NANOALLOYS
International Research Network

cnrs

UNIVERSITÉ PARIS SUD
Comprendre le monde, construire l'avenir®

Ageing of nanoalloys : Influence of size and concentration

F. Berthier

B. Legrand

ICMMO

SP2M
Synthèse, Propriétés et Modélisation des Matériaux

DE LA RECHERCHE À L'INDUSTRIE
cea

SRMP

Energetic model

$A_c B_{1-c}$

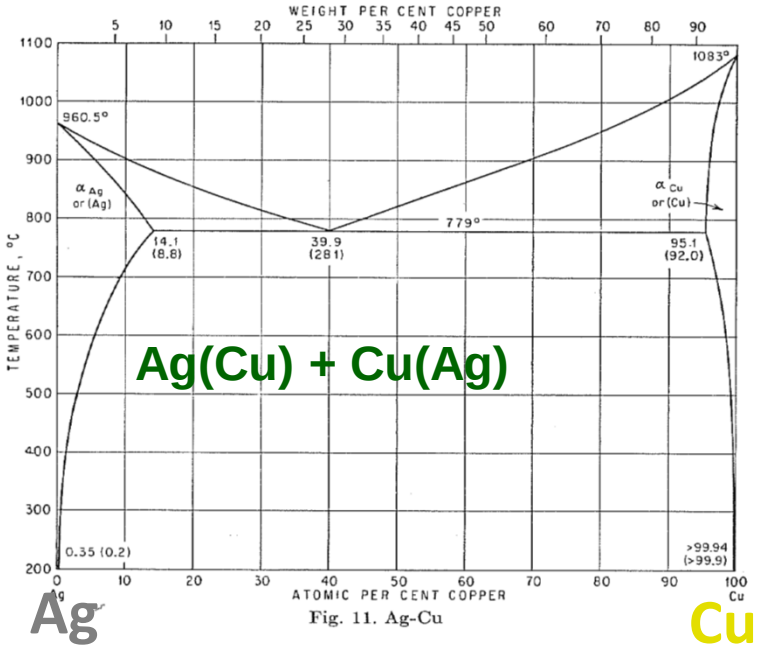


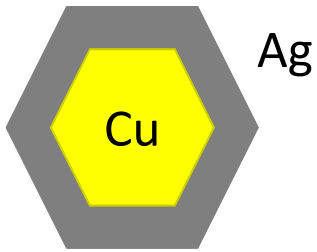
Fig. 11. Ag-Cu

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

$V < 0$: Phase separation

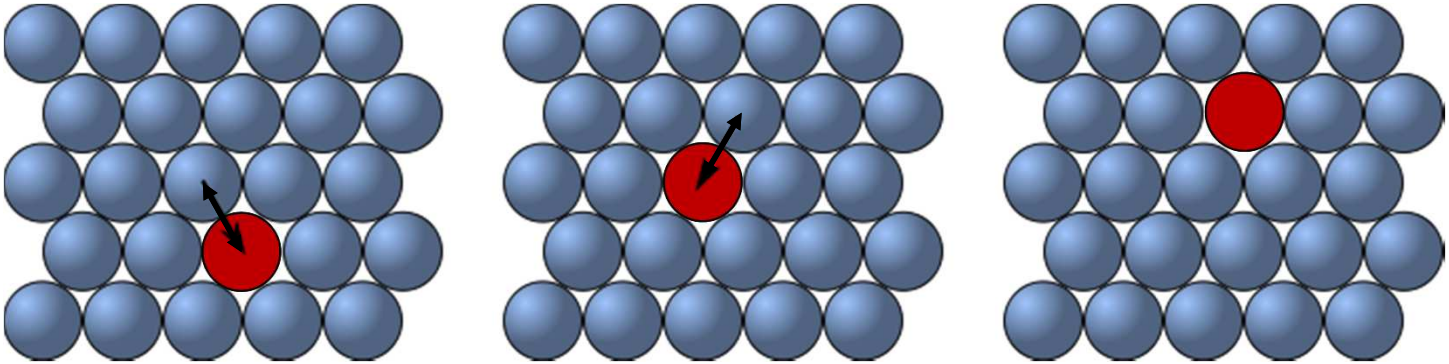
$$\tau = \frac{(V_{AA} - V_{BB})}{2}$$

$\tau > 0$: A superficial segregation

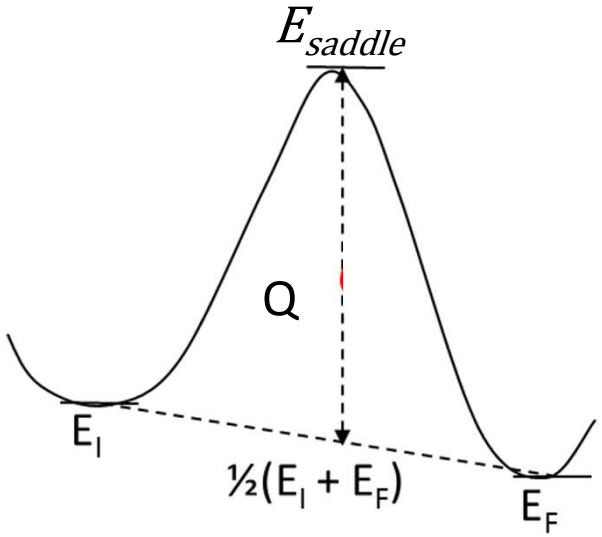


Diffusion mechanism

Direct exchange mechanism



Saddle energy model



$$P(E_I \rightarrow E_F) = \nu \exp\left(-\frac{E_{saddle} - E_I}{k_B T}\right)$$

Detailed balance

$$\frac{P(E_I \rightarrow E_F)}{P(E_F \rightarrow E_I)} = \exp\left(-\frac{E_F - E_I}{k_B T}\right)$$

$$E_I, E_{saddle} = \mathrm{f}(\tau, V, local\ environment)$$

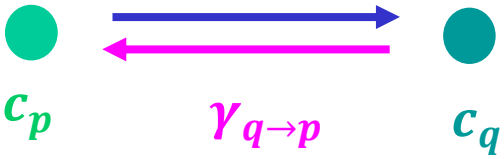
$$t_0 = \nu^{-1} \exp\left(\frac{Q}{k_B T}\right) \propto 1/D$$

$Q = 2{,}02$ eV/atome

$\nu = 4{,}8\ 10^{14}\ \mathrm{s}^{-1}$

J. Eugène *et al.*, Surface Science **241**, 1 (1991)

Mean Field Approximation Site Kinetics (MFA-SK)



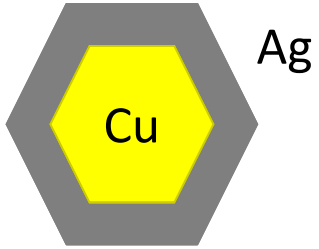
Site concentration

$$\frac{\partial c_p}{\partial\left({}^{t}/_{\boldsymbol{t_0}}\right)} = \sum_q \left[(1-c_p)c_q\gamma_{q\to p} - c_p(1-c_q)\gamma_{p\to q}\right]$$

$$\gamma_{q\to p} = \mathrm{f}(\tau, V, c_p, c_q, T)$$

$$\boldsymbol{t_0} = \boldsymbol{\nu}^{-1}\exp\left(\frac{\boldsymbol{Q}}{k_B T}\right) \propto 1/D$$

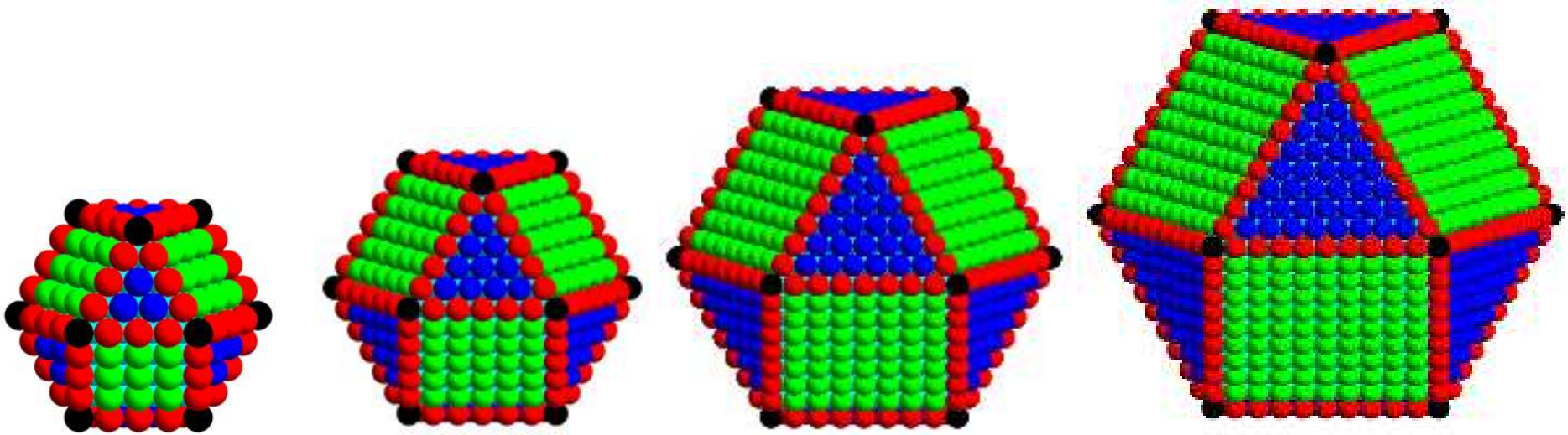
$$\frac{\partial c_p}{\partial t} = 0 \quad \leftrightarrow$$



Kinetic models contain the two driving forces leading to:

- Ag surface segregation
- phase separation

Cubo 5… 7… 9… 11



309 atoms

923 atoms

2057 atoms

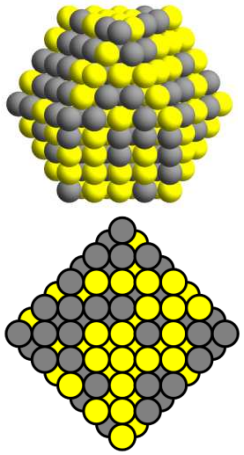
3871 atoms

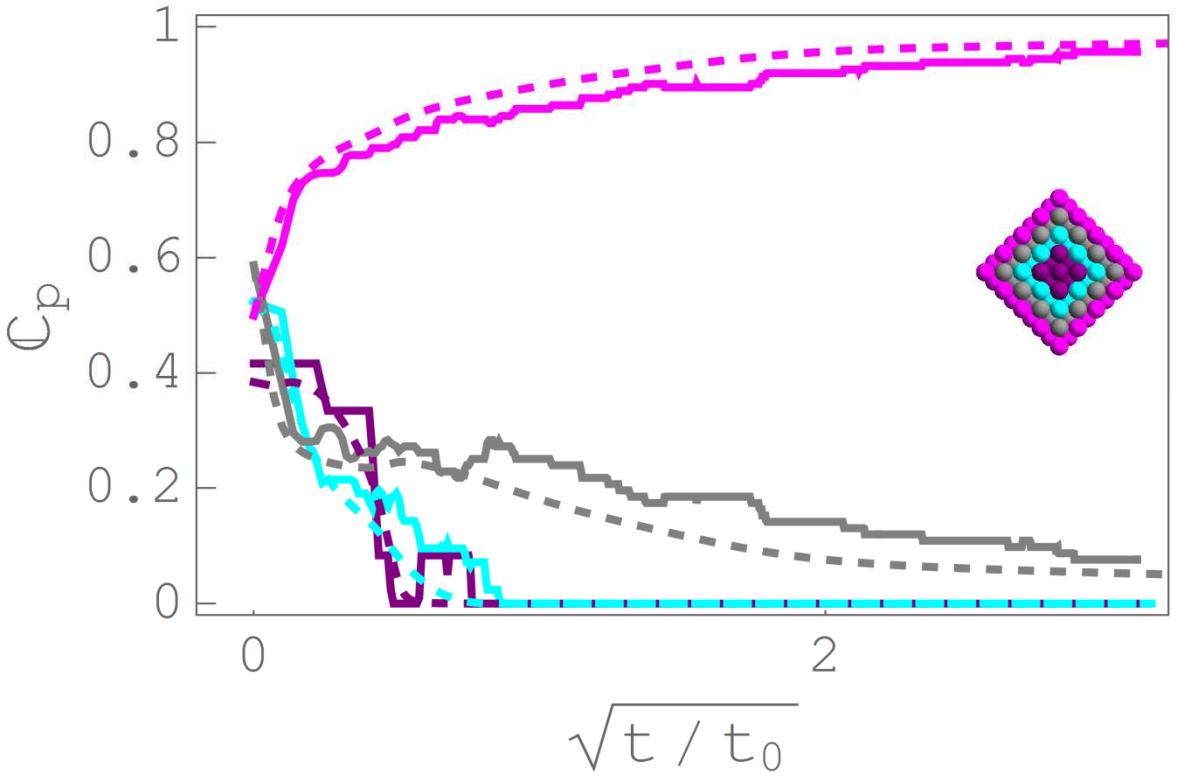
KMC ≡ MFA-SK

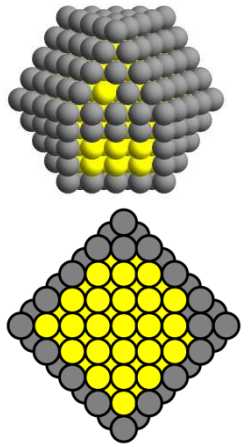
$c = 0{,}52$

Cubo 5

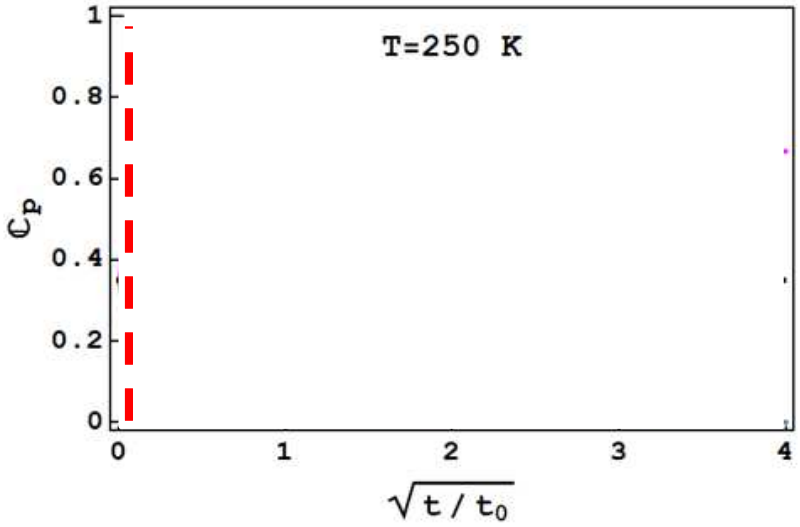
$T = 300K$

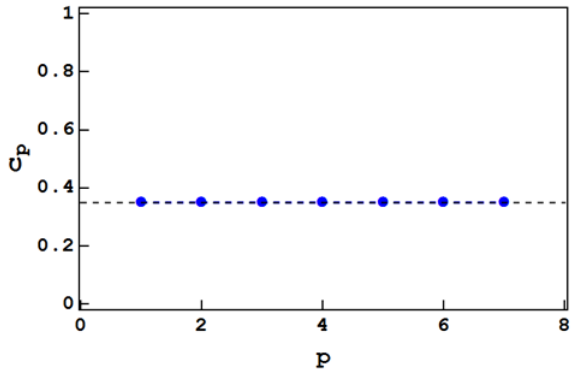


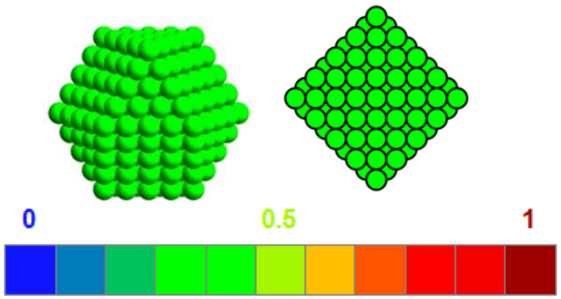




Ageing of initial uniform configurations (MFA-SK)

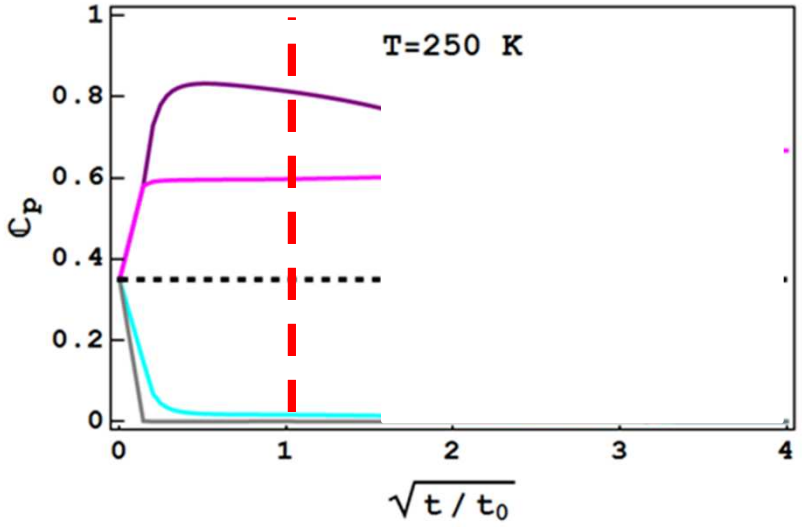




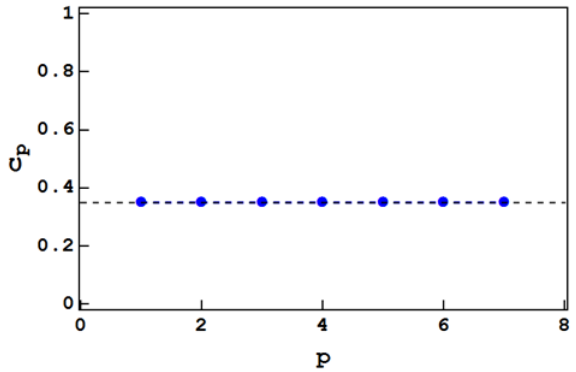


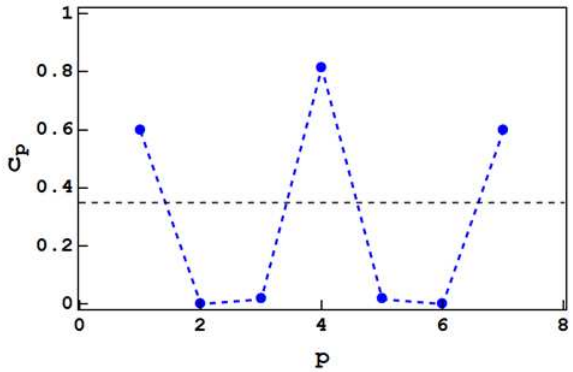
Cubo 5

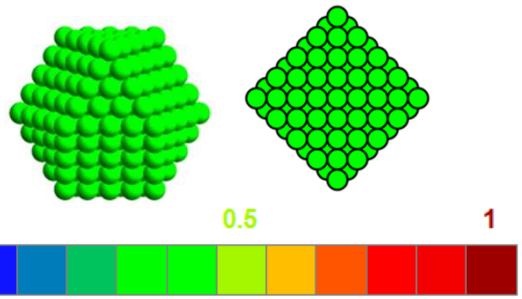
Ageing of initial uniform configurations (MFA-SK)

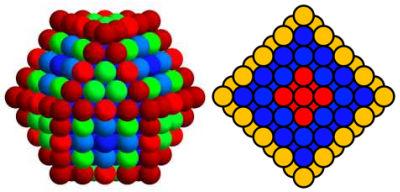


Cubo 5



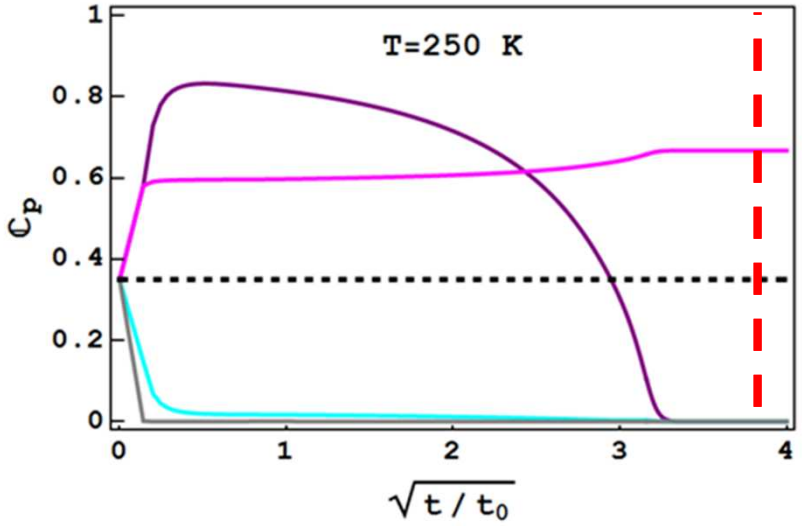




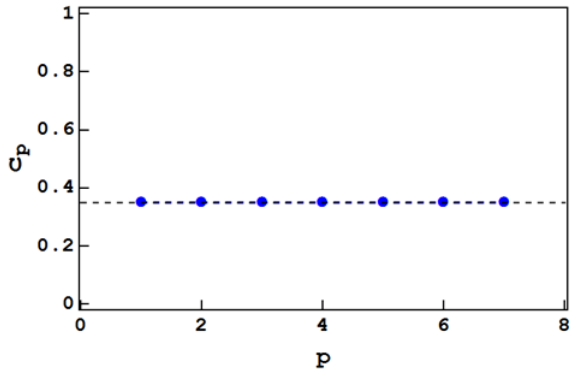


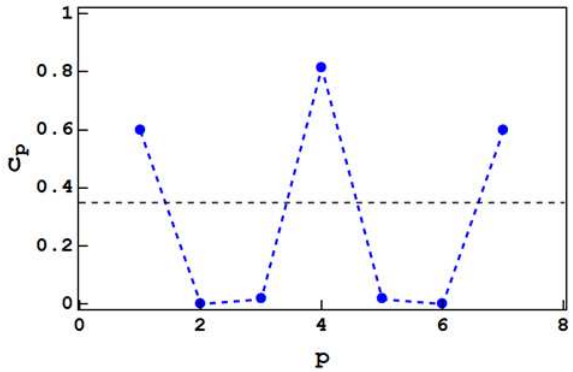
Metastable onion ?

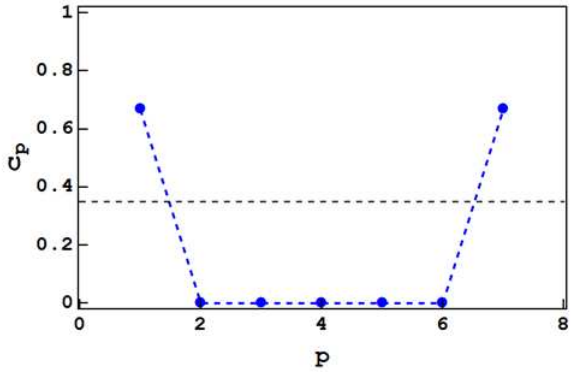
Ageing of initial uniform configurations (MFA-SK)

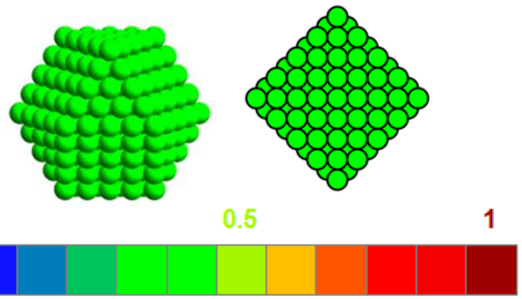


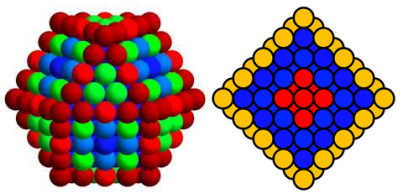
Cubo 5

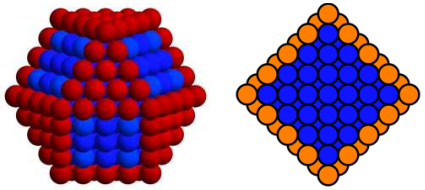




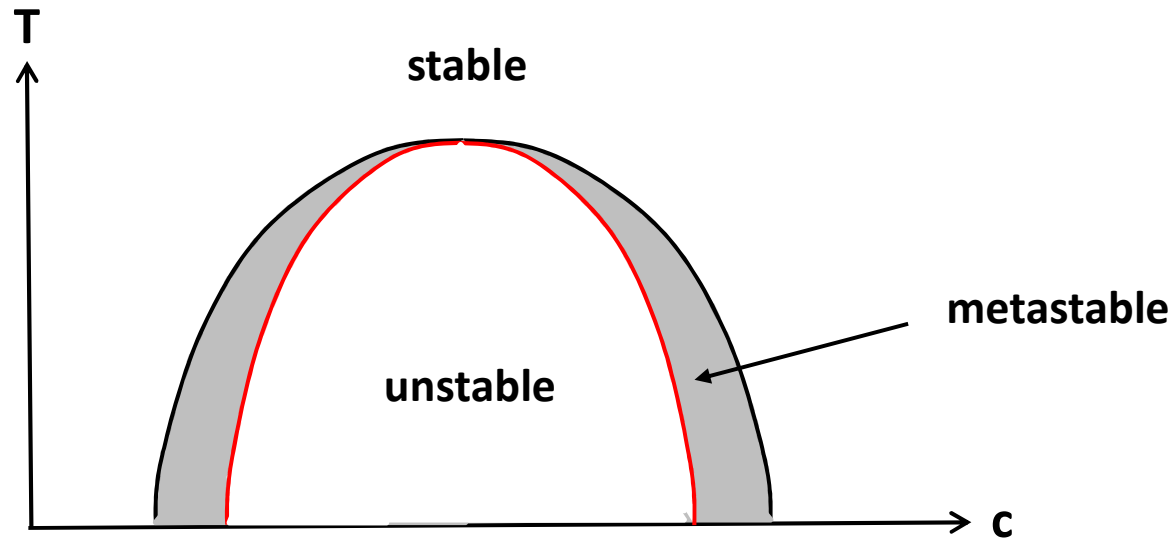








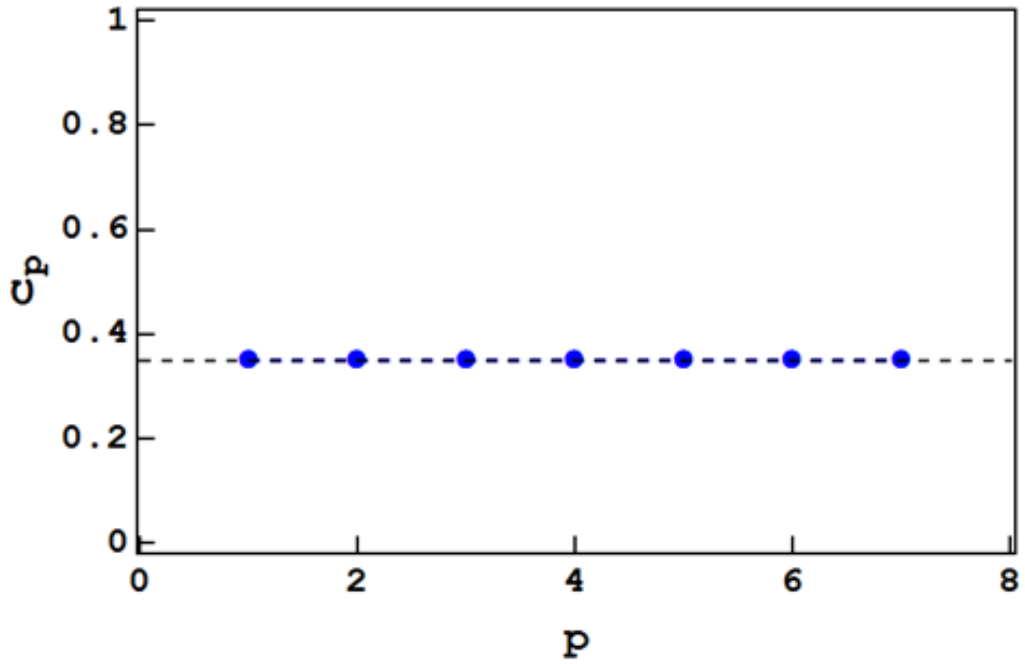
When the results raise questions



Unstable or metastable structure ??

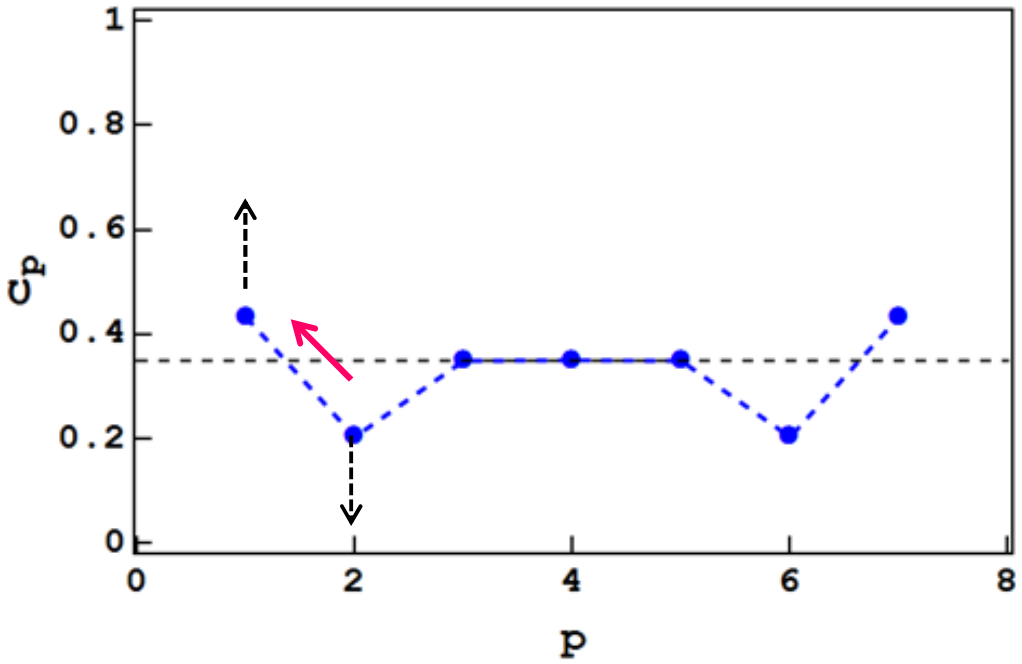
Nucleation-growth or spinodal decomposition??

Formation of the onion-like structure



Formation of the onion-like structure

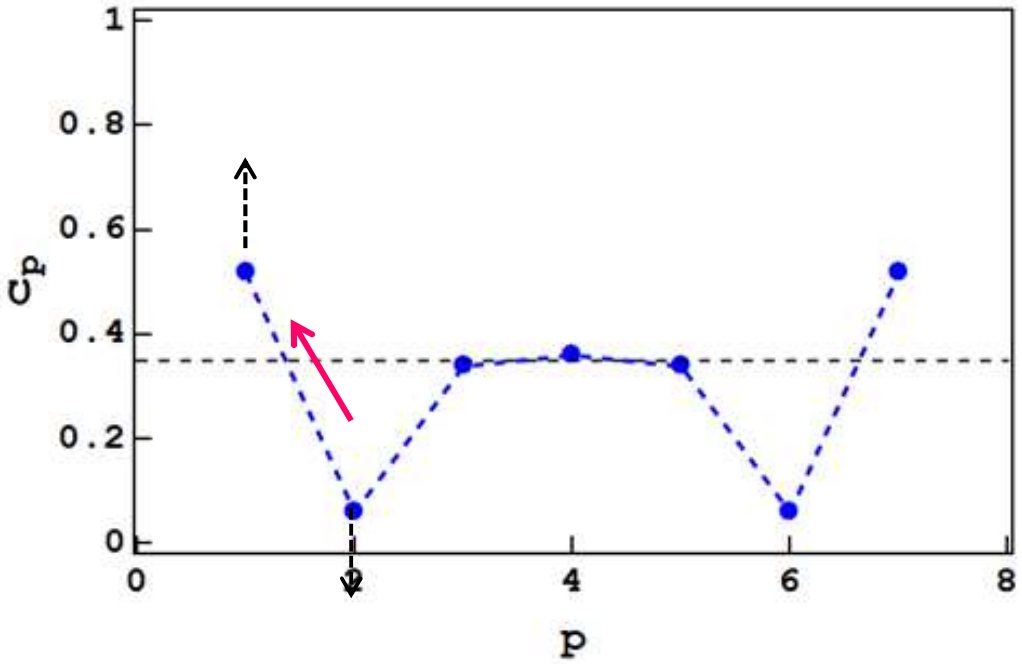
$$\frac{\partial c_p}{\partial\left({}^{t}/_{t_0}\right)} = \sum_q \left[\left(1-c_p\right)c_q\gamma_{q\to p}(\tau,V) - c_p\left(1-c_q\right)\gamma_{p\to q}(\tau,V)\right]$$



Ag surface segregation

Formation of the onion-like structure

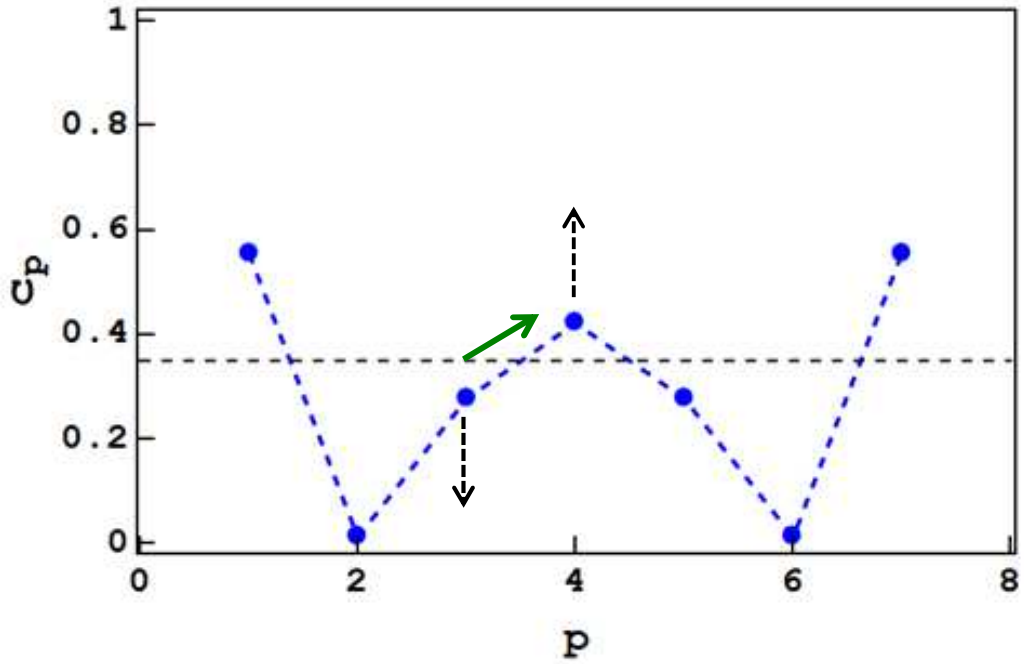
$$\frac{\partial c_p}{\partial\left({}^{t}/_{t_0}\right)} = \sum_q \left[\left(1-c_p\right)c_q\gamma_{q\to p}(\tau,V) - c_p\left(1-c_q\right)\gamma_{p\to q}(\tau,V)\right]$$



Ag surface segregation

Formation of the onion-like structure

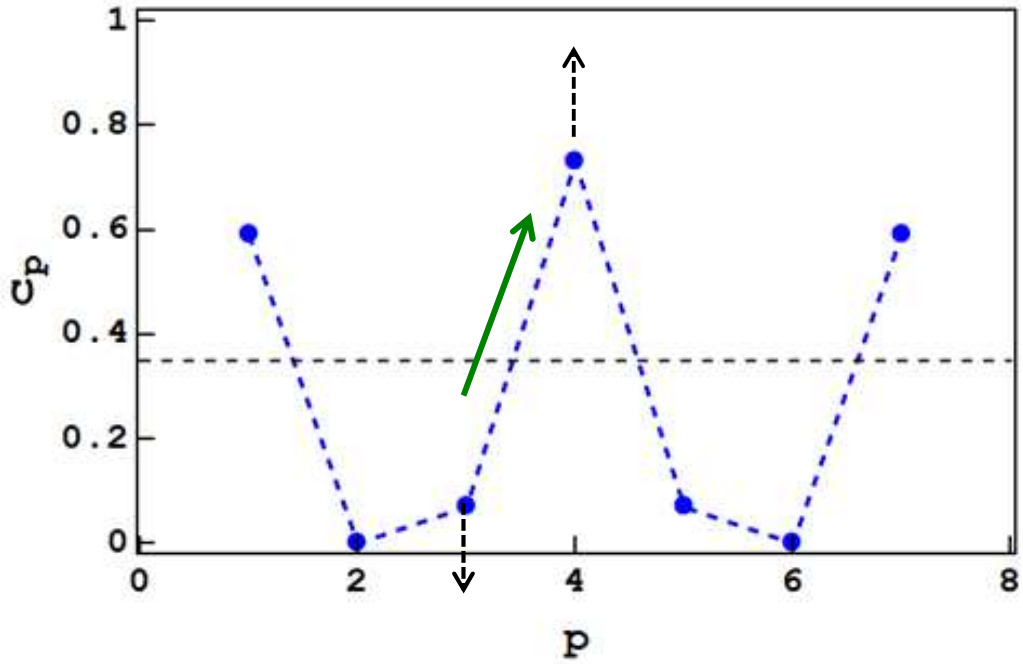
$$\frac{\partial c_p}{\partial\left({}^{t}/_{t_0}\right)} = \sum_q \left[\left(1-c_p\right)c_q\gamma_{q\to p}(\tau,V) - c_p\left(1-c_q\right)\gamma_{p\to q}(\tau,V)\right]$$



Ag surface segregation

phase separation

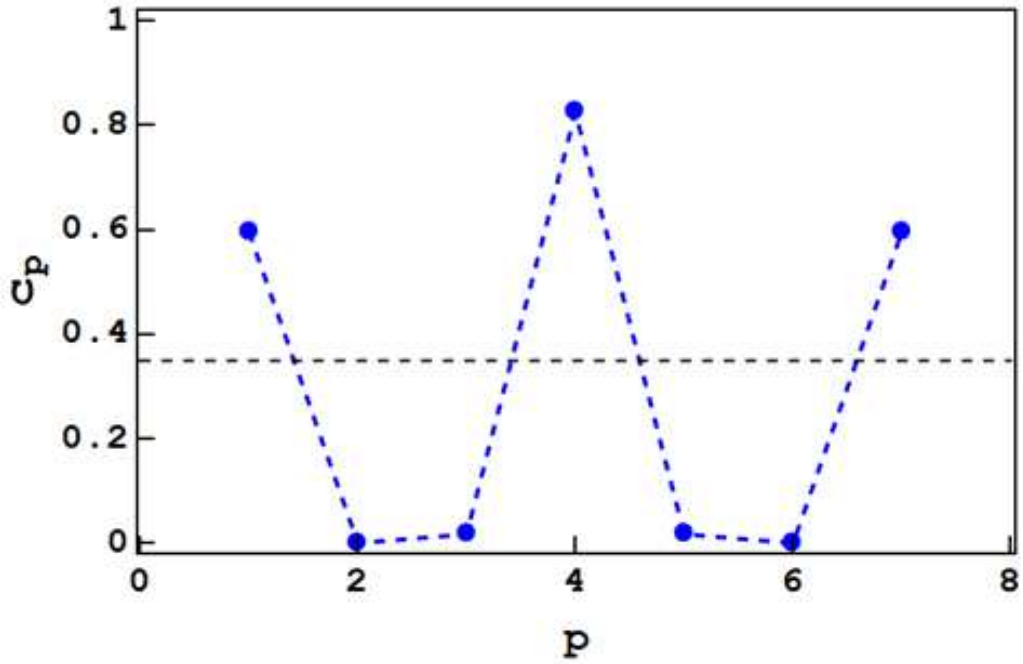
Formation of the onion-like structure



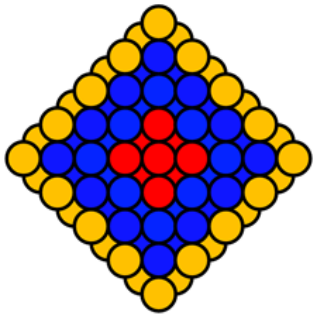
Ag surface segregation

phase separation

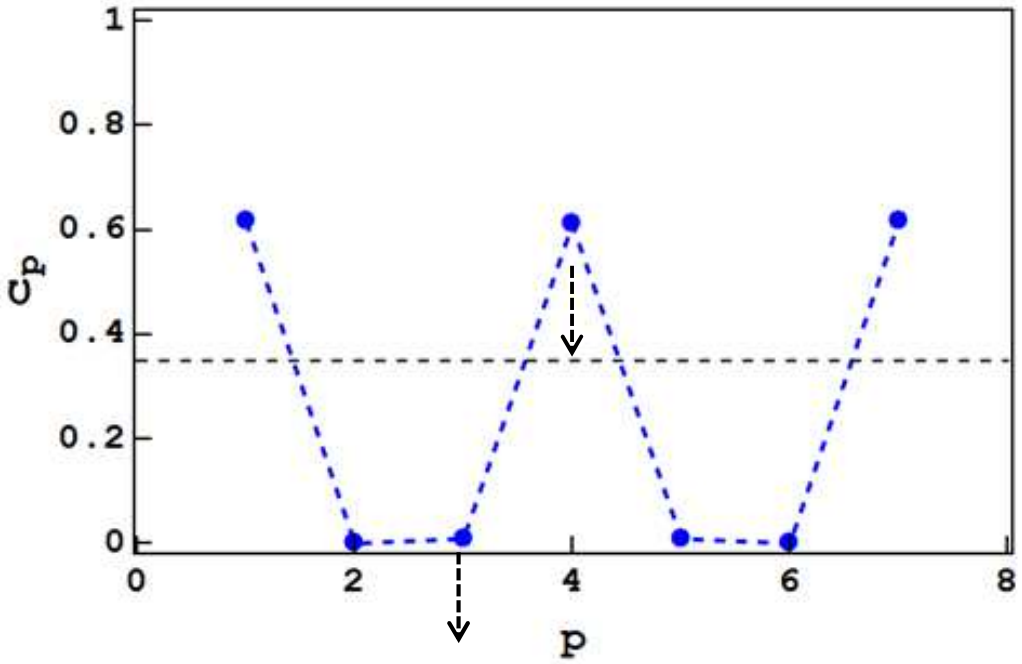
Formation of the onion-like structure



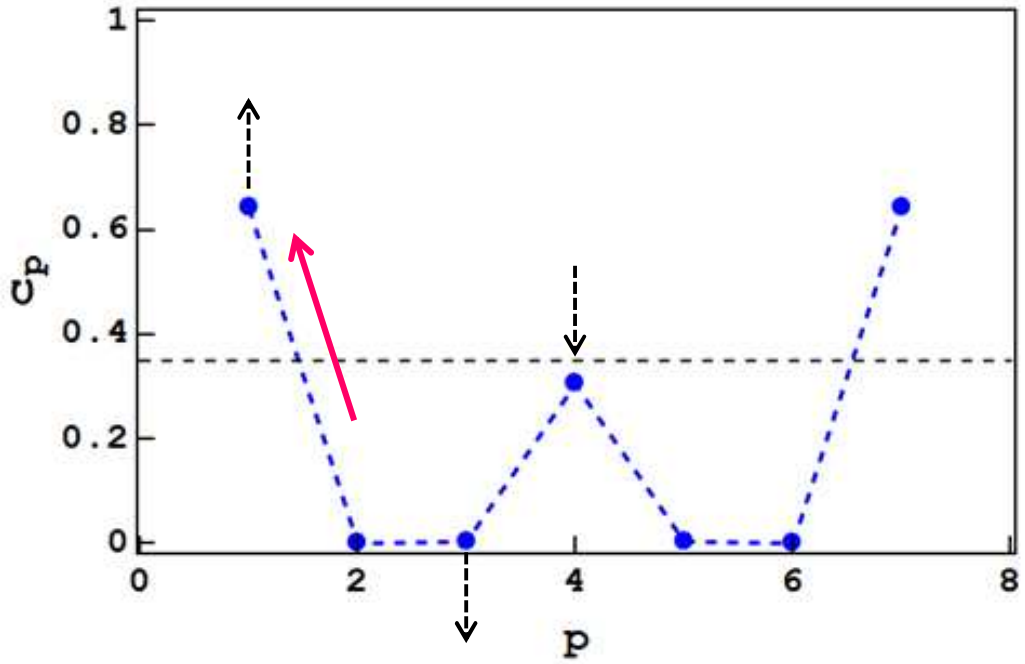
Onion-like structure : 2 interfaces Ag/Cu



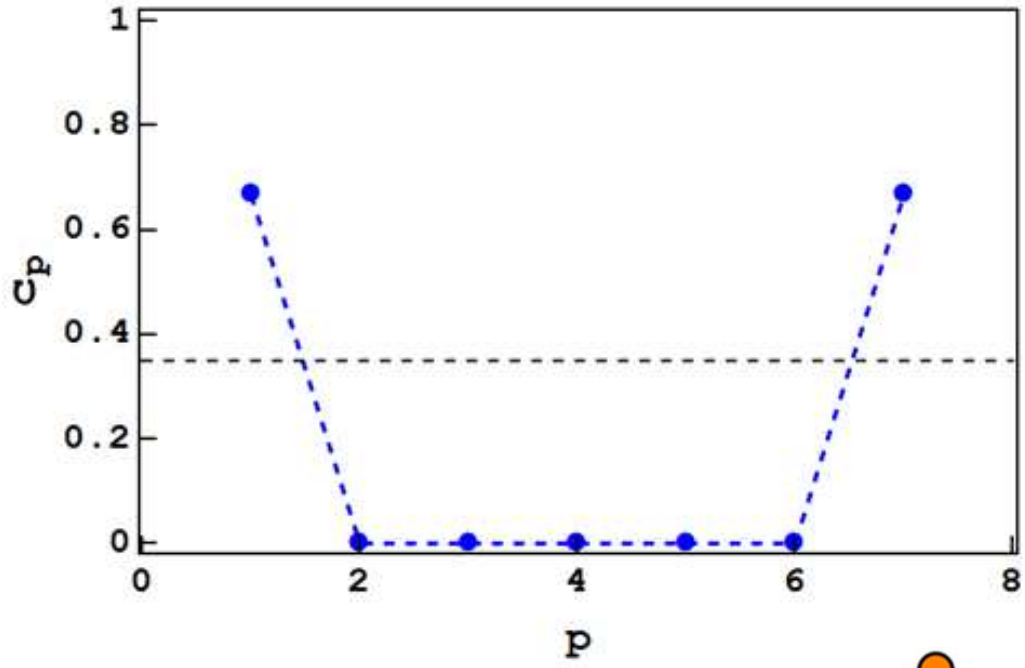
Dissolution of the onion-like structure



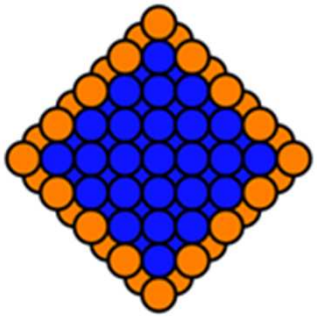
Dissolution of the onion-like structure

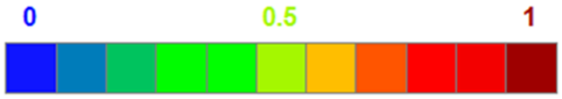


Dissolution of the onion-like structure

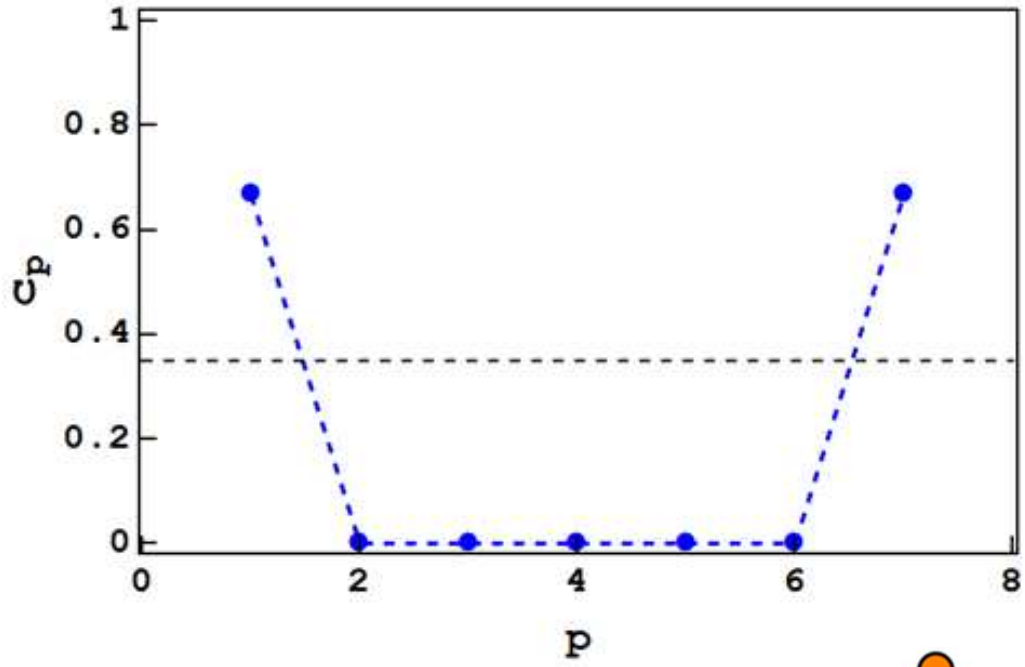


Core-Shell structure : 1 interface Ag/Cu

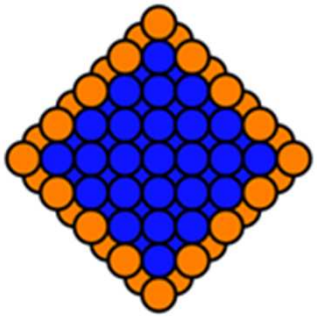




Dissolution of the onion-like structure

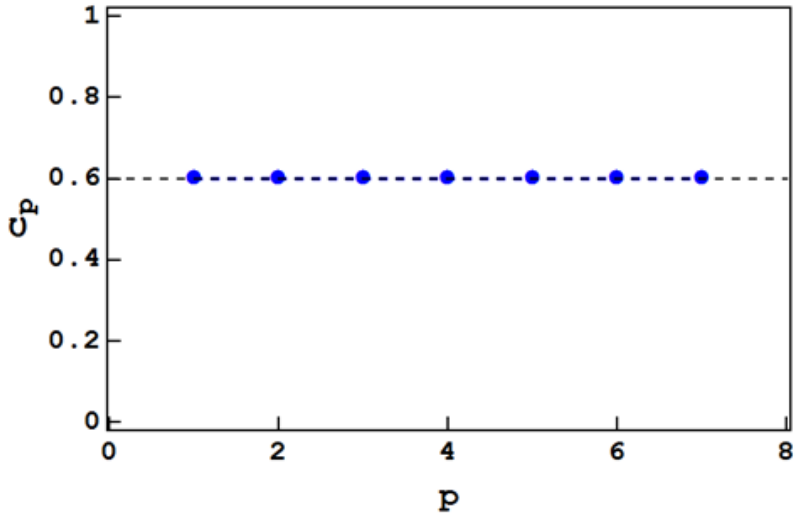


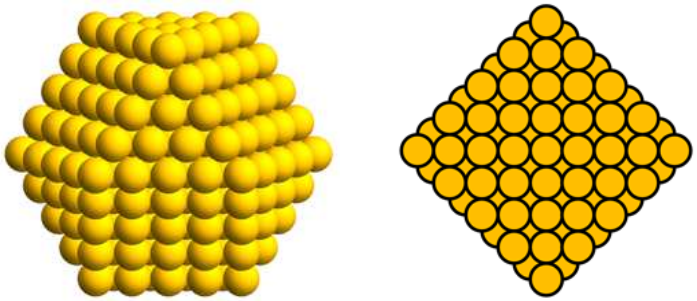
Core-Shell structure : 1 interface Ag/Cu



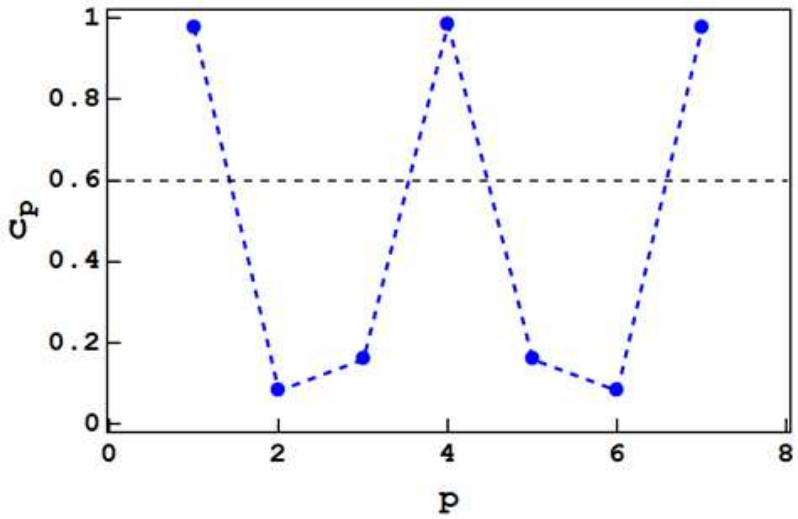
Nucleation-growth or spinodal decomposition??

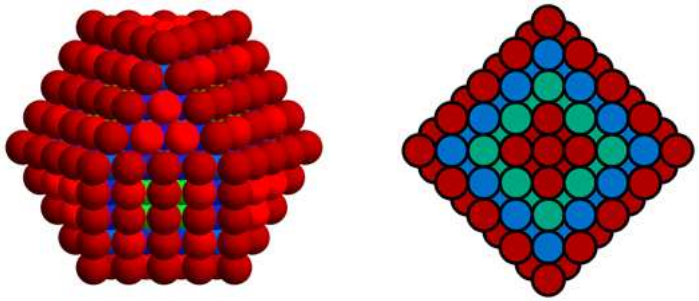
Influence of the concentration

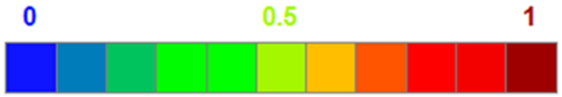




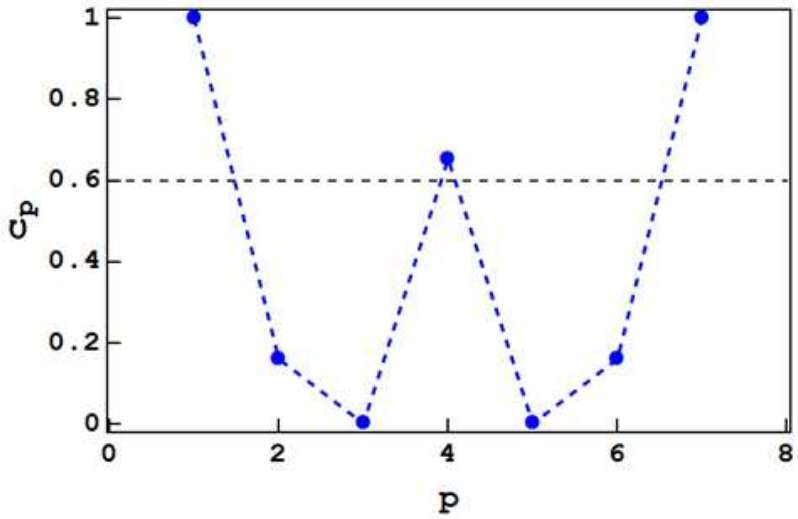
Influence of the concentration

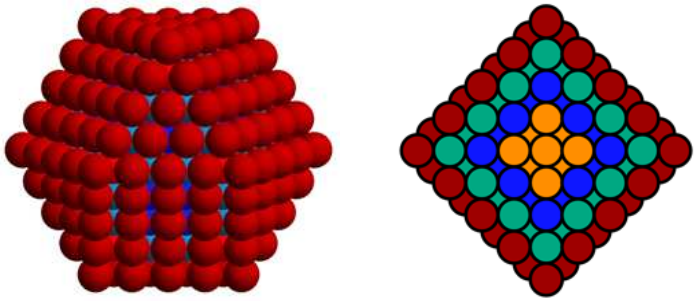


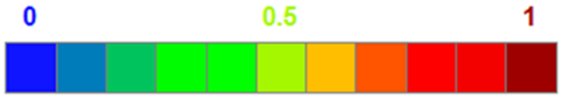




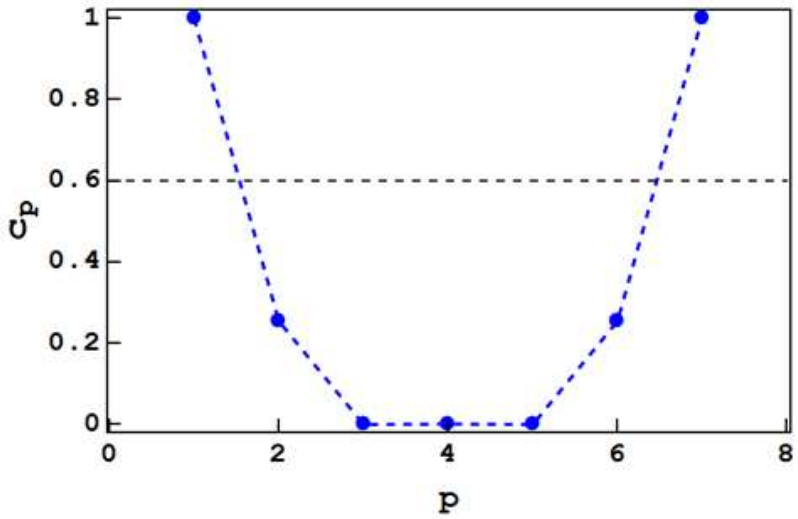
Influence of the concentration

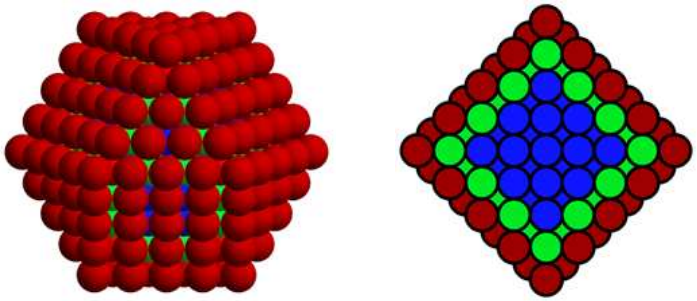


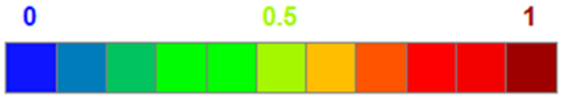




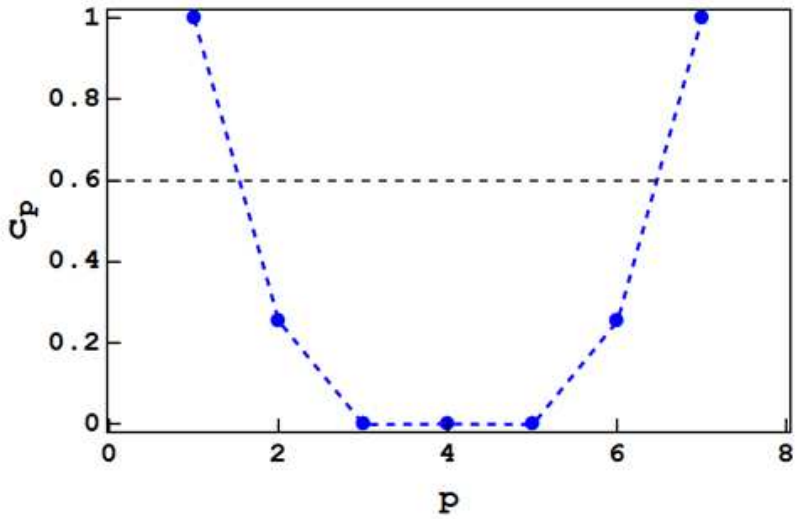
Influence of the concentration

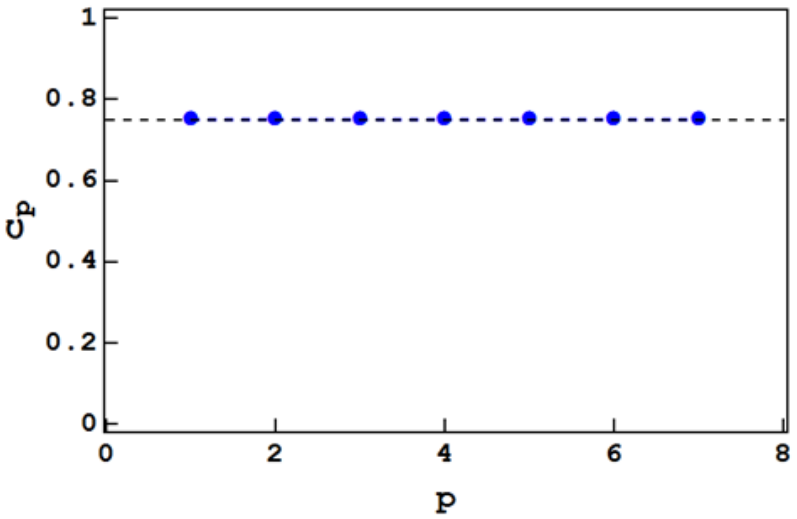


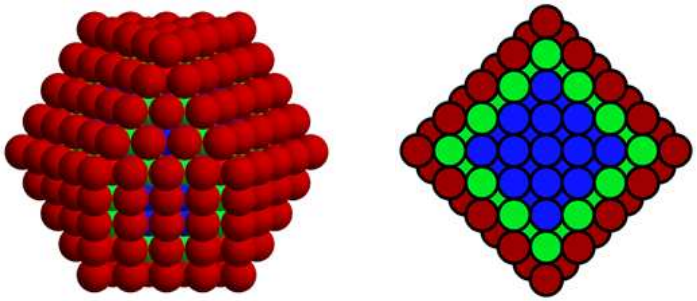


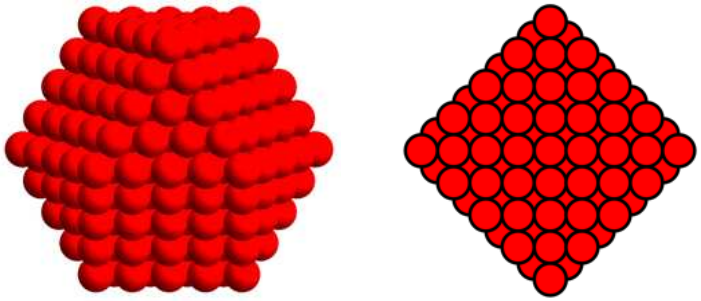


Influence of the concentration

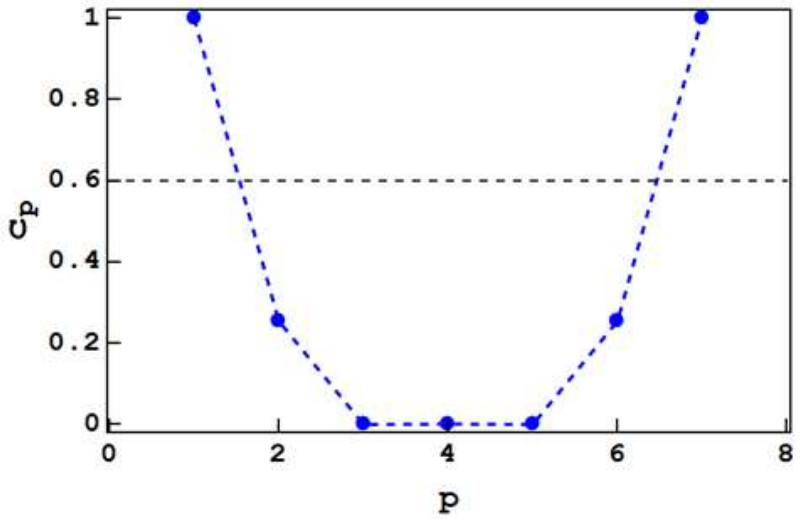


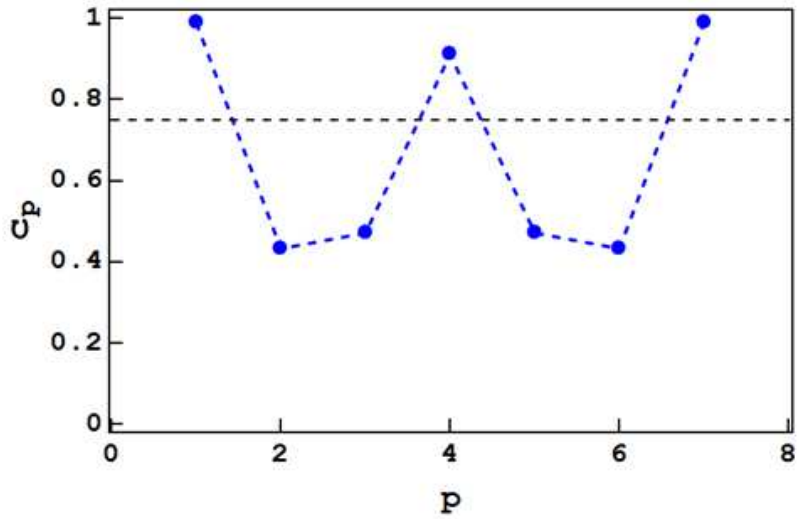


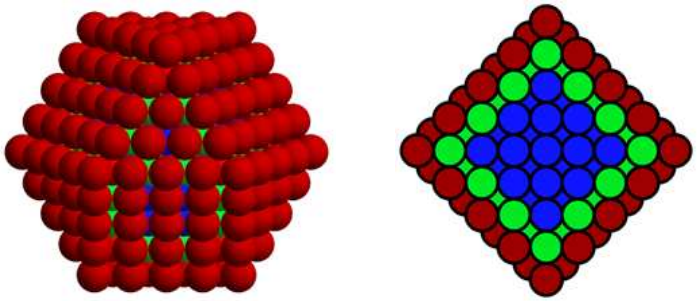


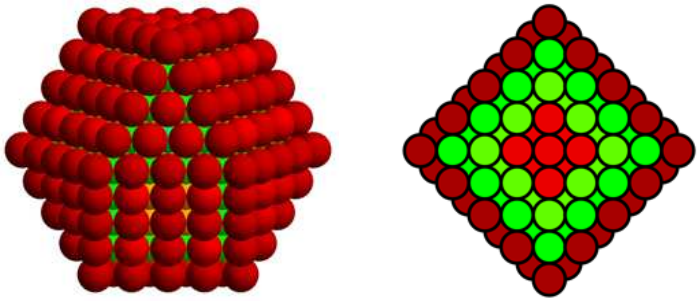


Influence of the concentration

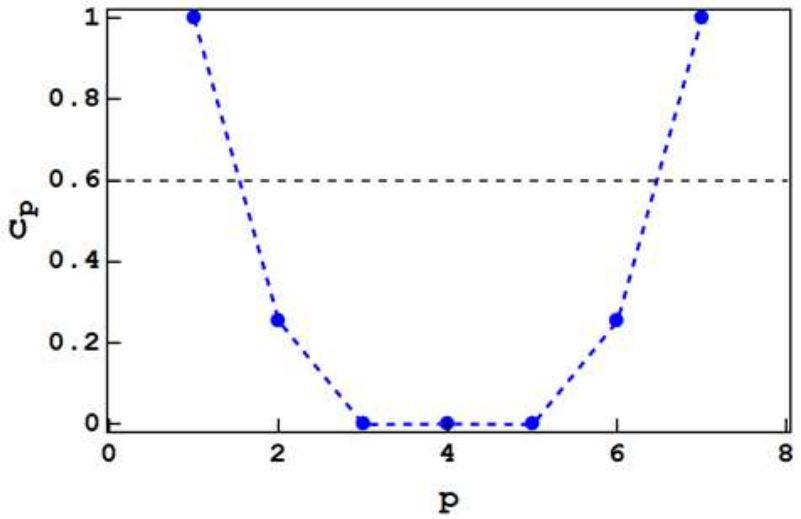


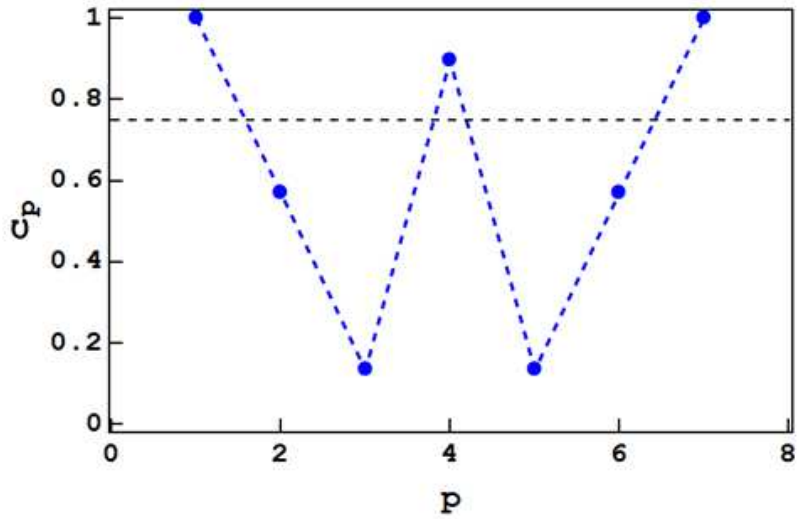


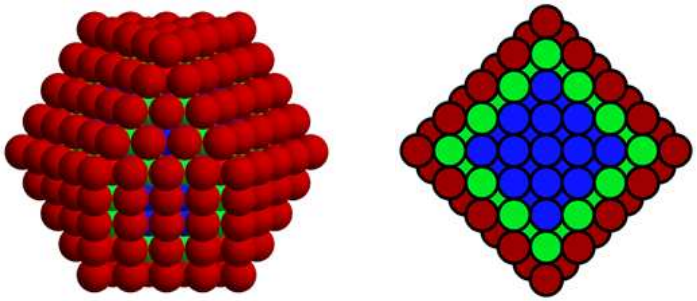


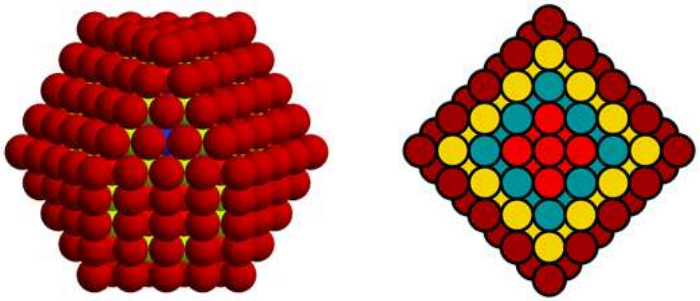


Influence of the concentration

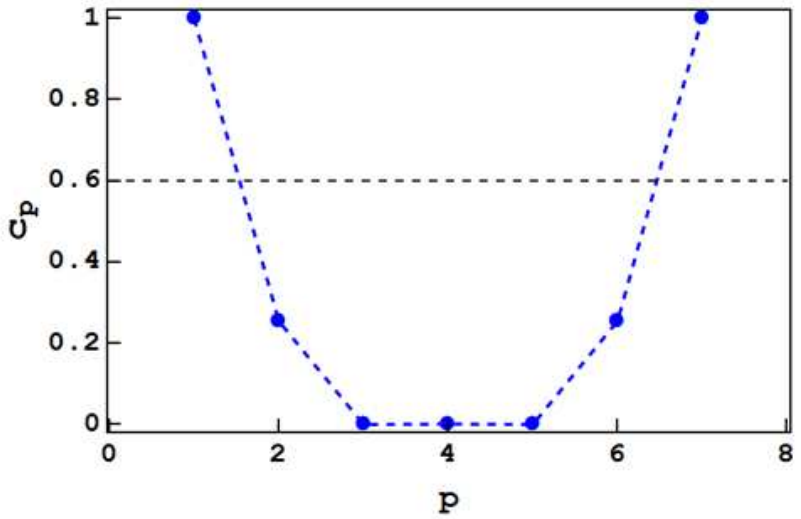


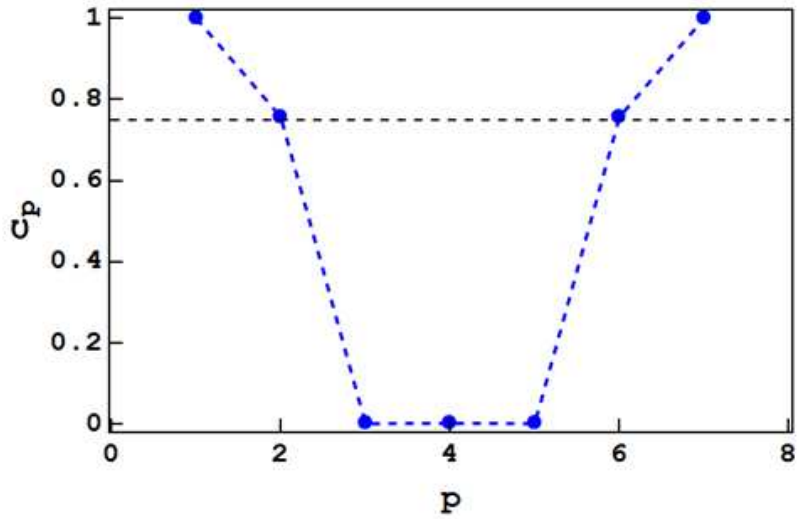


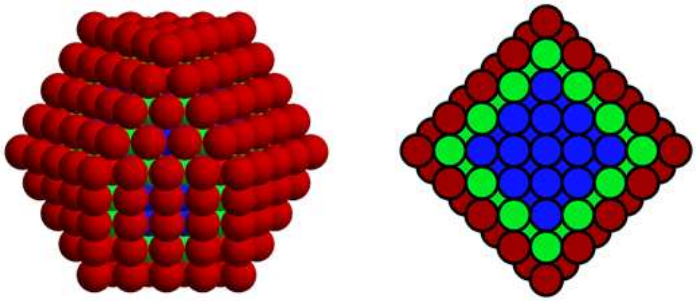


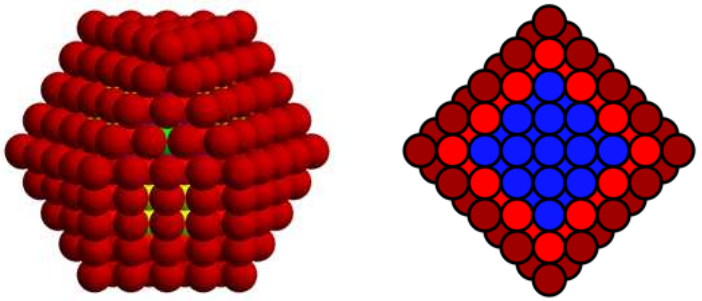


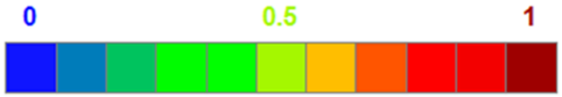
Influence of the concentration





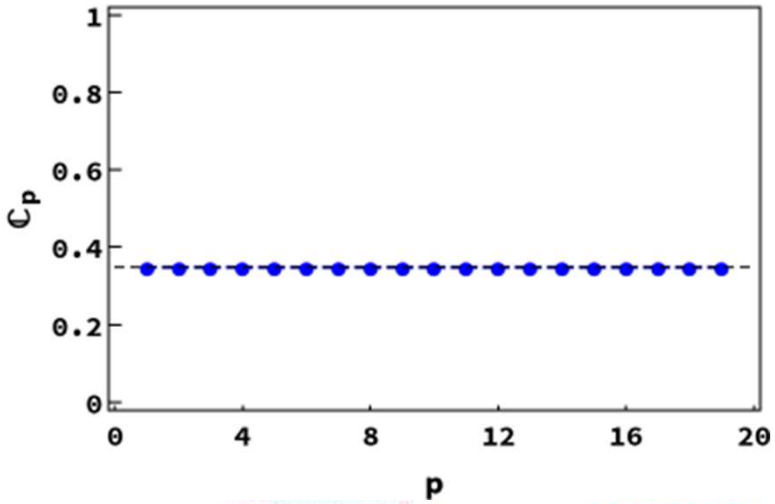


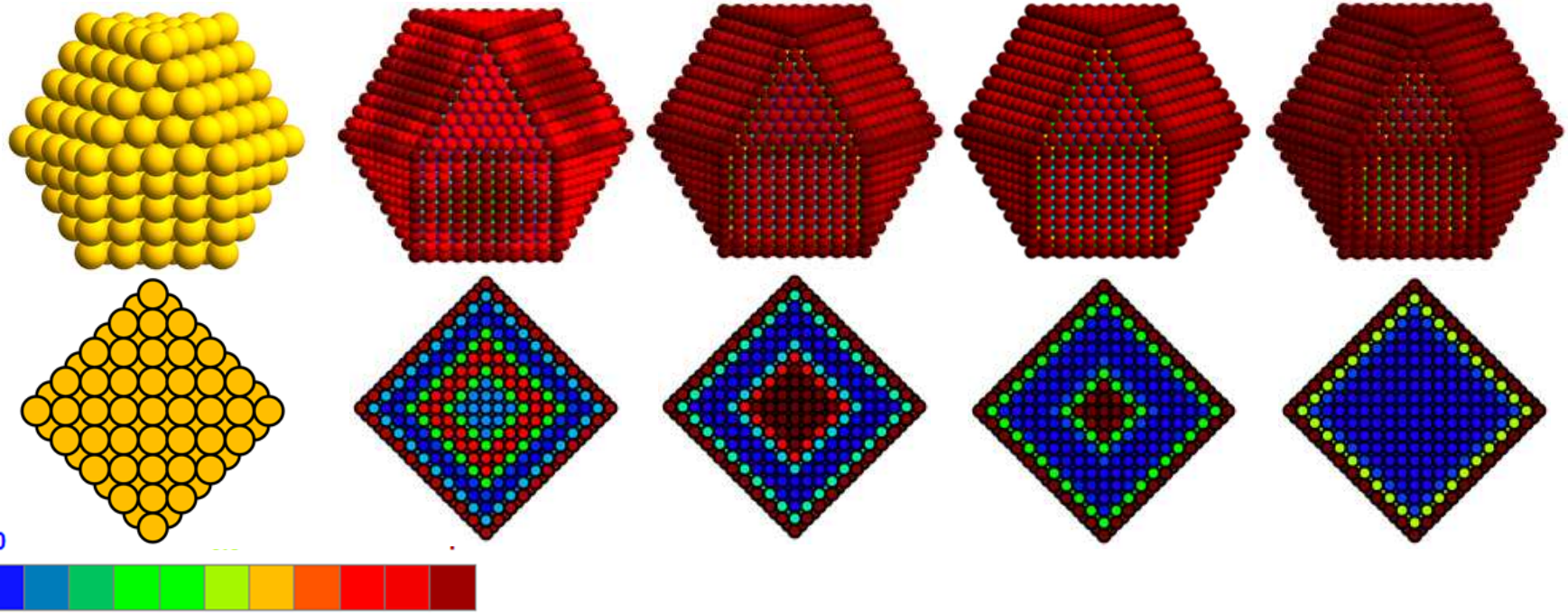




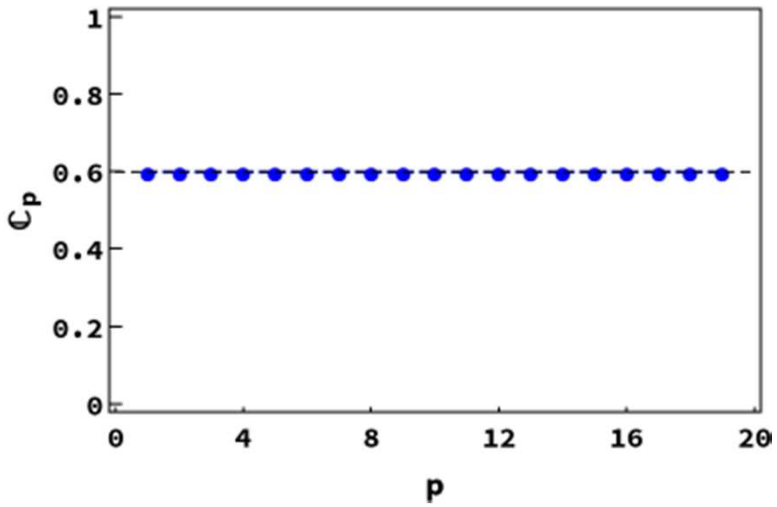
Nucleation-growth or spinodal decomposition??

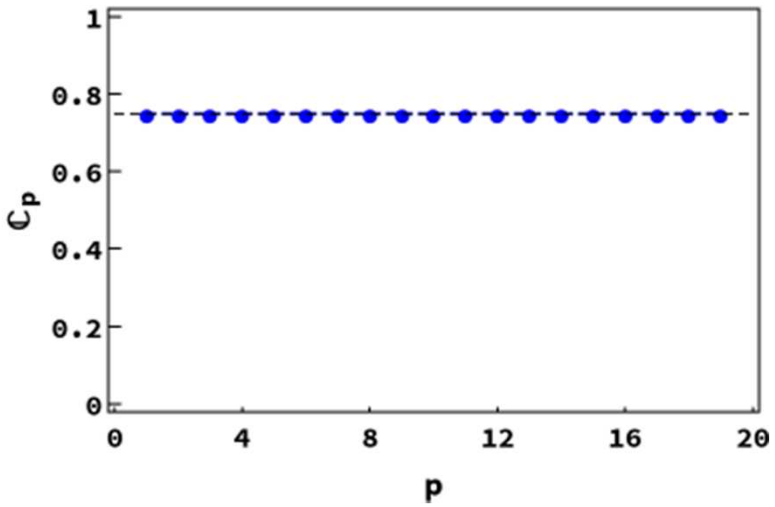
Influence of the size





Size and concentration



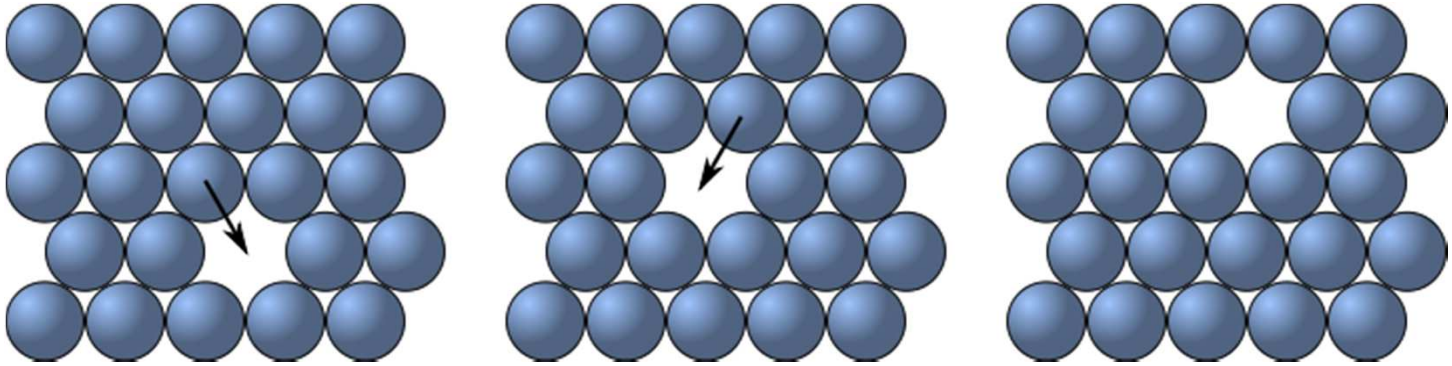


spinodal decomposition

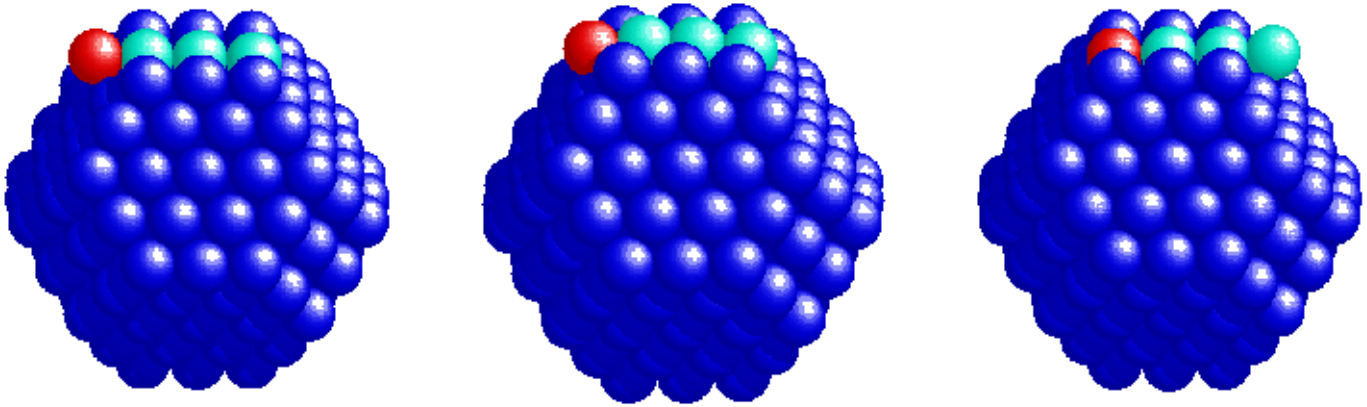
Conclusions

Diffusion mechanisms

Vacancy



Collective move of atoms



F. Baletto *et al.*, Surface Science **446** (2000) 31

Kinetic Monte Carlo (KMC)