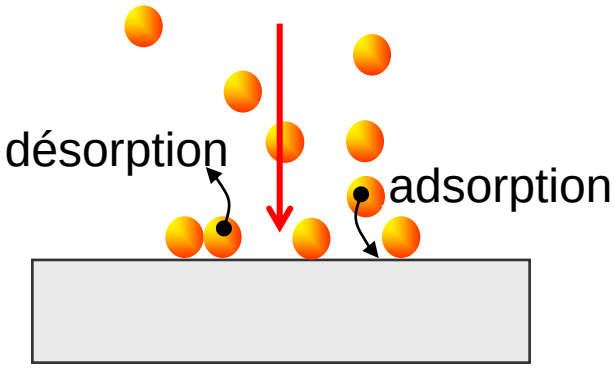
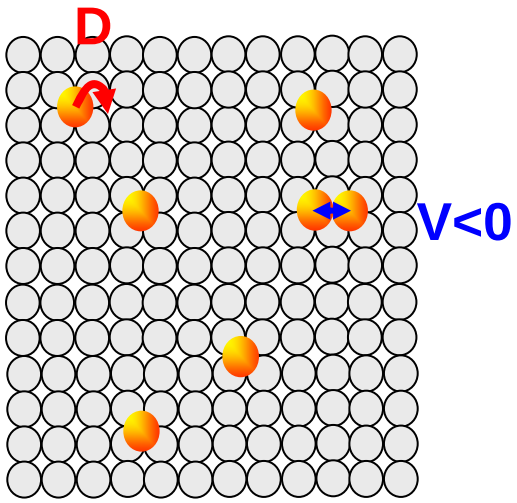
Dynamique d'amas et amas dynamiques

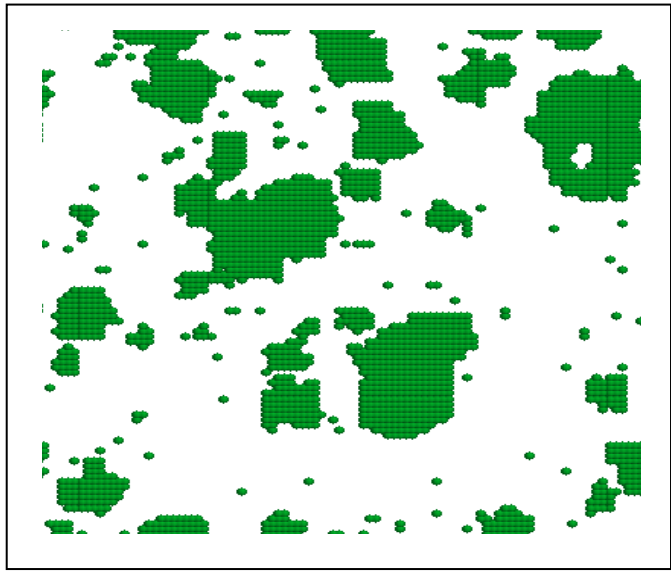
Isabelle, Émile, Fabienne, Bernard



Dépôt



Vieillissement



Ag/Cu (001)

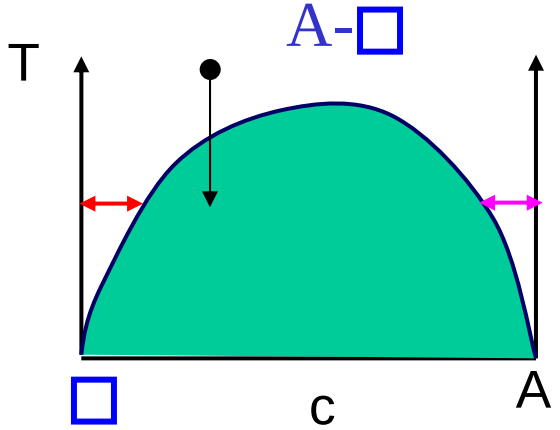
Problématique

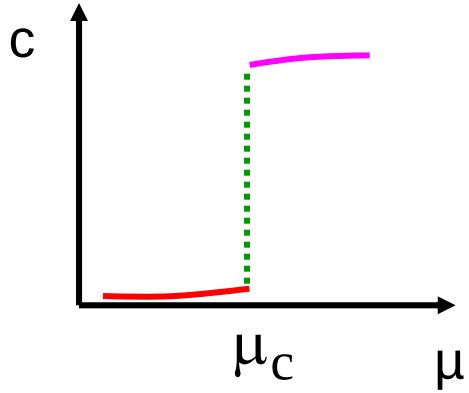
- ✓ Thermodynamique des agrégats purs
  - Energie libre des agrégats
  - Energie libre de surface des agrégats

- ✓ Agrégats au coeur des lacunes …
  Lacunes au coeur des agrégats !

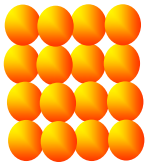
- ✓ Agrégats bimétalliques

Energie libre de formation des agrégats





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



$$\Delta F_n = F_n - n\mu$$

$$F_n = n\underbrace{\left(E_{ads} + ZV_{AA}/2\right)}_{\mu_c} + 4\left(\sqrt{n} - 2\right)\sigma_{côté} + 4\sigma_{sommet}$$

$$\sigma = \sigma_{côté} \qquad \sigma' = 4\sigma_{sommet} - 8\sigma_{côté}$$

$$\Delta\mu = \mu - \mu_c$$

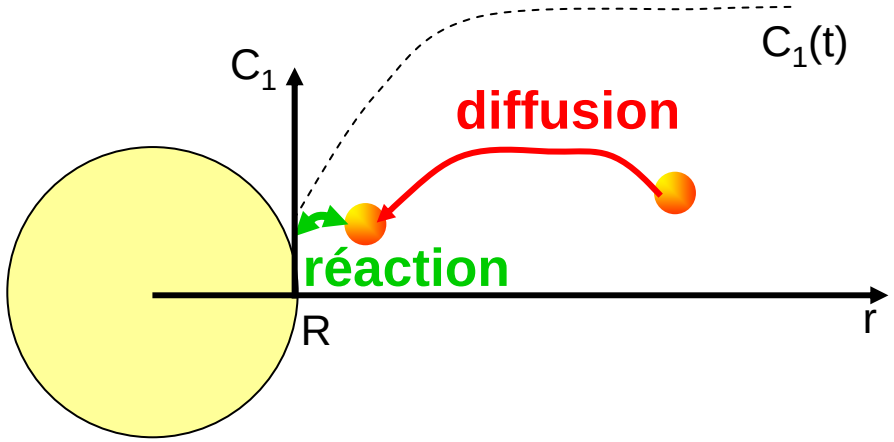
$$\Delta F_n = -n\Delta\mu + 4\sqrt{n}\,\sigma + \sigma'$$

Cinétique de précipitation

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

$D_n = 1$

$\beta_n, \alpha_n = ?$



$C_I = 0$

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

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

Energie libre de surface des agrégats

$\beta_n = k_n C_1$ Diffusion, indépendant de la thermo

état stationnaire ⇔ état d'équilibre

$$\frac{dC_n}{dt} = 0 \Rightarrow C_{n+1}\alpha_{n+1} = C_n\beta_n$$

$D_n = 1$

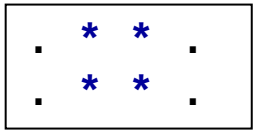
$$\alpha_{n+1} = \beta_n \exp\left(-\frac{\Delta F_{n+1} - \Delta F_n}{kT}\right) = k_n C_1 \exp\left(\frac{4\sigma\left(\sqrt{n+1} - \sqrt{n}\right) - \Delta\mu}{kT}\right)$$

nécessite la connaissance de ΔF_n ou de ♦

Petits agrégats…

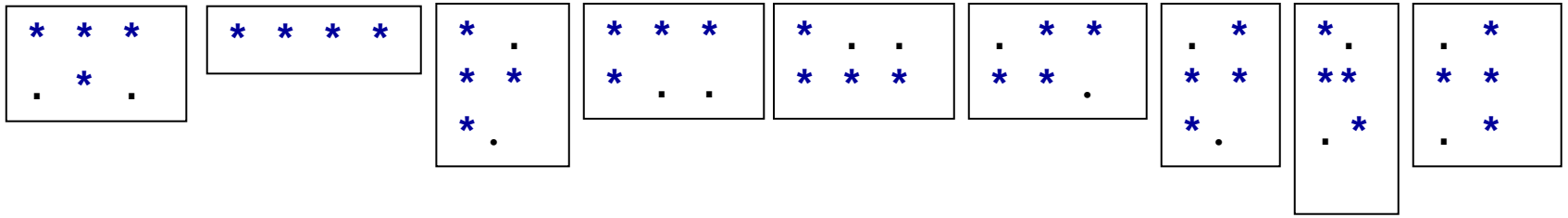
$$F_n = -kT \ln\left(\sum_p g_n^p e^{-E_n^p / kT} \right)$$

p = 0



$$E_4^0 = 4E_{ads} + 4V_{AA}, \quad g_4^0 = 1$$

p = 1



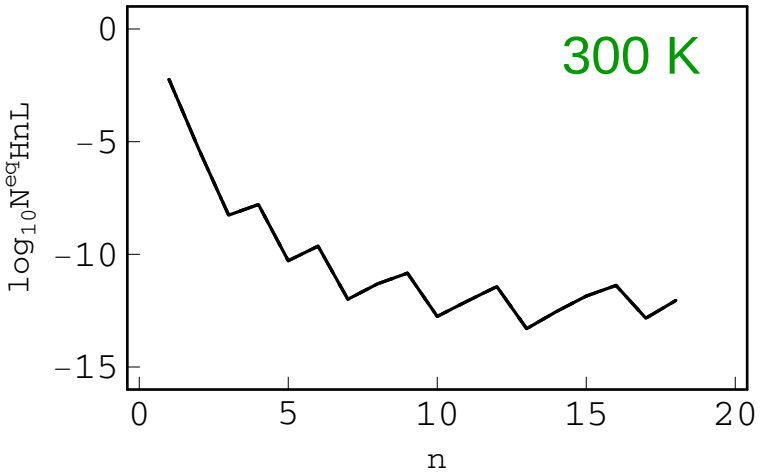
$$E_4^1 = 4E_{ads} + 3V_{AA},$$

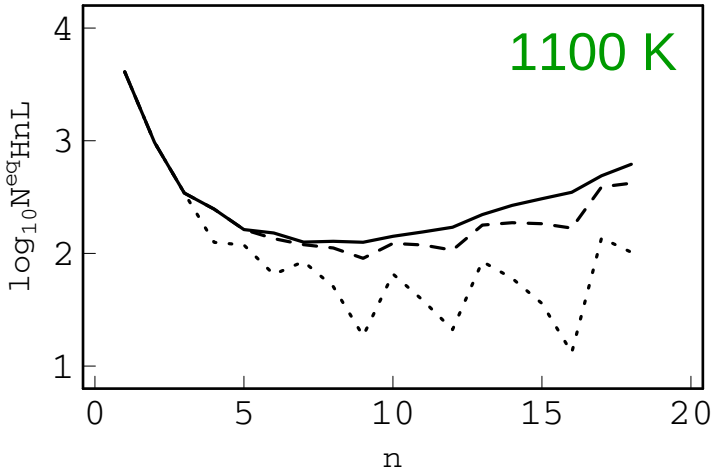
$$g_4^1 = 18$$

$$g_{21}^{12} = 25\ 424\ 079\ 339\ !!!$$

Pour les petites tailles détermination exacte de ΔF_n

Compétition énergie / entropie



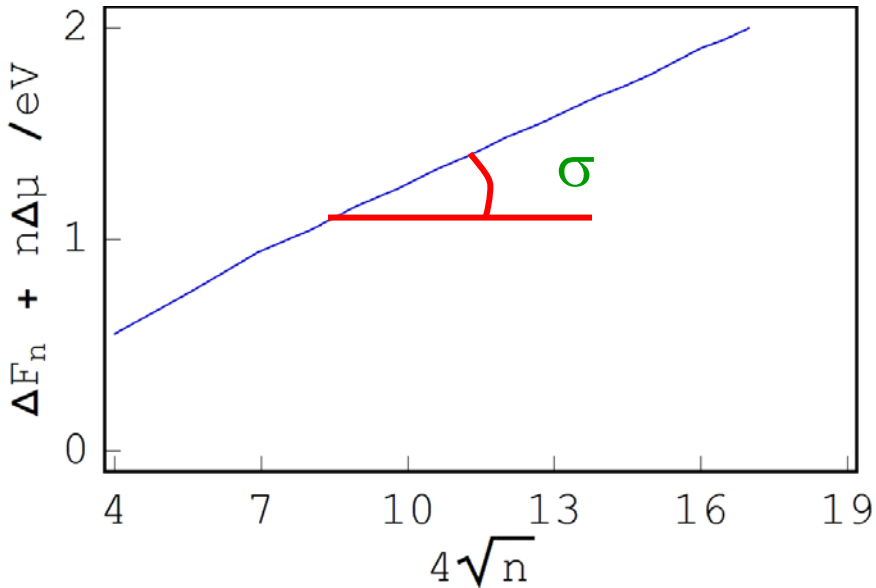


Nombres magiques

Détermination de σ

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

$$\Delta F_n = -n\Delta\mu + 4\sqrt{n}\,\sigma + \sigma'$$

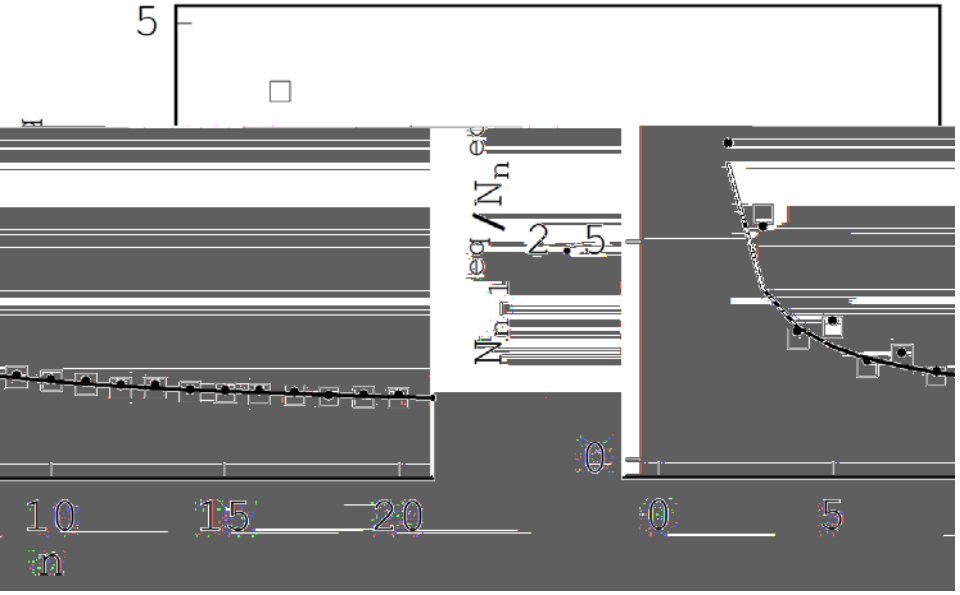


Energie libre de surface des agrégats

$$\beta_n \propto \sum_i N_n^{iL,ads} \exp\left(-\frac{iV_{AA}}{2kT}\right)$$

$$\alpha_n \propto \sum_i N_n^{iL,des} \exp\left(\frac{iV_{AA}}{2kT}\right)$$

Vérification du bilan détaillé



détermination de σ :

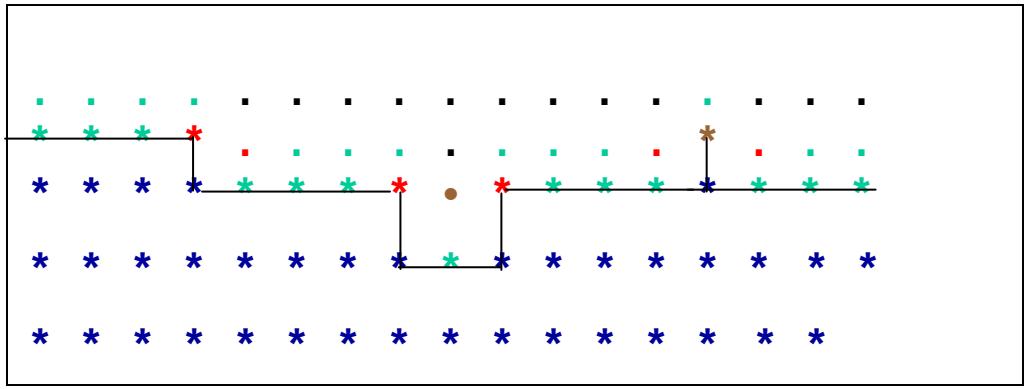
$$\sigma = -\frac{V_{AA}}{8\left(\sqrt{n+1}-\sqrt{n}\right)} + \frac{kT}{4\left(\sqrt{n+1}-\sqrt{n}\right)} \ln\left[\frac{\sum_{i=1}^{Z-1} N_n^{iL,des} \exp\left(\frac{i\,V_{AA}}{2kT}\right)}{\sum_{i=1}^{Z-1} N_{n-1}^{iL,ads} \exp\left(-\frac{i\,V_{AA}}{2kT}\right)}\right]$$

$$\left(N_n^{iL,ads}, N_n^{iL,des}\right) = ???$$

Champ moyen de lisière

1L désorption : *
2L désorption : *
3L désorption : *

1L adsorption : .
2L adsorption : .
3L adsorption : •



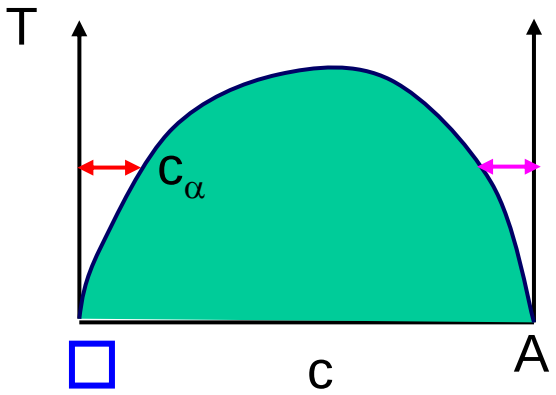
$$N^{3L,ads} = N^{1L,des}, N^{2L,ads} = N^{2L,des}, N^{1L,ads} = N^{3L,des}$$

$$\frac{\partial F}{\partial N^{iL,des}} = 0 \qquad N_n^{2L,des} = 4\sqrt{n}\,\frac{r}{1+r+r^2/2} \qquad r = 2\exp\left(\frac{V_{AA}}{2kT}\right)$$

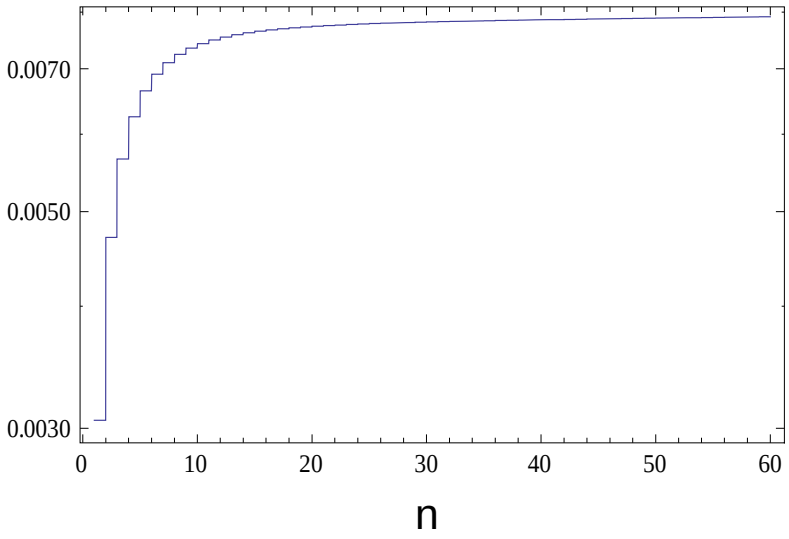
$$\sigma = -\frac{V_{AA}}{2} - kT\ln(1+r+r^2/2)$$

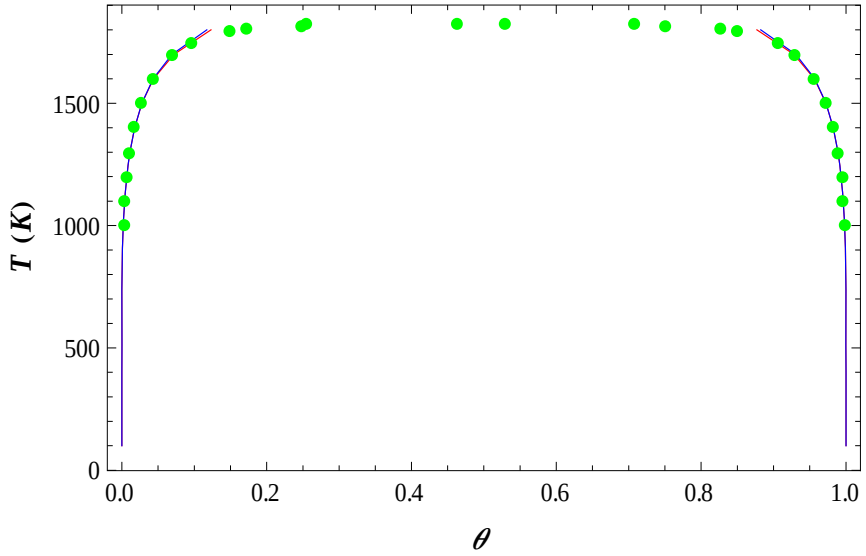
Bon accord entre toutes les différentes valeurs de σ obtenues

Liens entre σ et le diagramme de phases

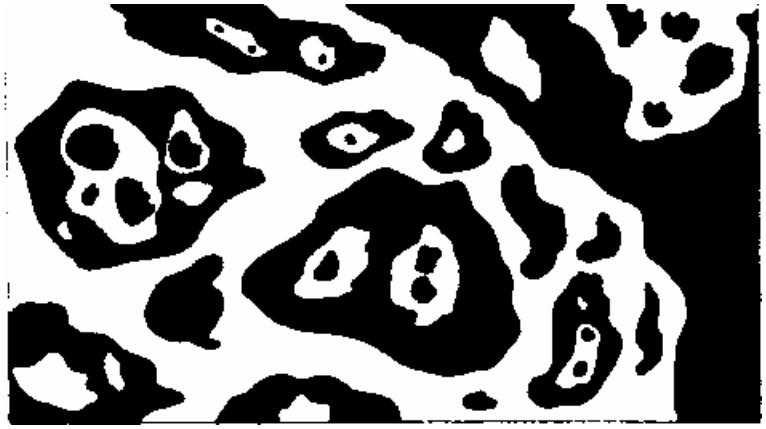


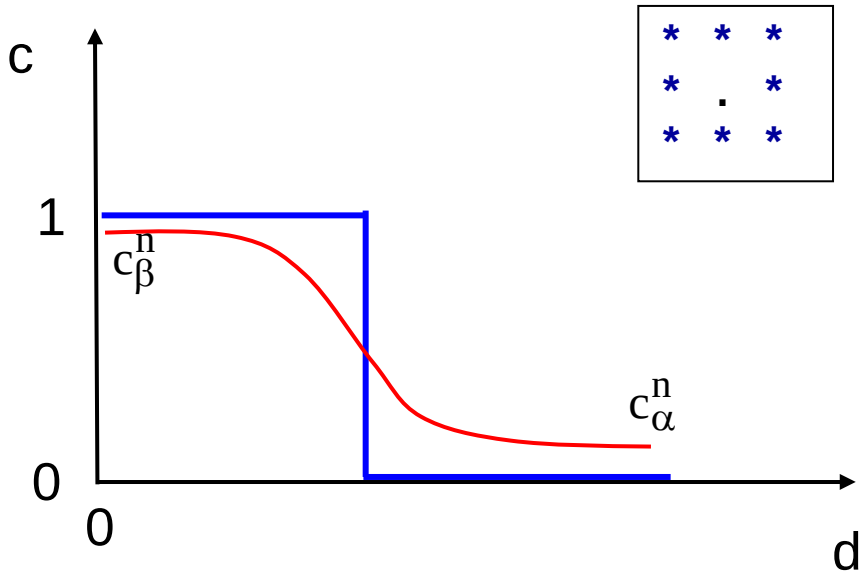
$\sum_k kC_k$



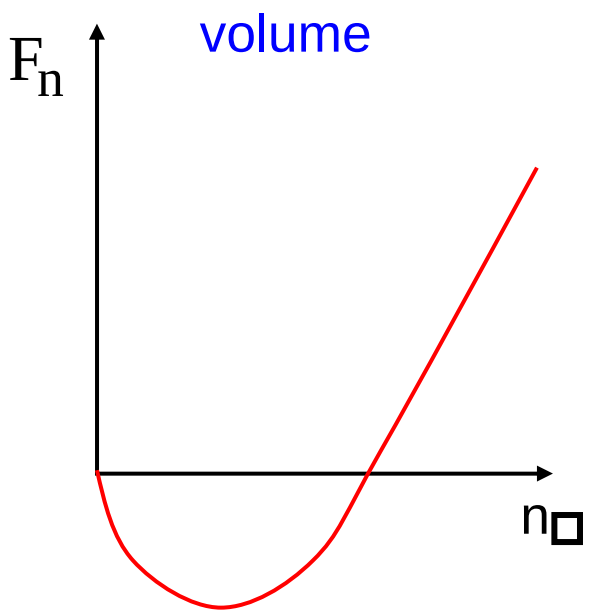


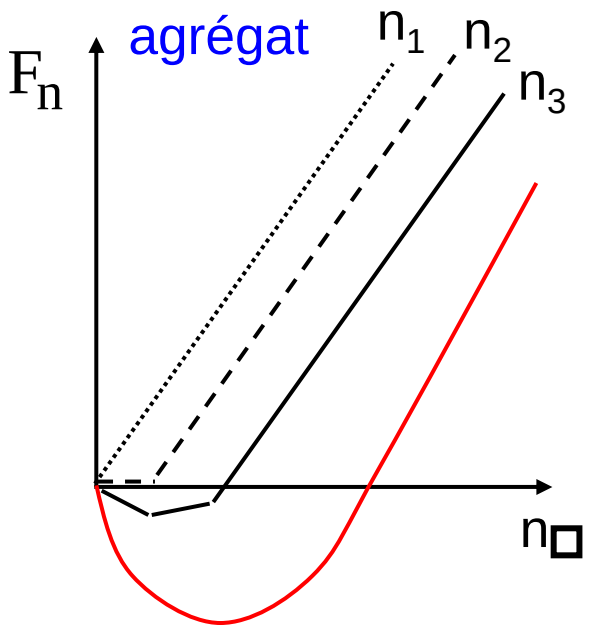
Quid des excitations de cœur ?





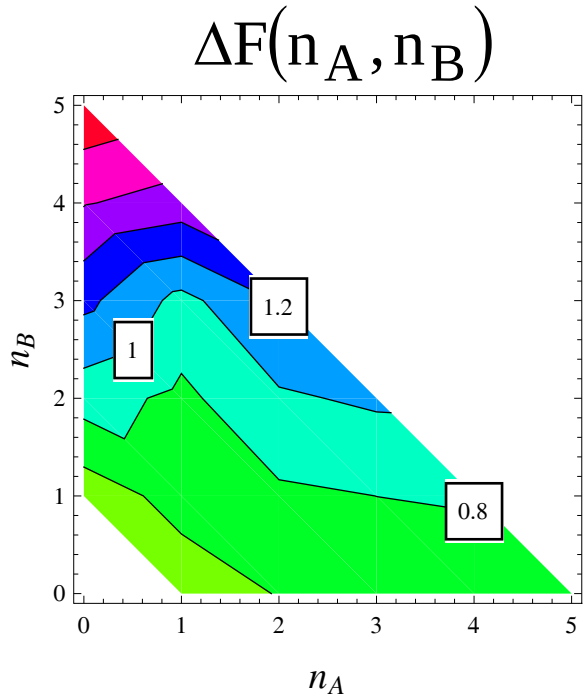
Concentration de □ dans un agrégat





Compétition énergie / entropie
Canonique / grand canonique… discret / continu

Agrégats bimétalliques



discret et limité !

- ✓système ternaire A-B-□
- ✓Énergie libre de surface ?
- ✓Taille critique de germination?
- ✓Influence des lacunes dans les amas ?