



Transition Ordre/Désordre ou Démixtion ?

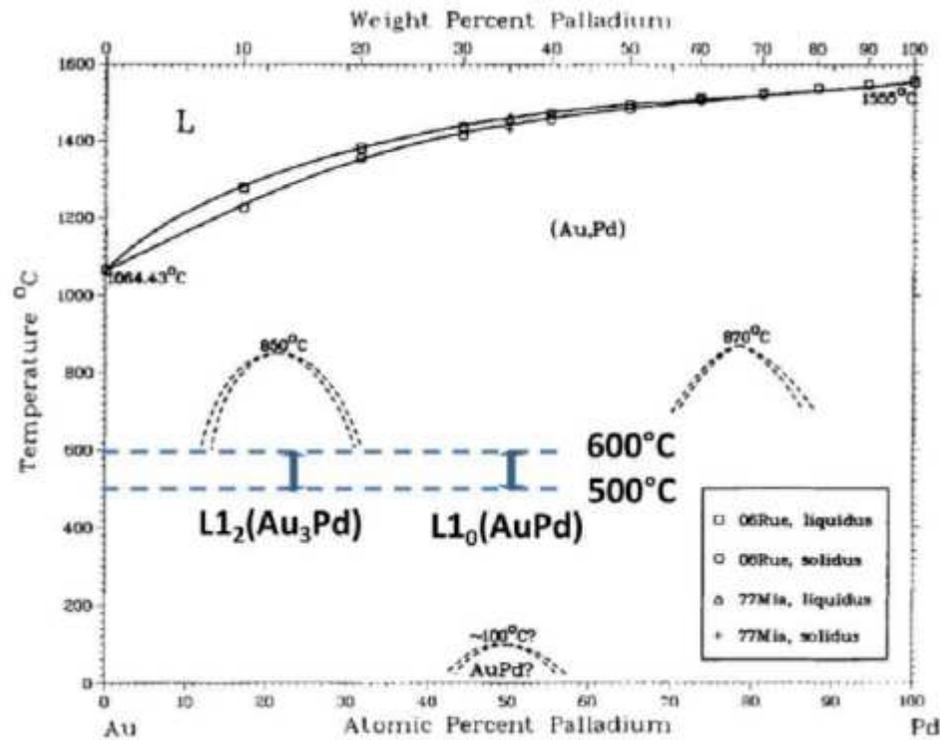
F. Berthier, J. Creuze, T. Gabard,



B. Legrand, M.-C. Marinica, C. Mottet



Un diagramme de phases controversé



Tendance à l'ordre

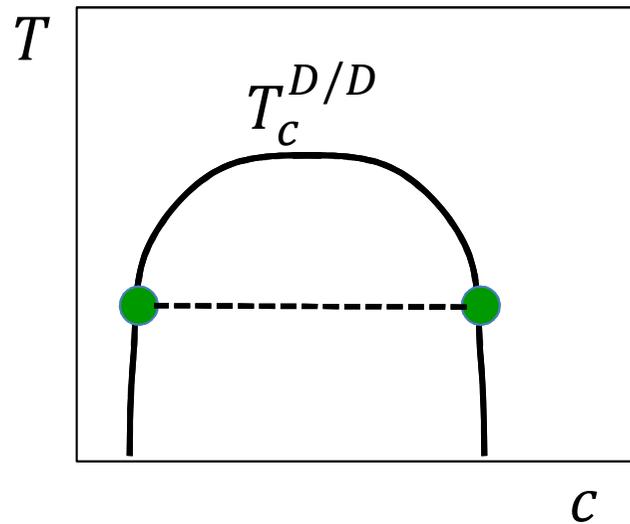
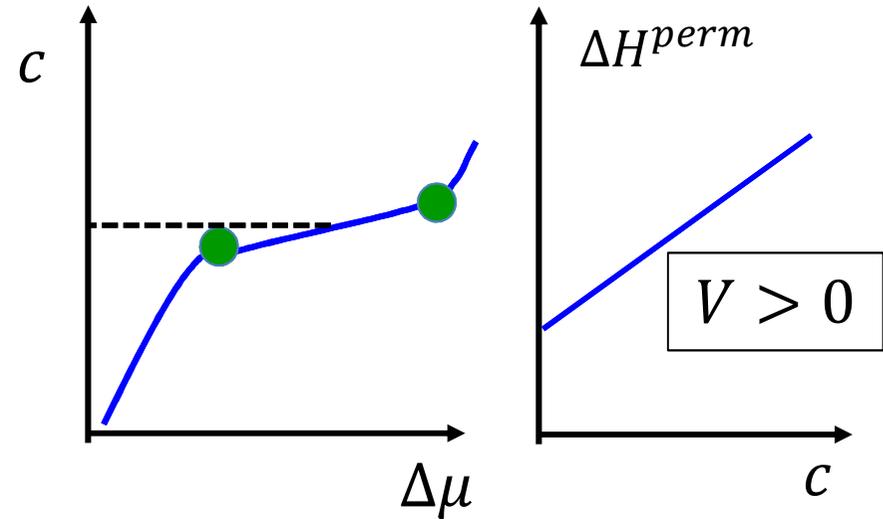
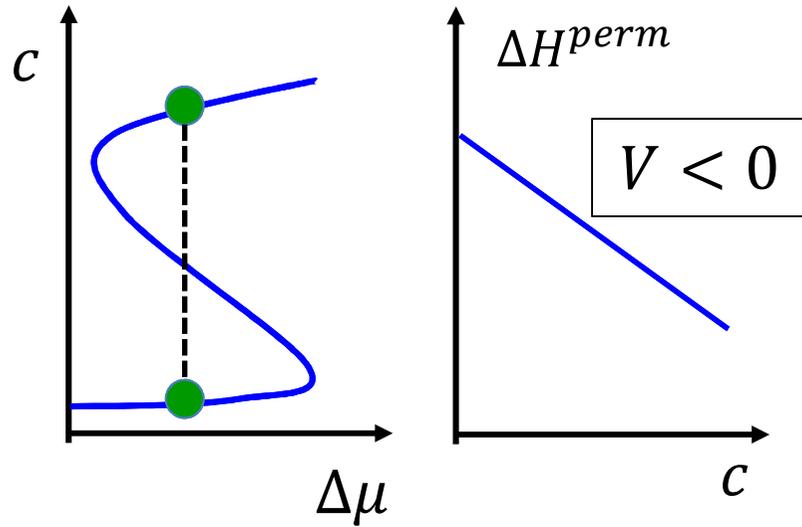
→ Isothermes Monte-Carlo SMA

Démixtion-Désordre versus Ordre-Désordre

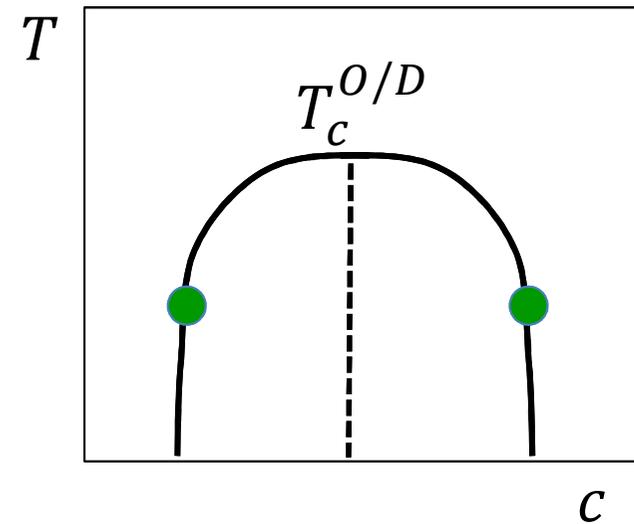
Tendance à la démixtion



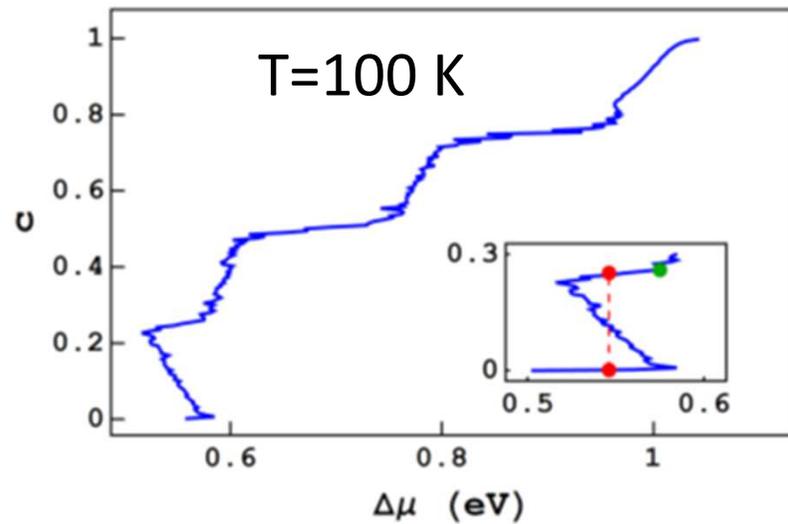
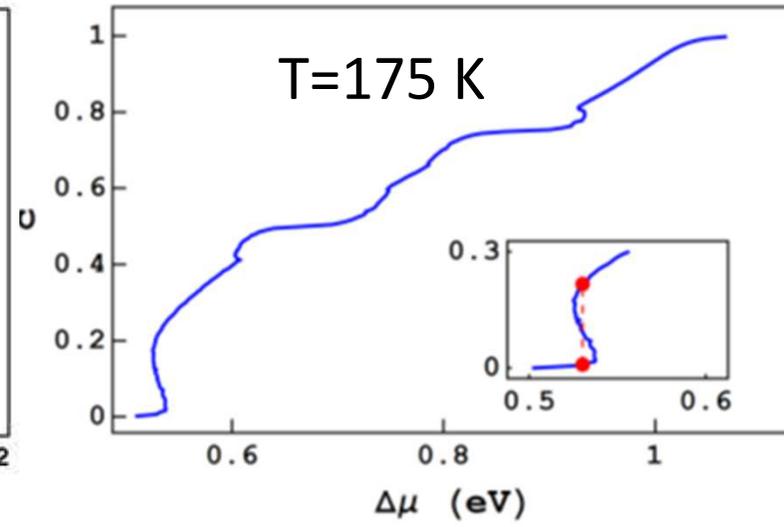
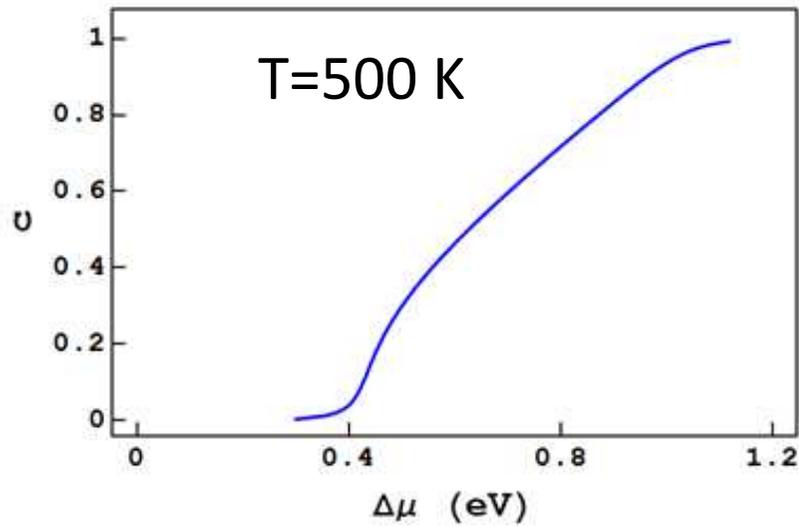
Tendance à l'ordre



Ising

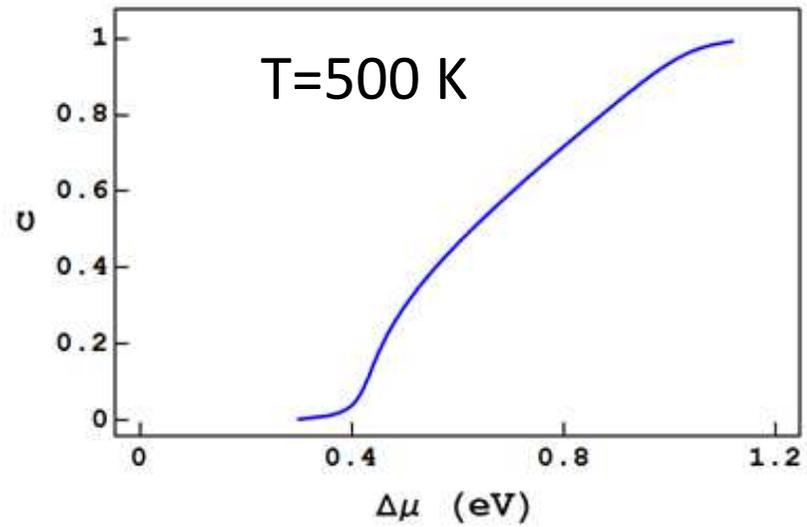


Isothermes $\text{Au}_c\text{Pd}_{1-c}$

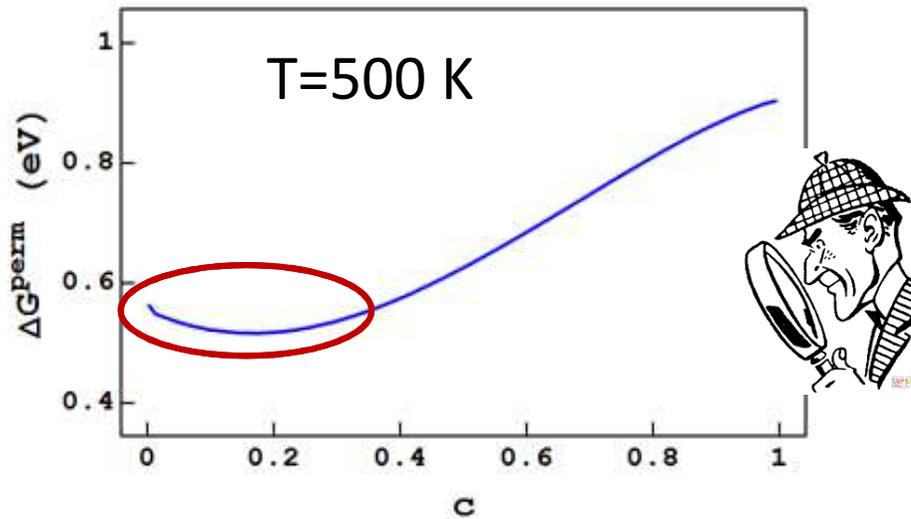


???

De l'isotherme à l'énergie libre de permutation

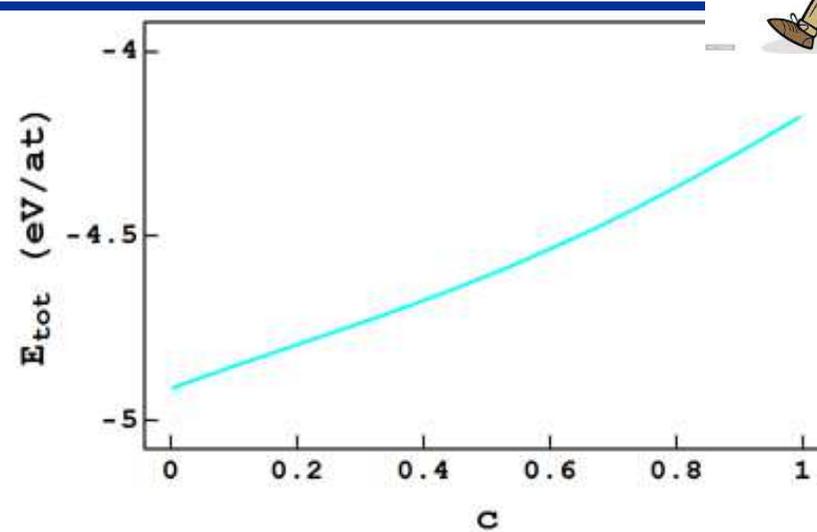
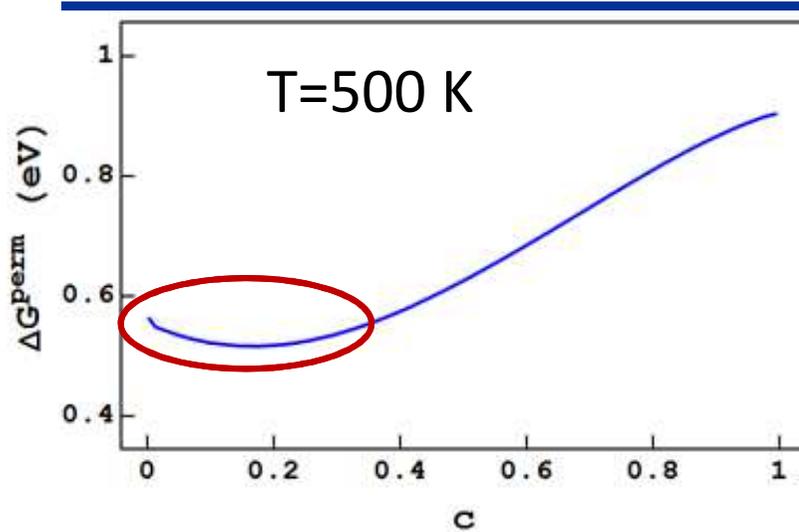


l'énergie libre de permutation : un sacré microscope !



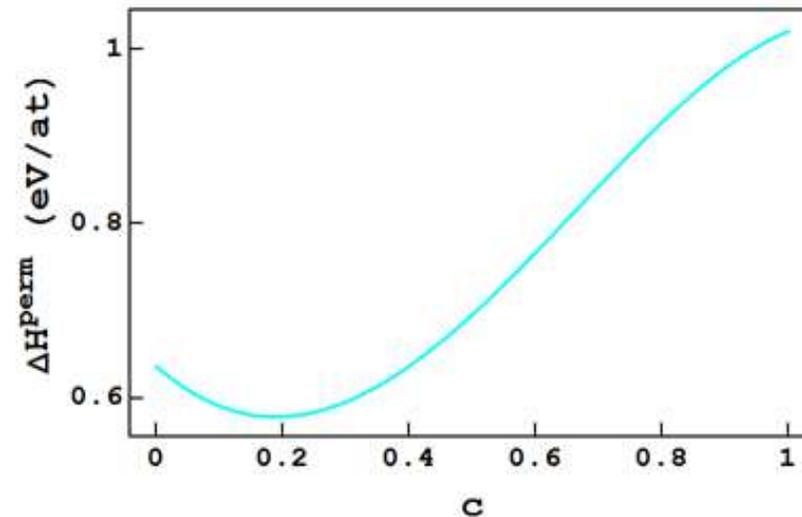
$$\Delta G^{perm} = \Delta\mu - k_B T \ln \frac{c}{1-c}$$

L'inspecteur mène l'enquête $\Delta G^{perm} = \Delta H^{perm} - T\Delta S^{perm}$

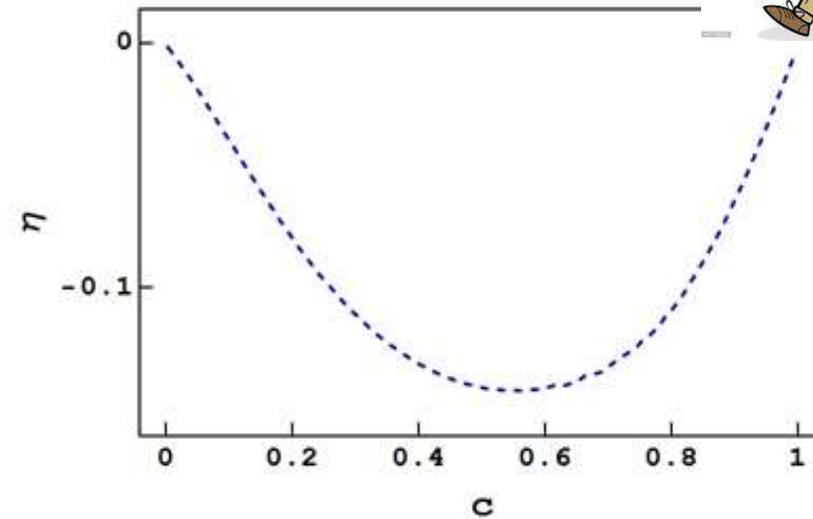
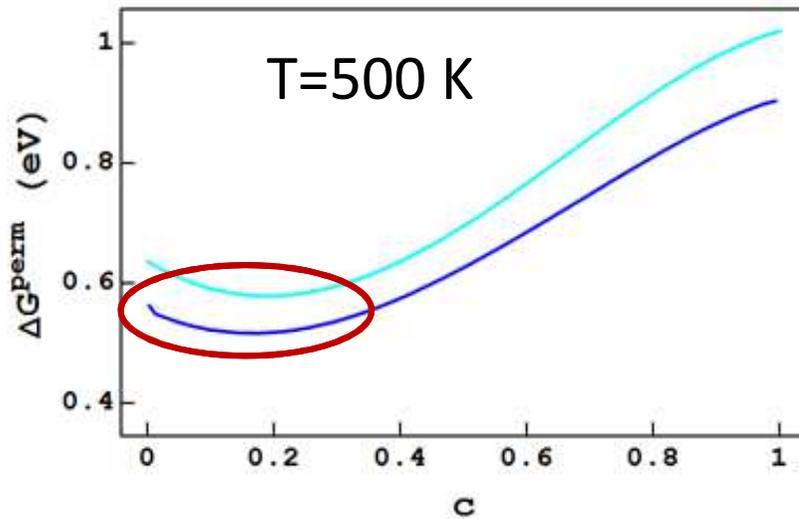


$$\Delta G^{perm} = \Delta\mu - k_B T \ln \frac{c}{1-c}$$

$$\Delta H^{perm}(c) = \frac{1}{Nat} \frac{\partial E_{tot}(c)}{\partial c}$$



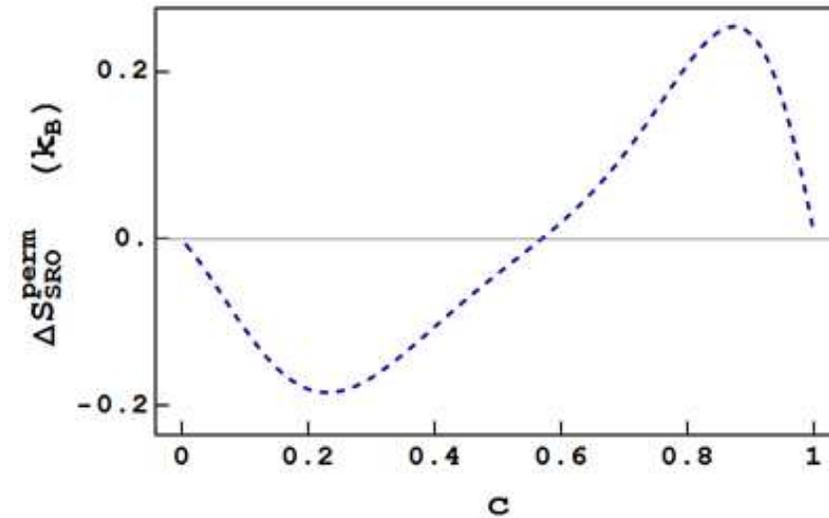
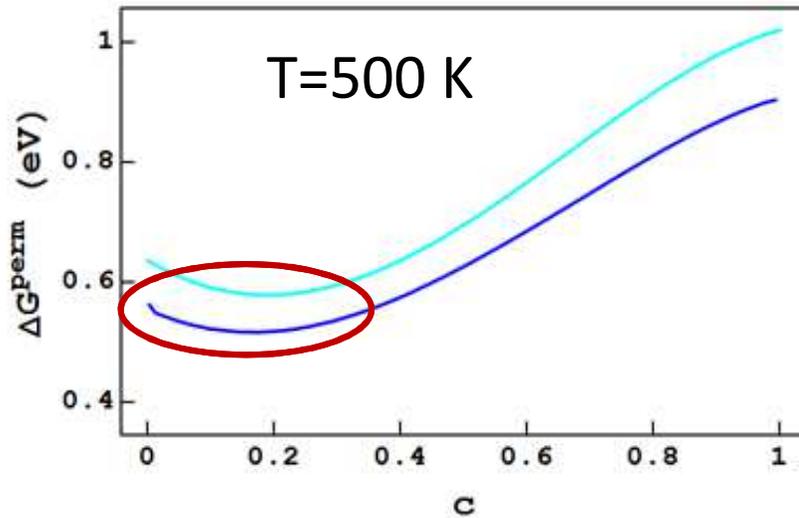
Le bon coupable ? $\Delta G^{perm} = \Delta H^{perm} - T\Delta S^{perm}$



$$\Delta G^{perm} = \Delta\mu - k_B T \ln \frac{c}{1-c}$$

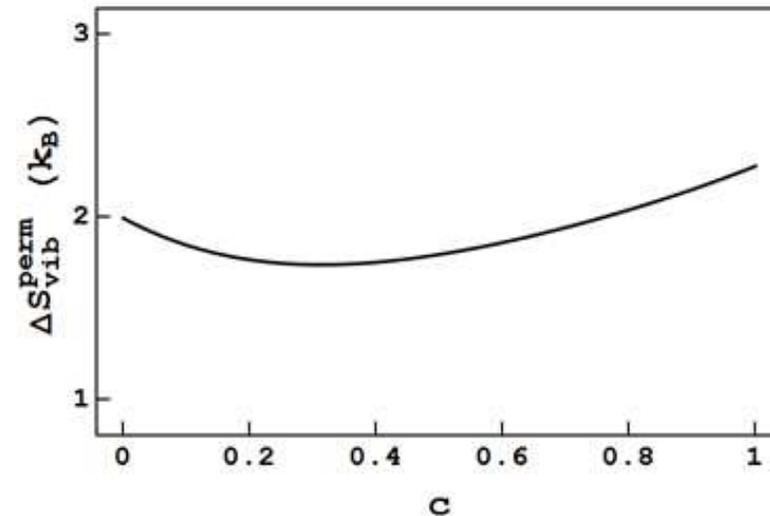
$$\Delta S^{perm} = \Delta S_{SRO}^{perm} + \Delta S_{vib}^{perm}$$

Le bon coupable ? $\Delta G^{perm} = \Delta H^{perm} - T\Delta S^{perm}$

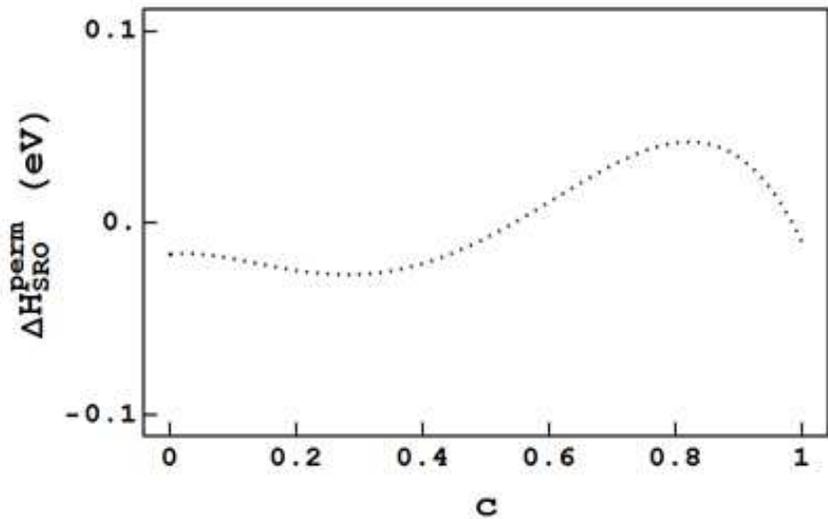
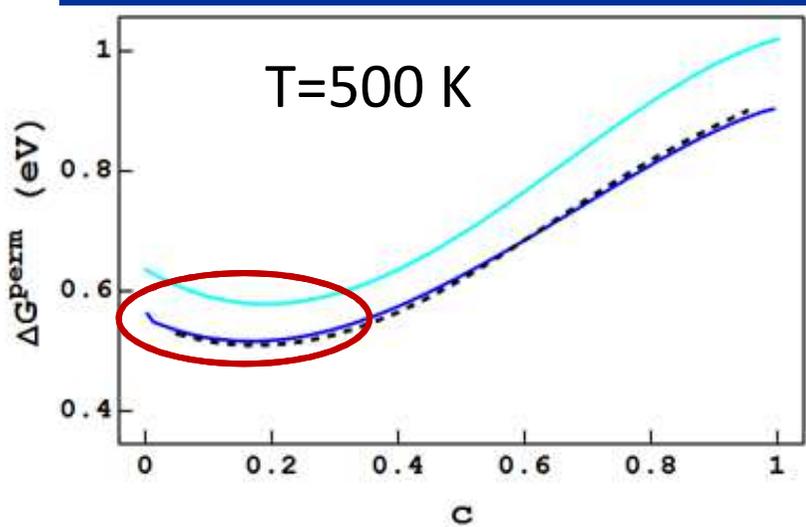


$$\Delta G^{perm} = \Delta\mu - k_B T \ln \frac{c}{1-c}$$

$$\Delta S^{perm} = \Delta S_{SRO}^{perm} + \Delta S_{vib}^{perm}$$



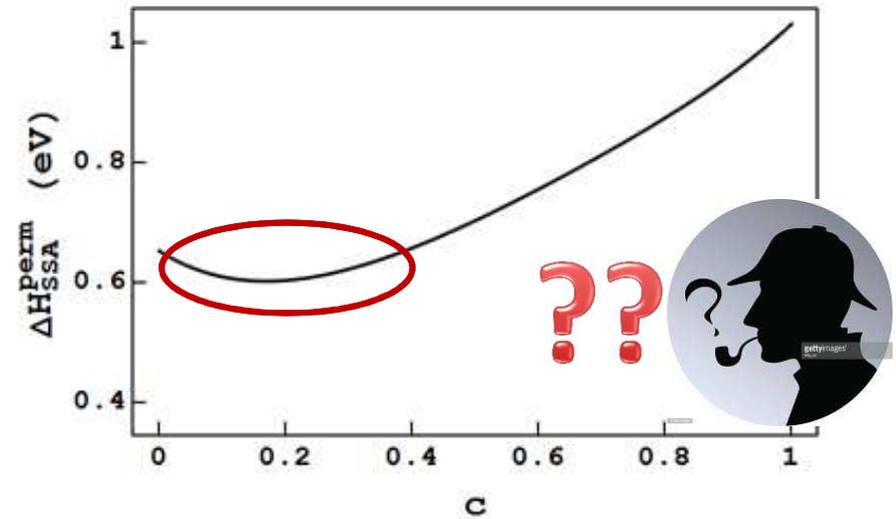
Ultime reconstitution... vers une solution ?



$$\Delta G^{perm} = \Delta\mu - k_B T \ln \frac{c}{1-c}$$

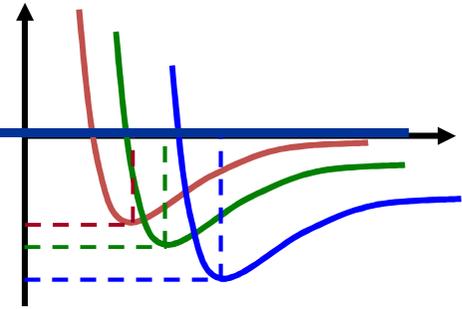
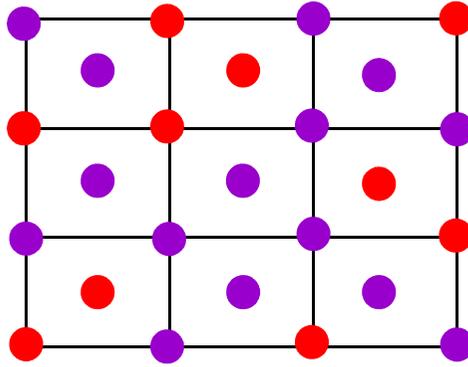
$$\Delta G^{perm} = \Delta H^{perm} - T\Delta S^{perm}$$

$$\Delta H^{perm} = \Delta H_{SSA}^{perm} + \Delta H_{SRO}^{perm}$$

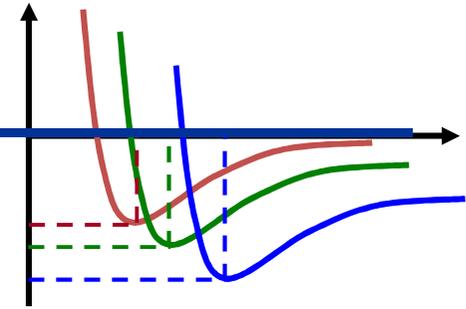
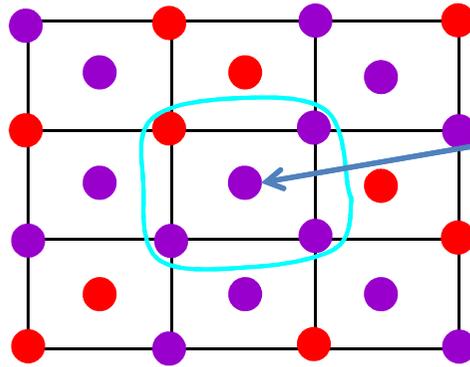


Comment expliquer le comportement de ΔH_{SSA}^{perm} ?

Les énergies de site à la rescousse

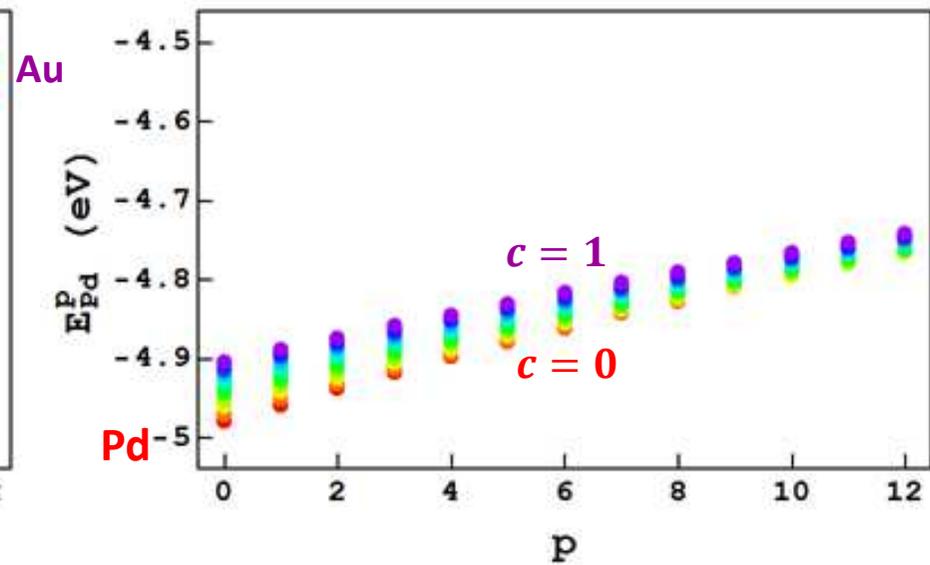
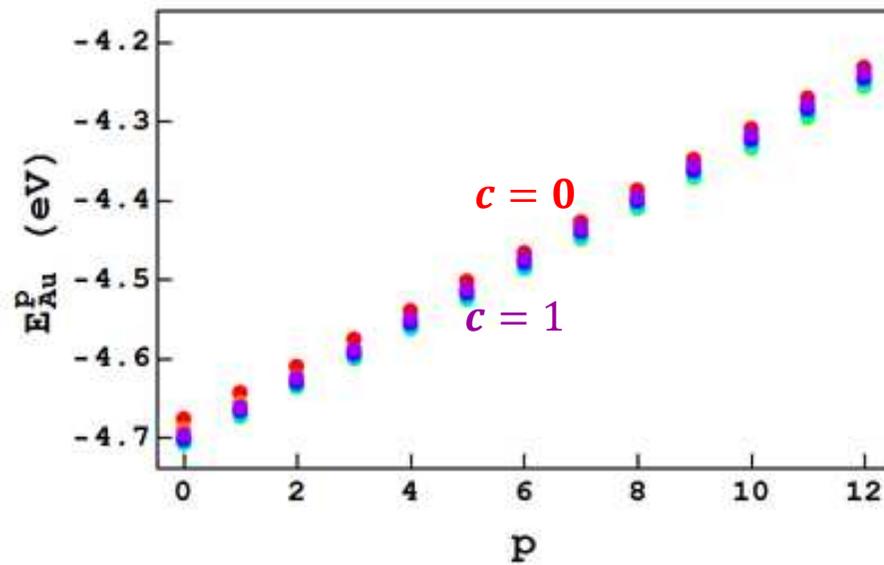
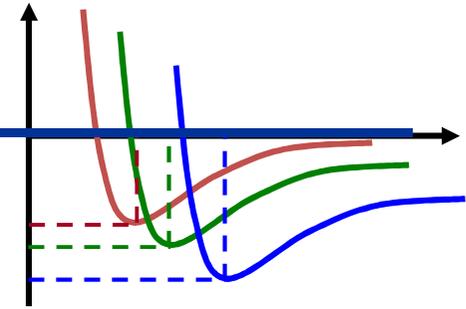
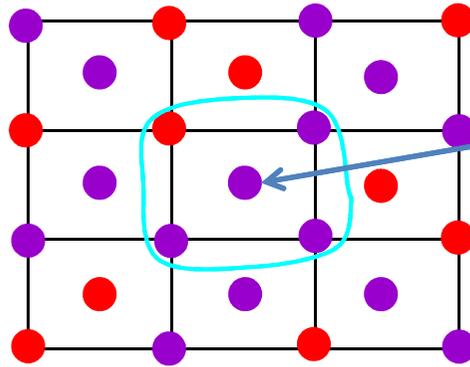


Les énergies de site à la rescousse



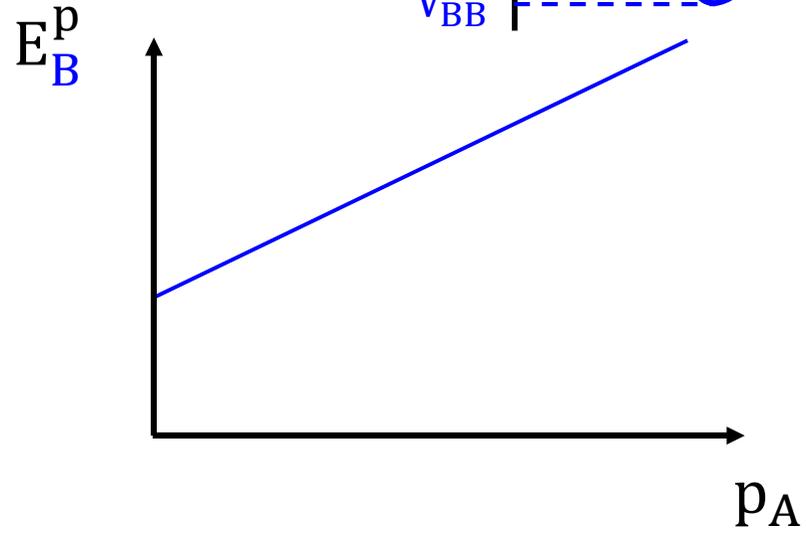
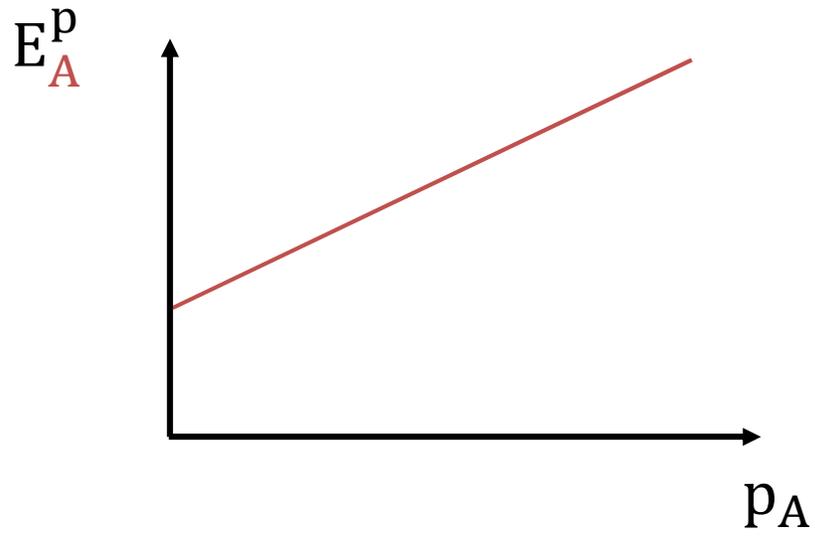
$$H(c) = N_{at} \sum_{p=0}^Z C_Z^p c^p (1-c)^{Z-p} \left(c E_{Au}^p(c) + (1-c) E_{Pd}^p(c) \right)$$

Les énergies de site à la rescousse

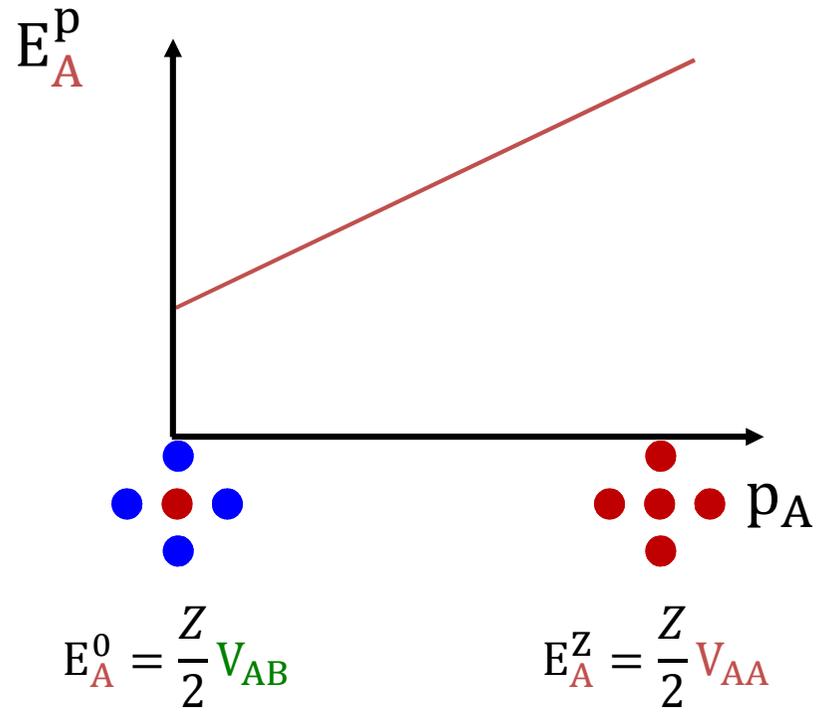


Non-linéarité en p : chimie locale
 Dépendance en c : élasticité

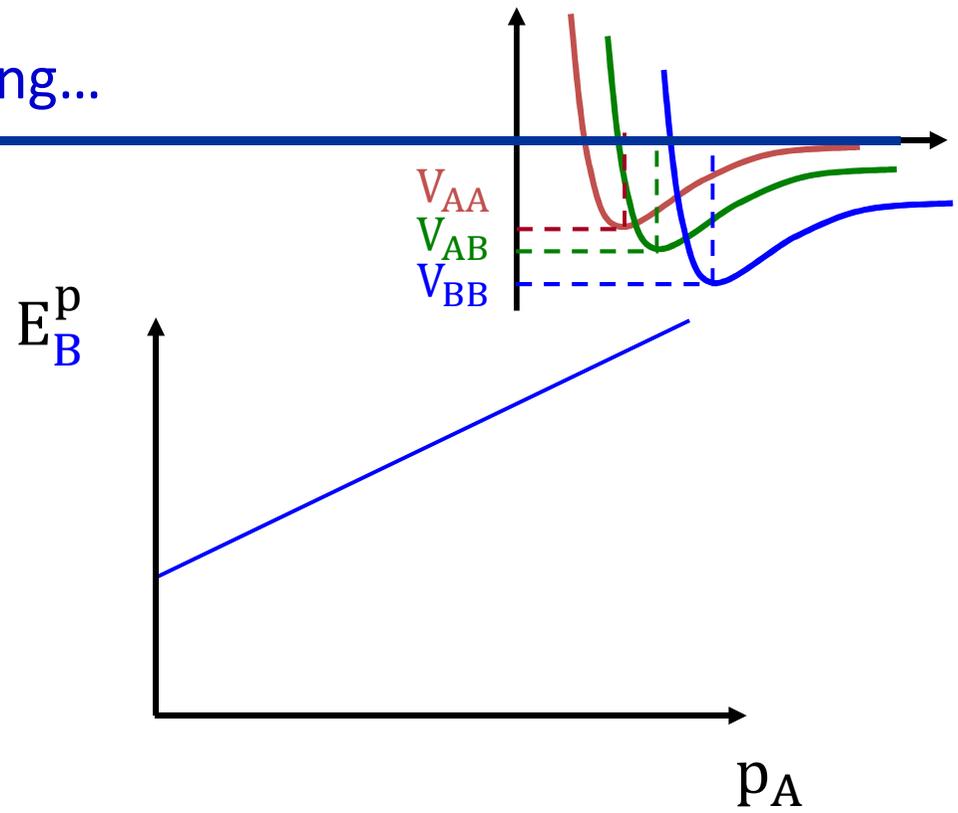
De la linéarité du modèle d'Ising...



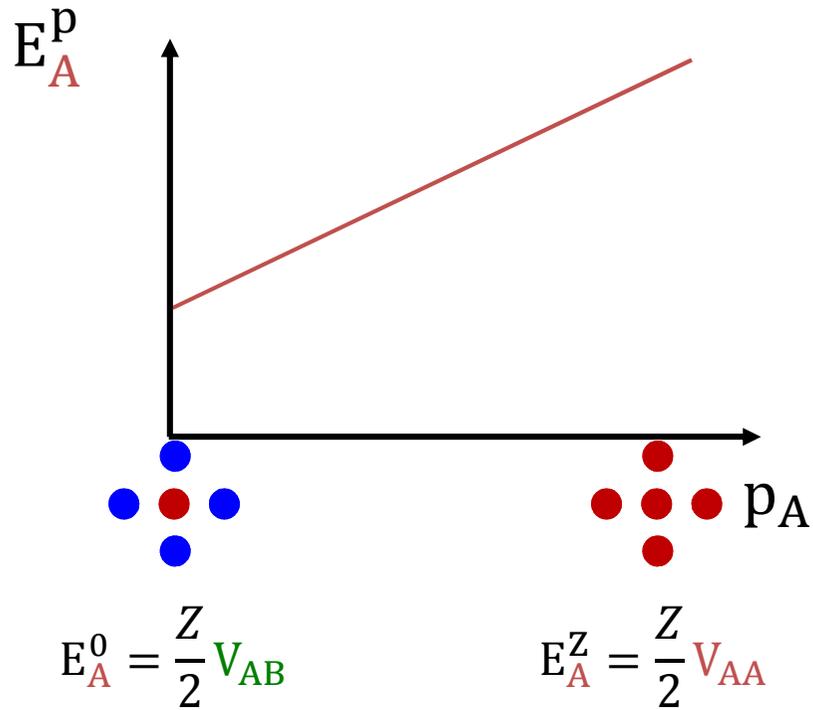
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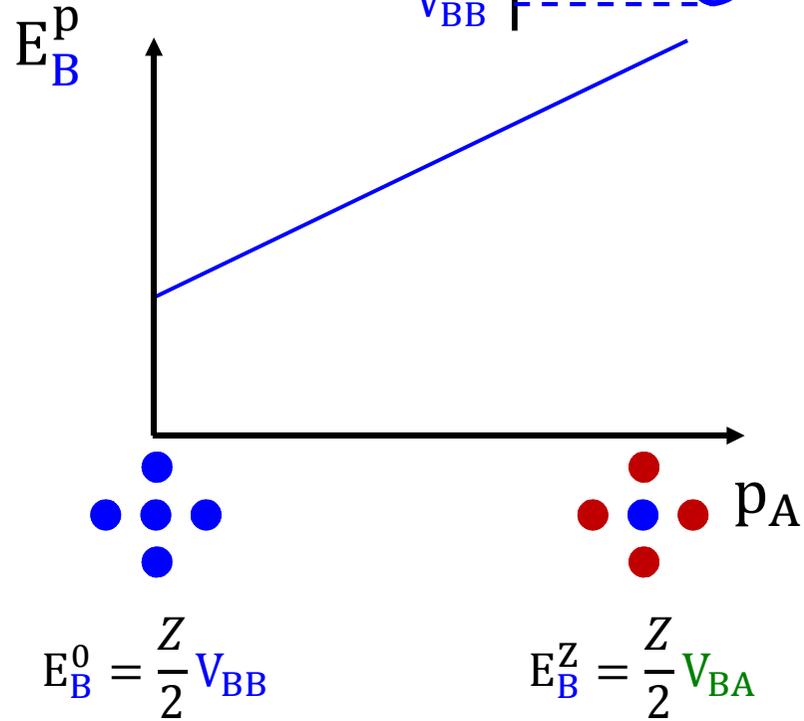
pende = $V_{AA} - V_{AB}$



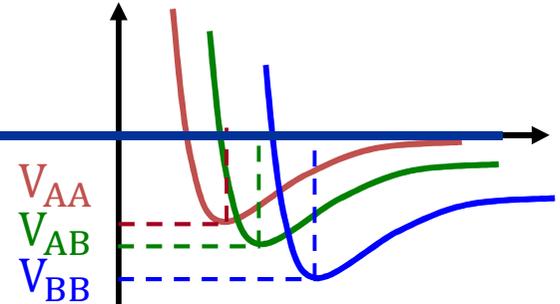
De la linéarité du modèle d'Ising...



pende = $V_{AA} - V_{AB}$

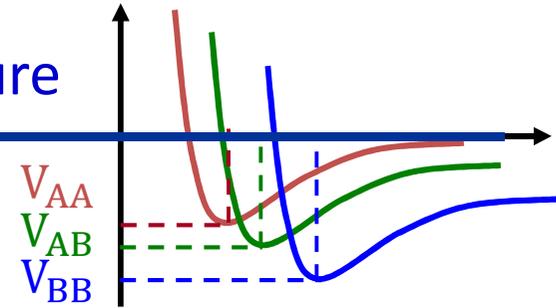
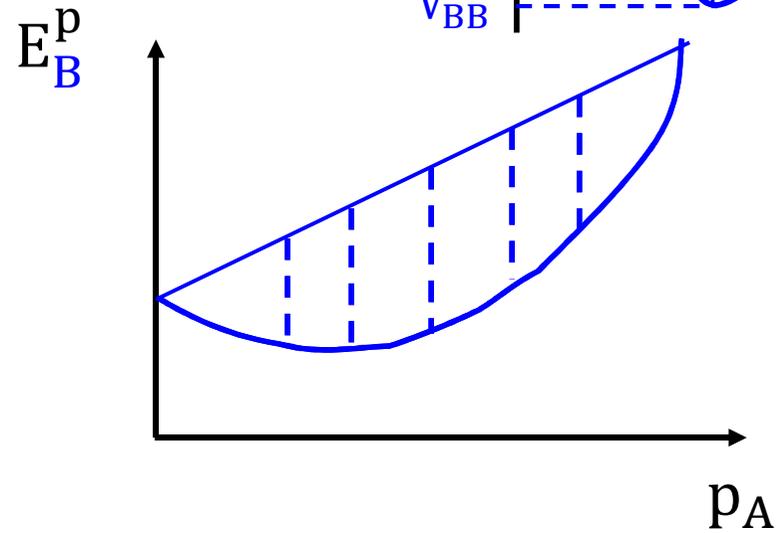
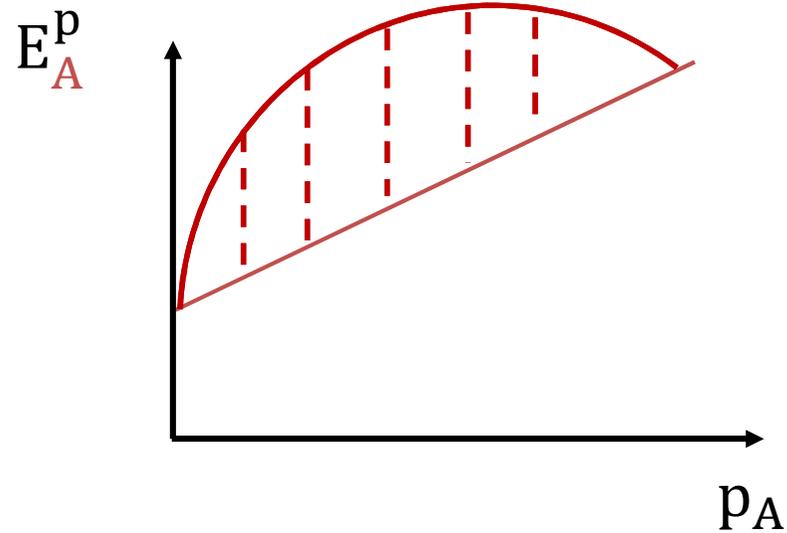


pende = $V_{AB} - V_{BB}$



Différence des pentes : $V = (V_{AA} + V_{BB} - 2V_{AB})/2$
 4 quantités (E_X^0, E_X^Z) pour 3 inconnues (V_{AA}, V_{BB}, V_{AB})

De la linéarité du modèle d'Ising... à la courbure



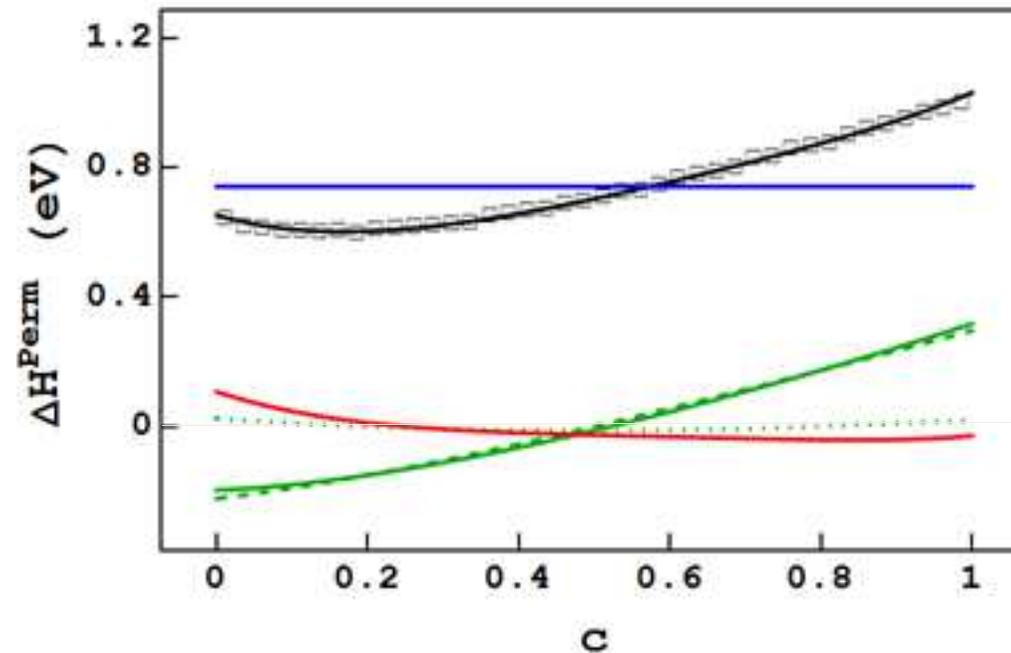
$$H(c) = H_{Ising}(c) + H_{triplets}(c)$$

Avec

$$H_{triplets}(c) = Z(Z - 1)c(1 - c)(1 - 2c)(c\kappa_A + (1 - c)\kappa_B)$$

Quand les énergies de site mettent un point final à l'enquête

$$\Delta H_{SSA}^{perm}(c) = \frac{\partial H(c)}{N_{at} \partial c} = \Delta H_{Coh}^{perm}(c) + \Delta H_{Chem}^{perm}(c) + \Delta H_{Size}^{perm}(c)$$



L'enquête est close !



Ultime dénouement !

