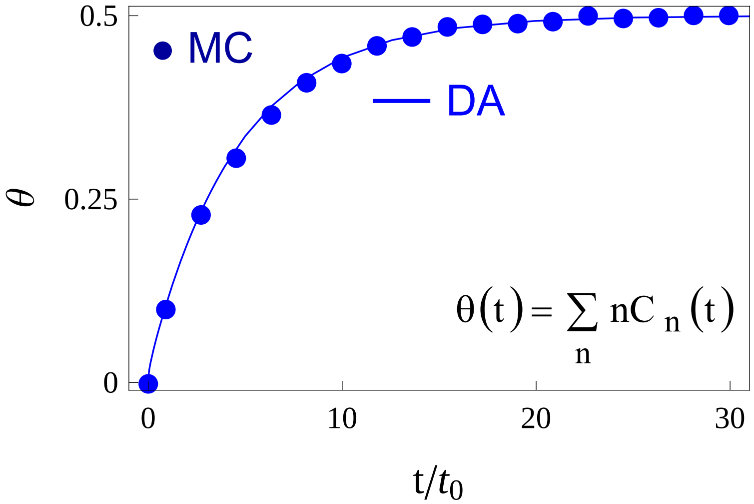




Retour au Yin avec lacunes

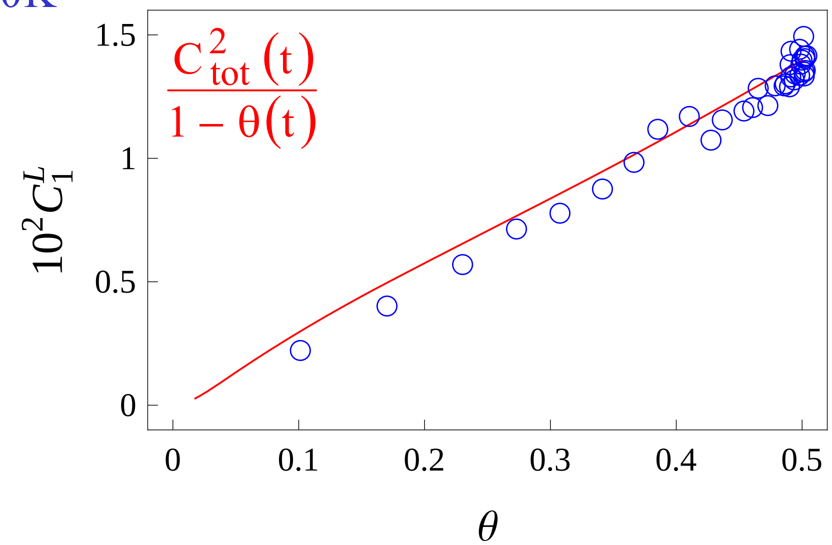
Equilibre : $C_1^L = \dfrac{C_{tot}^2}{1-\theta}$

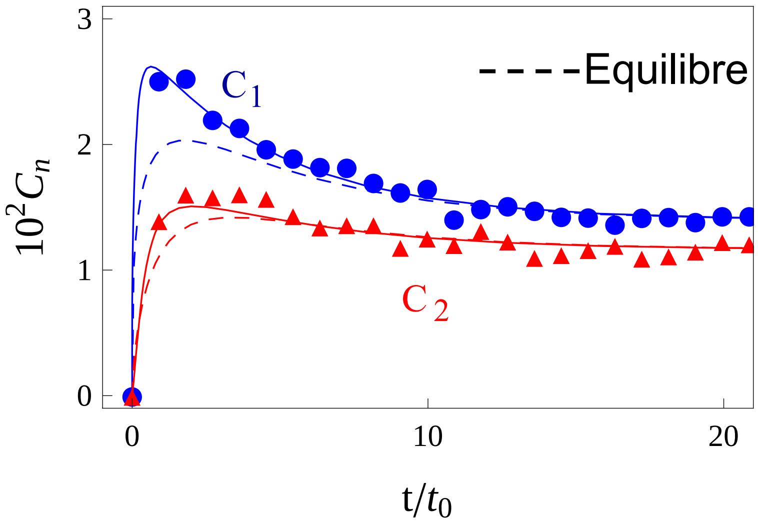
Cinétique : $C_1^L(t) = \dfrac{C_{tot}^2(t)}{1-\theta(t)}$???



$T = 1000K$

$C_{tot}(t) = \sum_n C_n(t)$





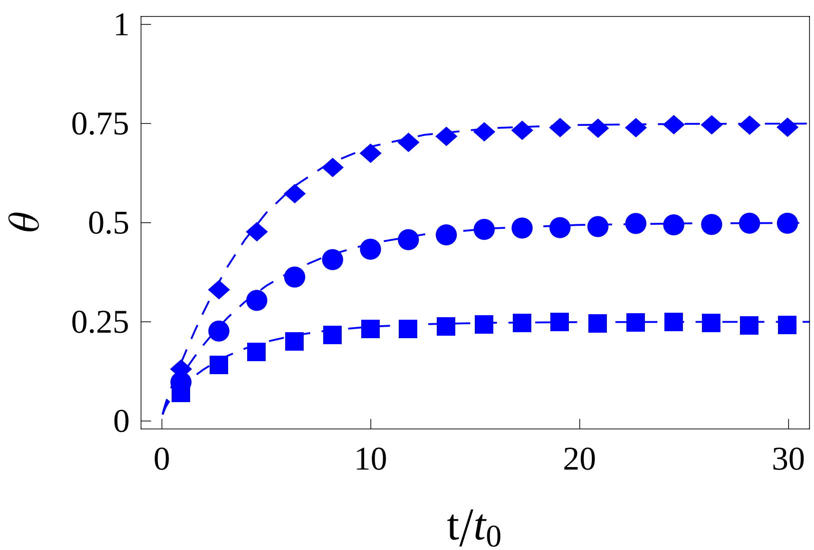
Caractère nécessaire de 2 variables,
… suffisant ?

D’où la DA à 2 variables

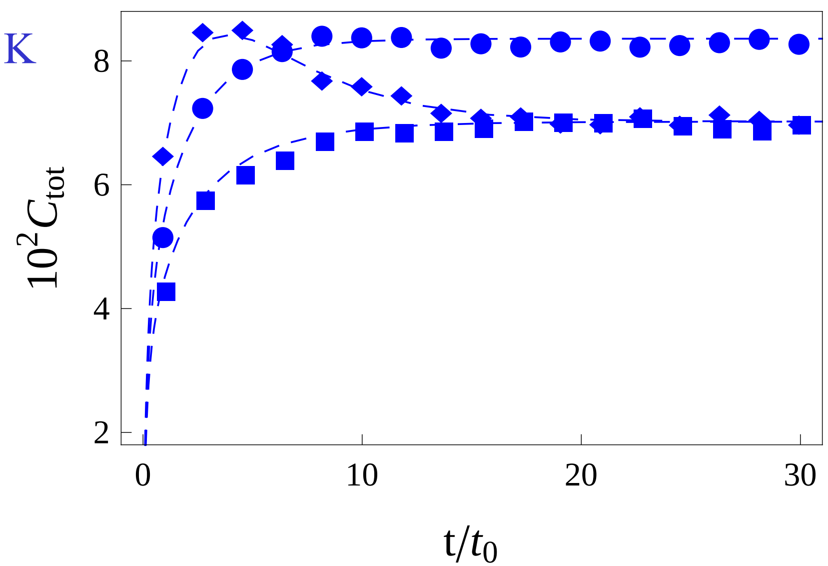
$$\begin{cases} \dfrac{d\theta}{dt} = (\beta_0 D_1 - \alpha_0 C_1) + \left(\beta_1 \dfrac{D_{n+1}}{D_n} - \alpha_1 \dfrac{D^L_{n+1}}{D^L_n}\right) C_{tot} + \left(\beta_2 C^L_1 - \alpha_2 D^L_1\right) \\ \dfrac{dC_{tot}}{dt} = (\beta_0 D_1 - \alpha_0 C_1) - \left(\beta_2 C^L_1 - \alpha_2 D^L_1\right) \end{cases}$$

$$\begin{cases} C_1 = \dfrac{C_{tot}^{\;2}}{\theta} \\ C^L_1 = \dfrac{C_{tot}^{\;2}}{1-\theta} \end{cases}$$

$$D_1 = (1-\theta)\left(1 - \frac{C_{tot}}{1-\theta}\right)^2 \quad D^L_1 = \theta\left(1 - \frac{C_{tot}}{\theta}\right)^2 \quad \frac{D_{n+1}}{D_n} = \left(1 - \frac{C_{tot}}{1-\theta}\right) \quad \frac{D^L_{n+1}}{D^L_n} = \left(1 - \frac{C_{tot}}{\theta}\right)$$



T = 1000K



DA ≡ 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 : $P_{AB} = C_{tot}$

Equilibre

SRO de paire
≡
DA (θ)

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

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

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

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

Cinétique

PPM de paire
≡
DA (θ, C_{tot})

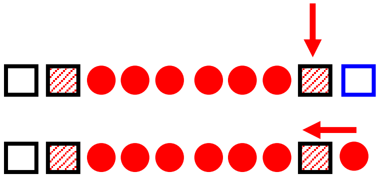
Approximation de paire exacte à 1D

- ≡ DA (θ, C_{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

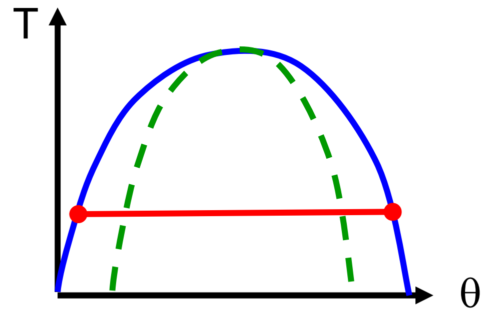
- D_n
- coagulation : utilisation des D_n
- fragmentation : nb de sites conduisant à la perte de connexité

2D $\Delta F_n = -n\Delta\mu + 4\sqrt{n}\,\sigma + \sigma'$ $\Delta\mu = \mu - \mu_c, \mu_c = ZV_{AA}/2$

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

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

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



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

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

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