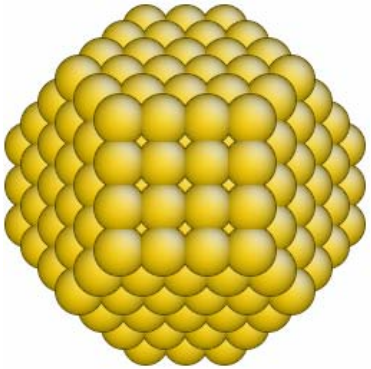
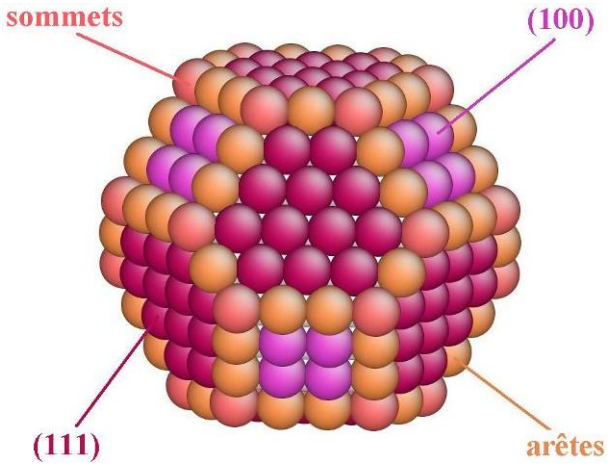
Agrégats bimétalliques: qu'y a-t-il avant le «cœur-coquille»?

L. Delfour, J. Creuze, F. Berthier, B. Legrand
(ICMMO/LEMHE - Orsay; SRMP- Saclay)



PW : 405 atomes



GDR - Decembre 2009

Problématique

Thermodynamique des agrégats bimétalliques :

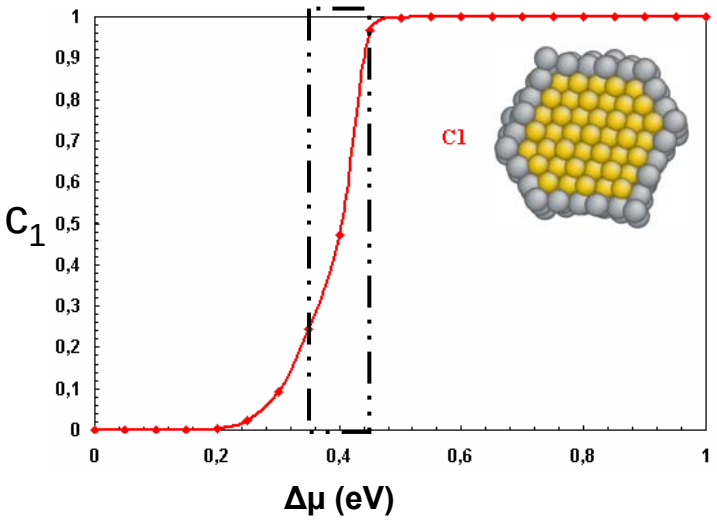
Influence de la dimension finie sur la ségrégation superficielle et les transitions de phases

- Simulations Monte Carlo avec relaxation dans l'ensemble pseudo grand-canonique (N_{tot} et $\Delta\mu$ fixés)

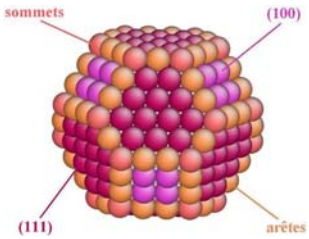
-Interprétation par un formalisme de Champ Moyen sur réseau

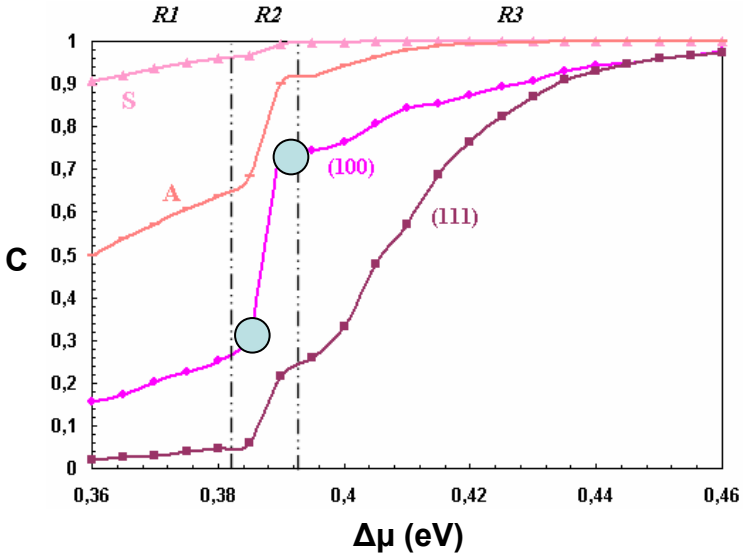
- Système Cu-Ag
  - ségrégation superficielle d'Ag
  - $r_{Ag} > r_{Cu}, \Delta r / r = 13\%$
  - forte tendance à la démixtion en volume

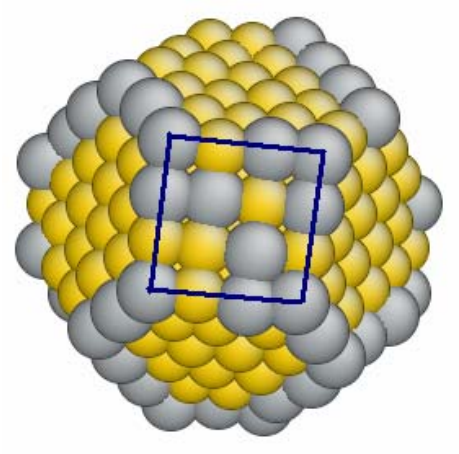
Formation de la coquille



T = 300 K

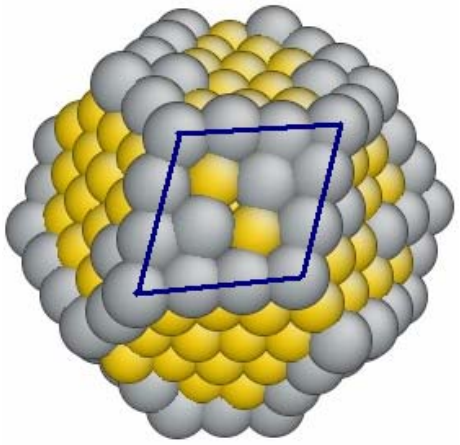




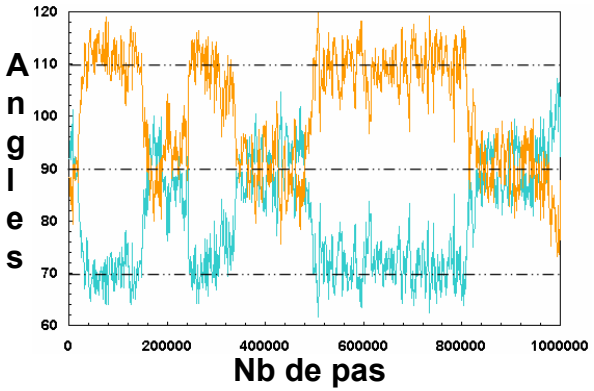


Ag

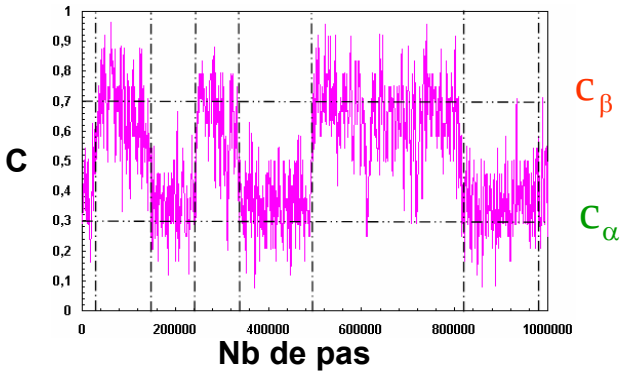
Cu



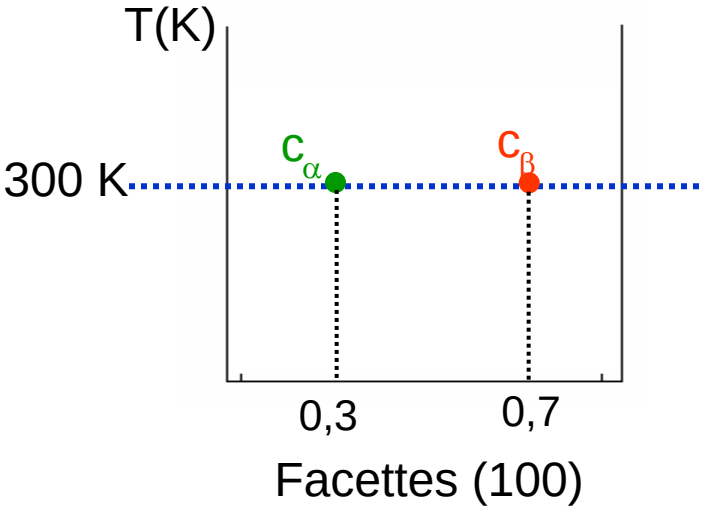
Bi-stabilité chimico-structurale



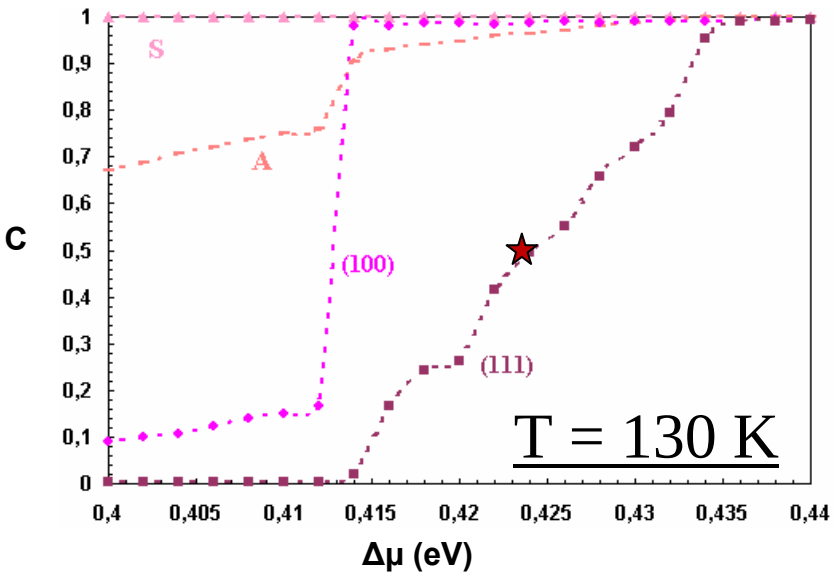
équilibre dynamique
structural collectif

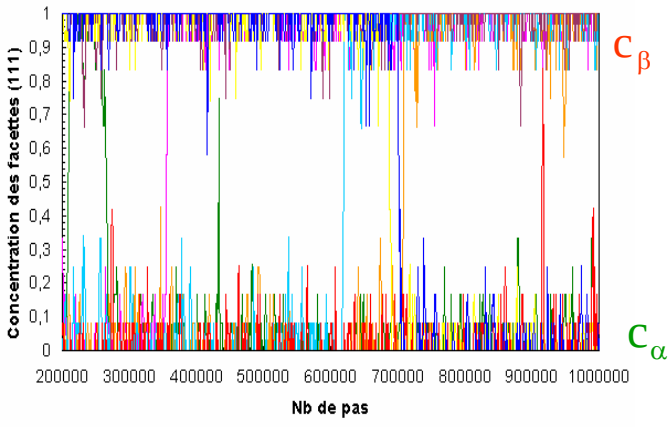


équilibre dynamique
chimique collectif

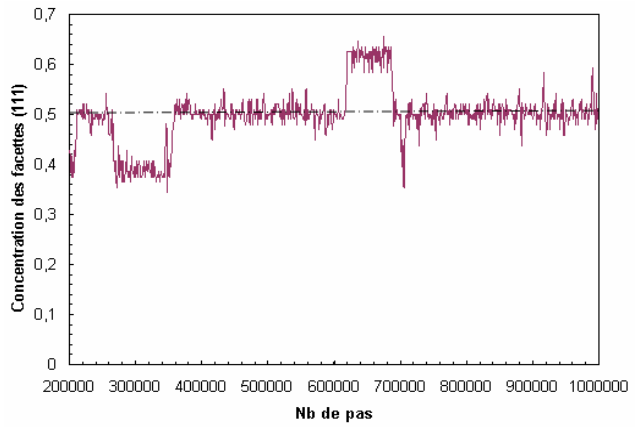


Des facettes (100) aux facettes (111)

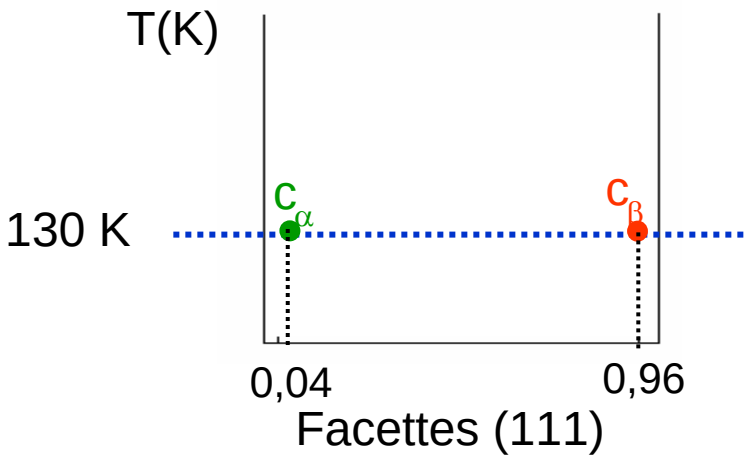




par facette (111)



toutes les facettes (111)



équilibre dynamique chimique individuel

Champ Moyen sur réseau pour A_cB_{1-c}

$$\frac{c_p}{1-c_p} = \exp\left(-\frac{\Delta H_p^{perm} - \Delta\mu}{k_B T}\right)$$

$$\Delta H_p^{perm} = \Delta H_p^{perm,\,imp\,A} + 2\sum_q Z_{pq} V_{pq} c_q$$

$$\Delta H_p^{perm,\,imp\,A} = Z_p(\tau - V)$$

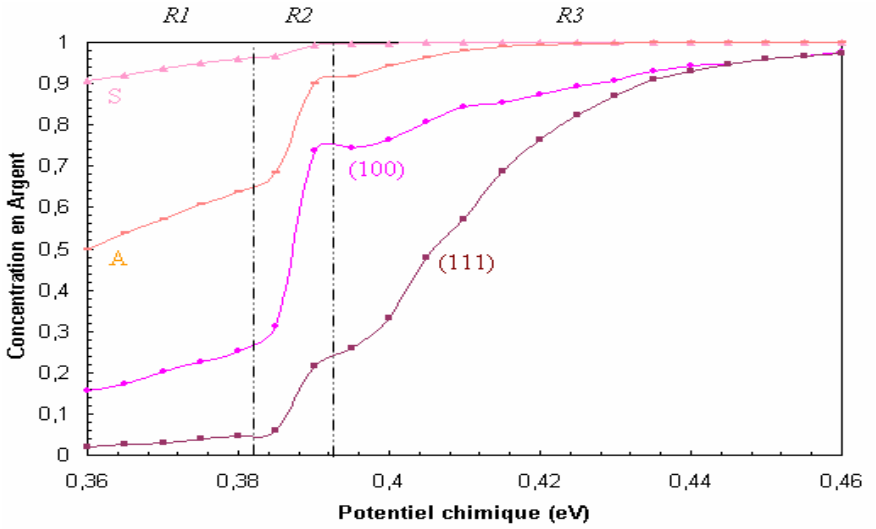
$$V = (V_{AA} + V_{BB} - 2V_{AB})/2$$

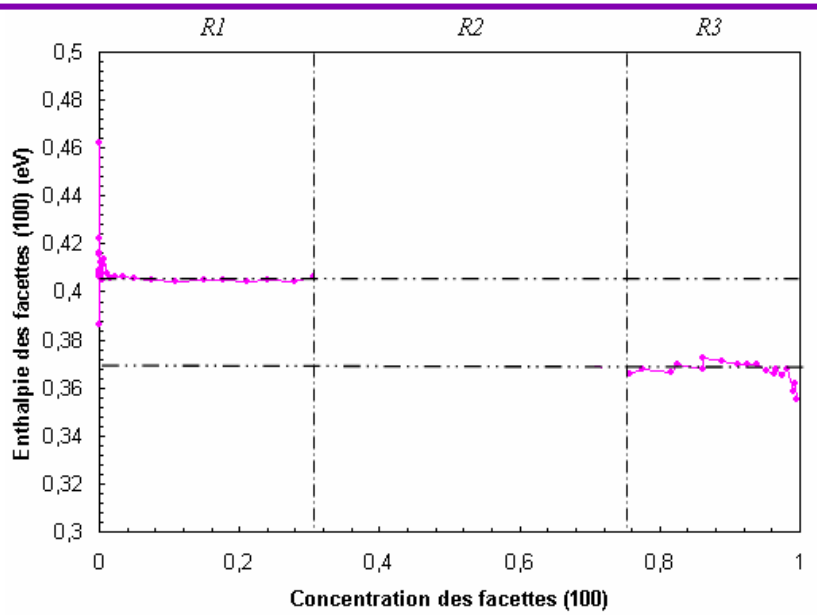
$$\tau = (V_{AA} - V_{BB})/2$$

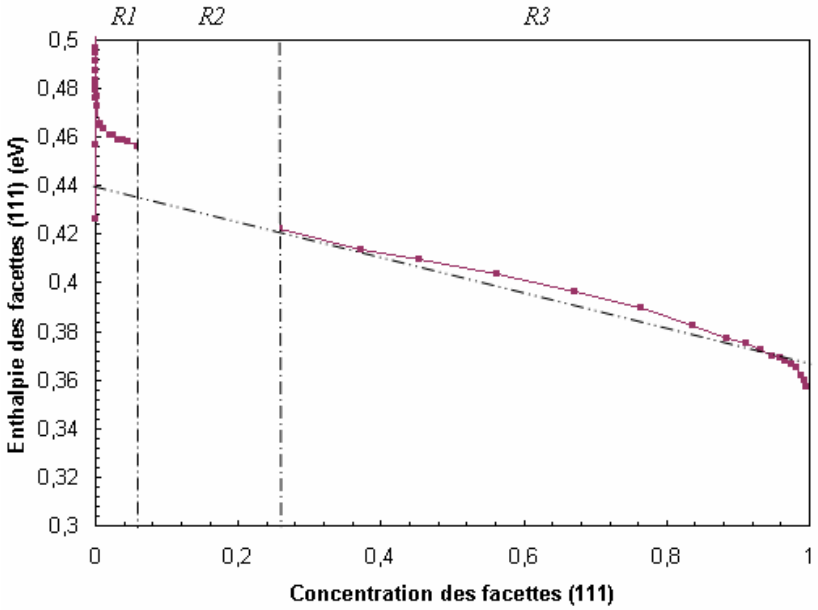
⇒ exploitation des isothermes MC :

$$\Delta\mu - k_B T \ln\left(\frac{c_p}{1-c_p}\right) = \Delta H_p^{perm,\,imp} + 2\sum_q Z_{pq} V_{pq} c_q$$

$$\Delta\mu - k_B T \ln\left(\frac{c_p}{1-c_p}\right) = \Delta H_p^{perm,\,imp} + 2\sum_q Z_{pq} V_{pq} c_q$$



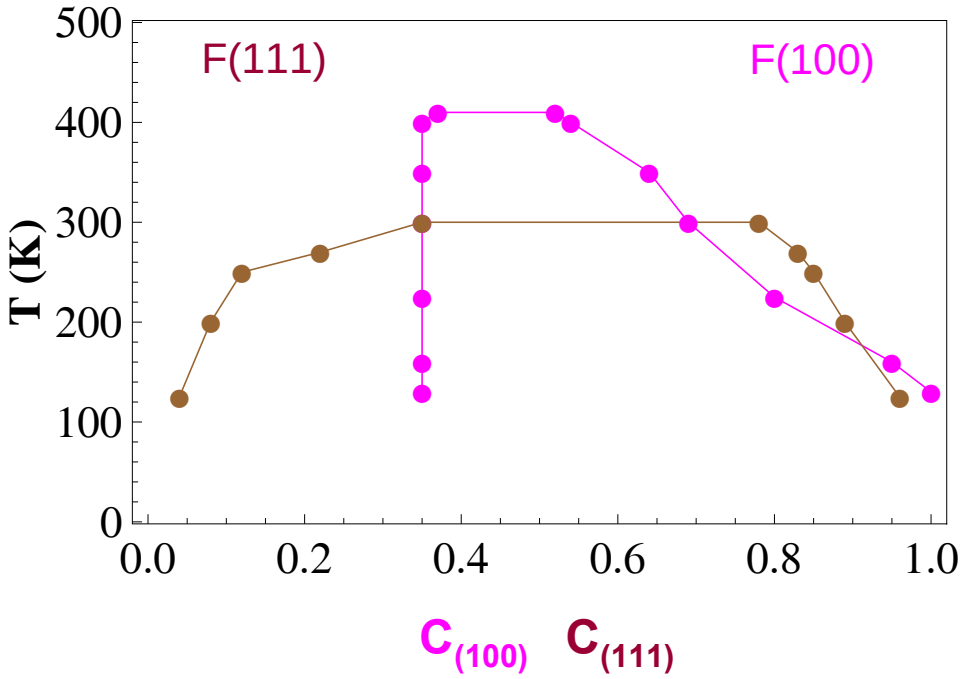




$\Delta H_p^{perm,\,imp}$ (meV)		(100)	(111)
Cu(Ag)	□	415	500
	◊	-	440

V (meV)		(100)	(111)
Cu(Ag)	□	≈ 0	-
	◊	≈ 0	– 7.5

Multiplicité des diagrammes de phases

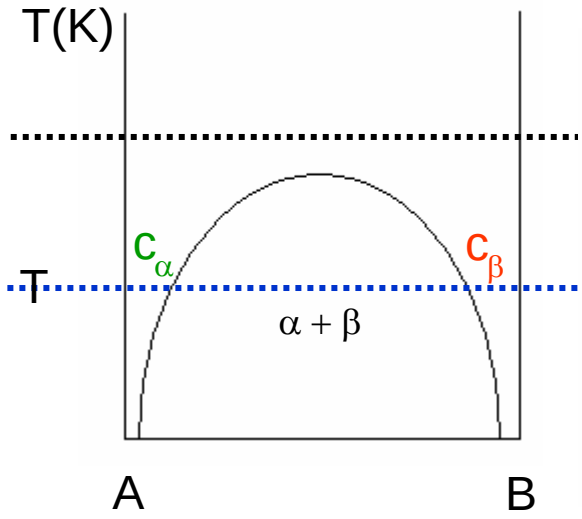


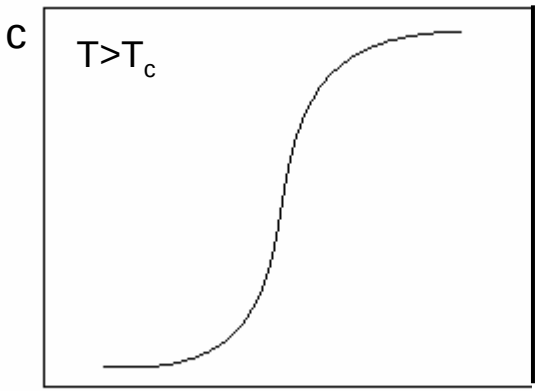
F(100) : Instabilité structurale

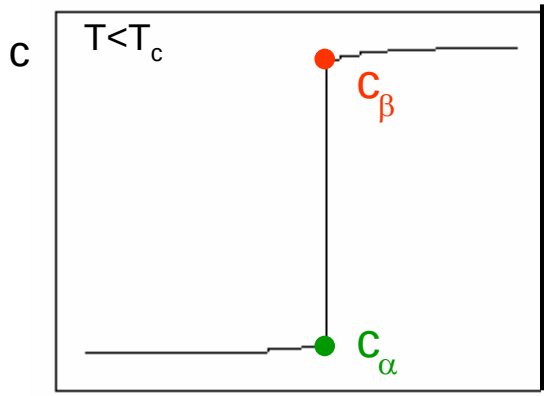
F(111) : Ising standard

Calculs *ab initio* des V : crucial mais diabolique !

Réactivité : bi-stabilité …







Champ Moyen (CM) sur réseau pour A_cB_{1-c} :

$$\frac{c_p}{1-c_p} = \exp\left(-\frac{\Delta H_p^{perm} - \Delta\mu}{k_B T}\right)$$

$$\Delta H_p^{perm} = \Delta H_p^{perm,\,imp\,A} + 2\sum_q Z_{pq} V_{pq} c_q$$

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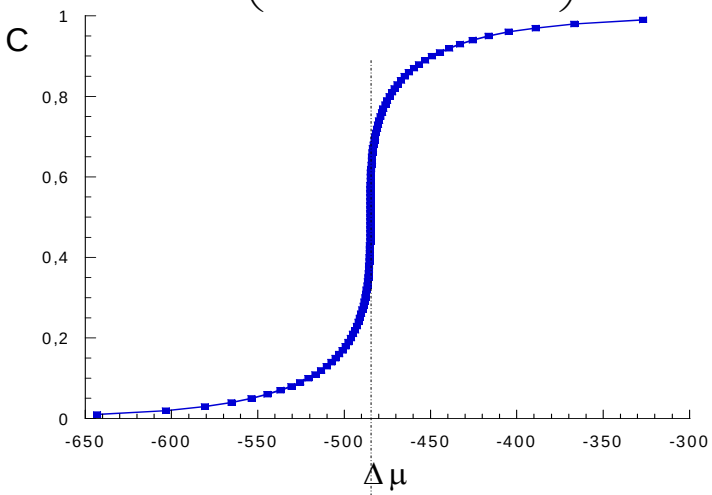
$$V = (V_{AA} + V_{BB} - 2V_{AB})/2$$

$$\tau = (V_{AA} - V_{BB})/2$$

exploitation des isothermes des simulations MC

$$\frac{c}{1-c} = \exp\left(-\frac{\Delta H^{perm}(c) - \Delta\mu}{k_B T}\right)$$

$$\Delta H^{perm} = \Delta H^{perm,\ imp\ A} + 2\ Z\ \ V\ \ c$$



$\Delta H = \Delta\mu - kT \ln (c/1\text{-}c)$