MULTISCALE SIMULATIONS OF ELECTRODEPOSITION : EFFECT OF SUPERFICIAL DIFFUSION

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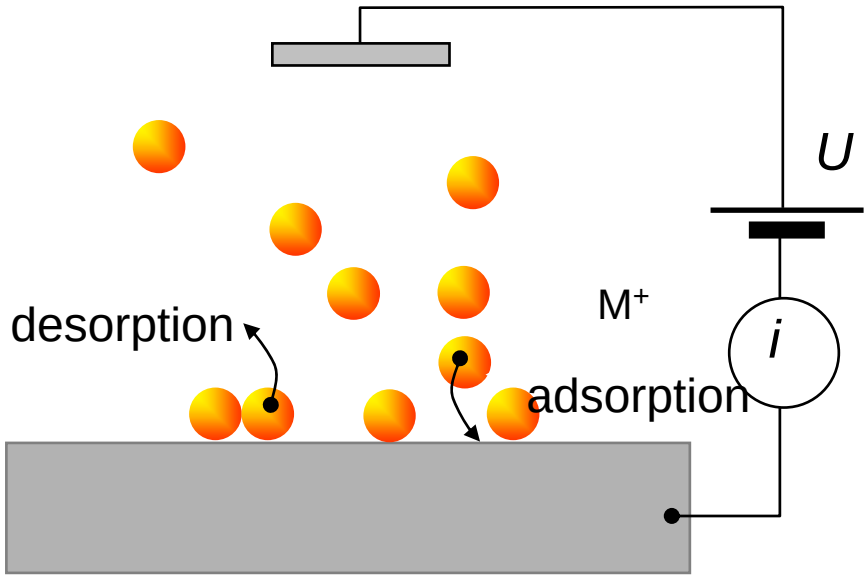
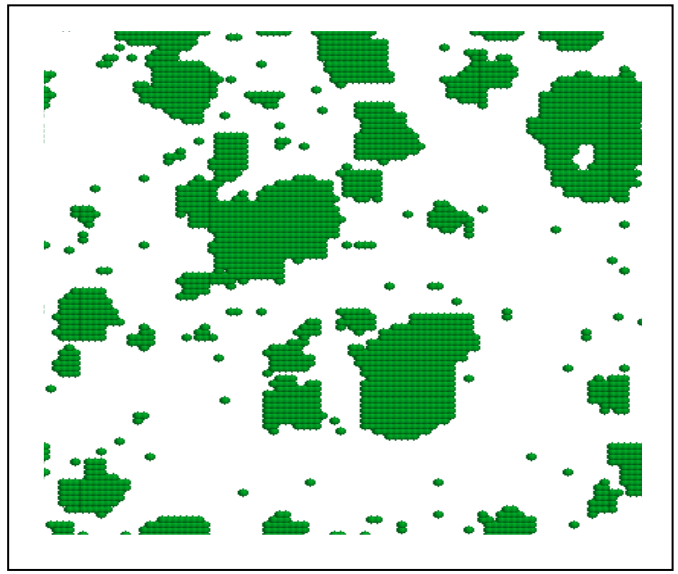
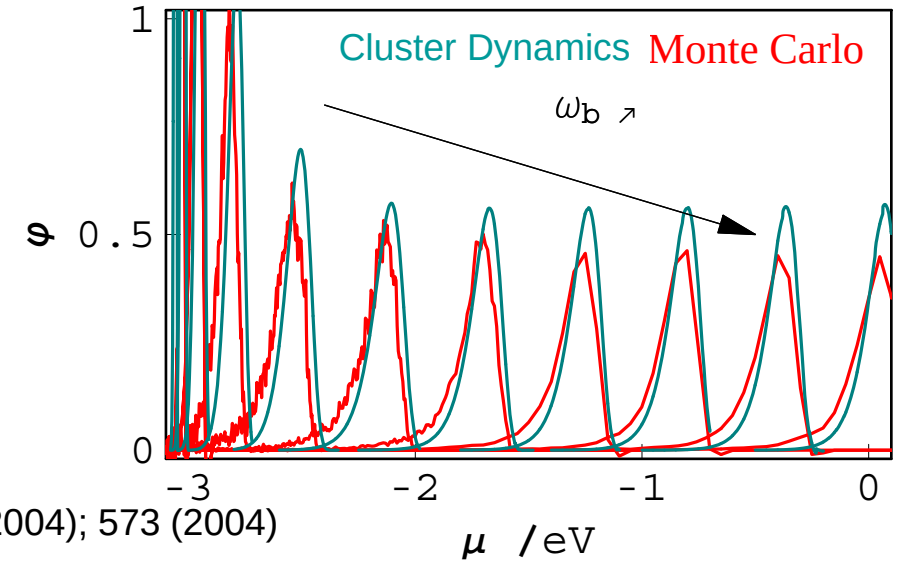
Multiscale simulations of adsorption/desorption



Ag/Cu (001)



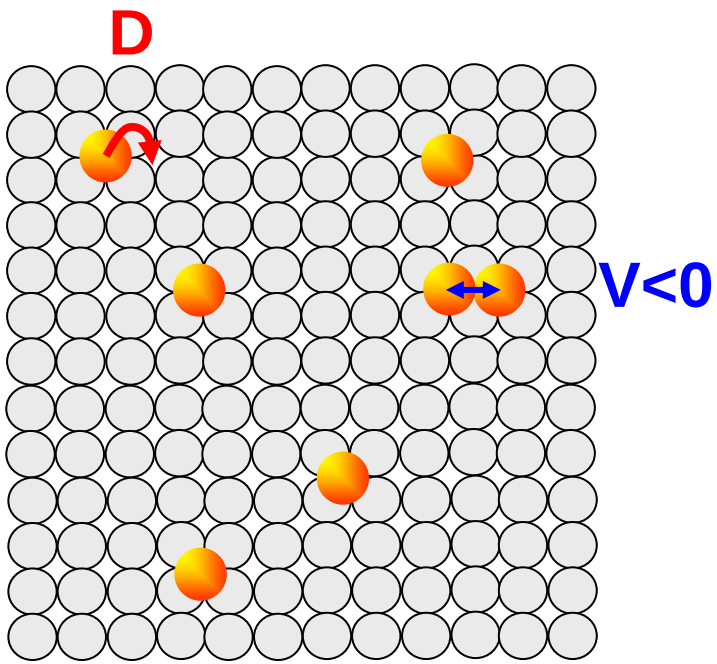
adsorption/desorption and superficial diffusion ?



F. Berthier ..., *J. Electroanal. Chem.* 561 (2004); 562 (2004); 573 (2004)

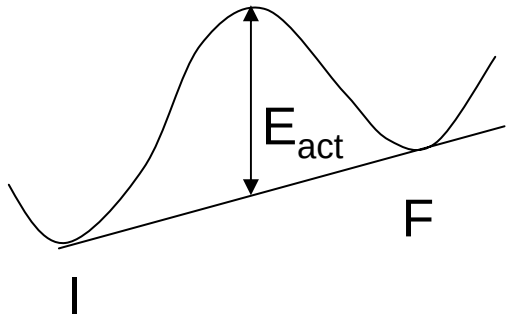
Preliminary study : Ageing of deposition

Ag/Cu (001)



Atomistic simulations : KMC

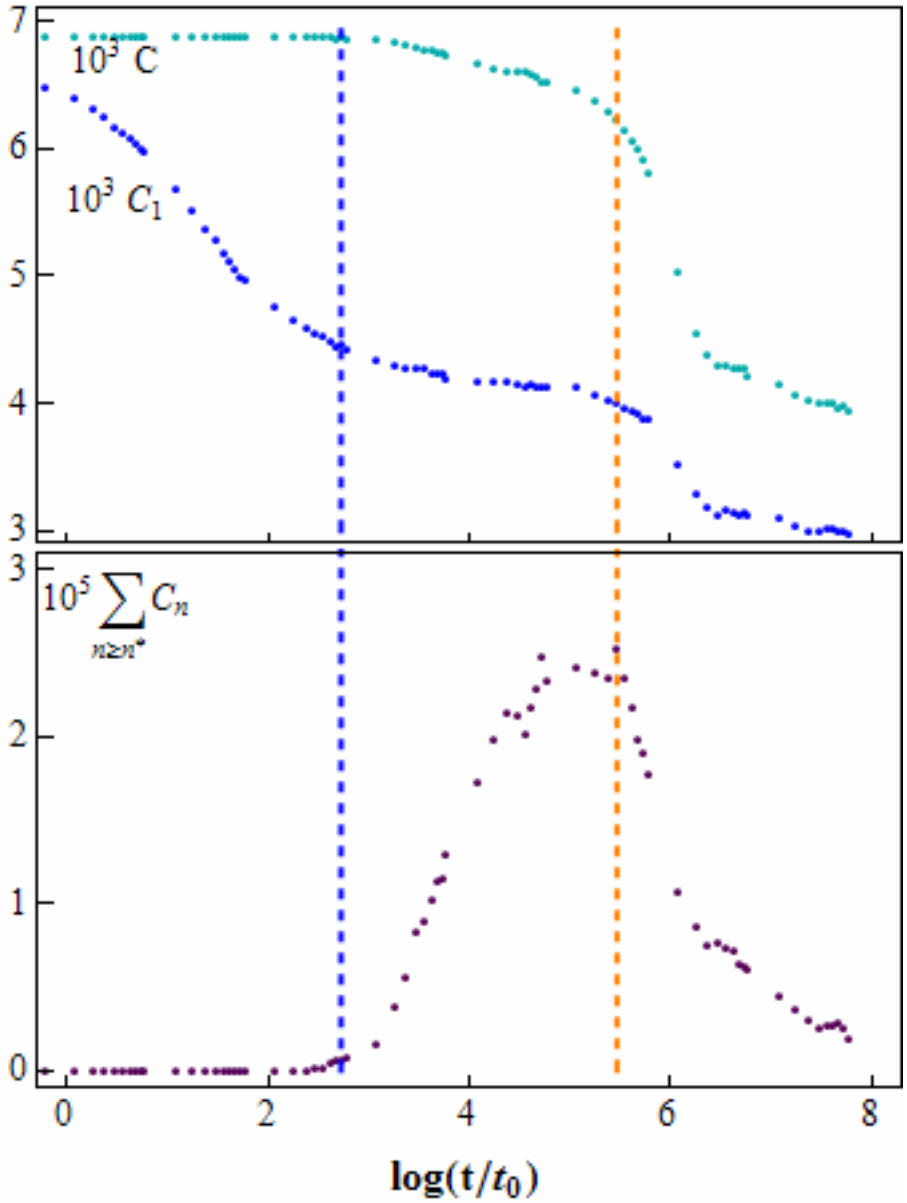
$$P_{I \to F} = \exp\left(-\frac{E_{act}}{k_B T}\right) \exp\left(-\frac{(n_F - n_I)V}{k_B T}\right)$$



$$D \propto \nu \exp\left(-\frac{E_{act}}{k_B T}\right)$$

$$t = N^{KMC} / \nu$$

Monte Carlo Kinetics



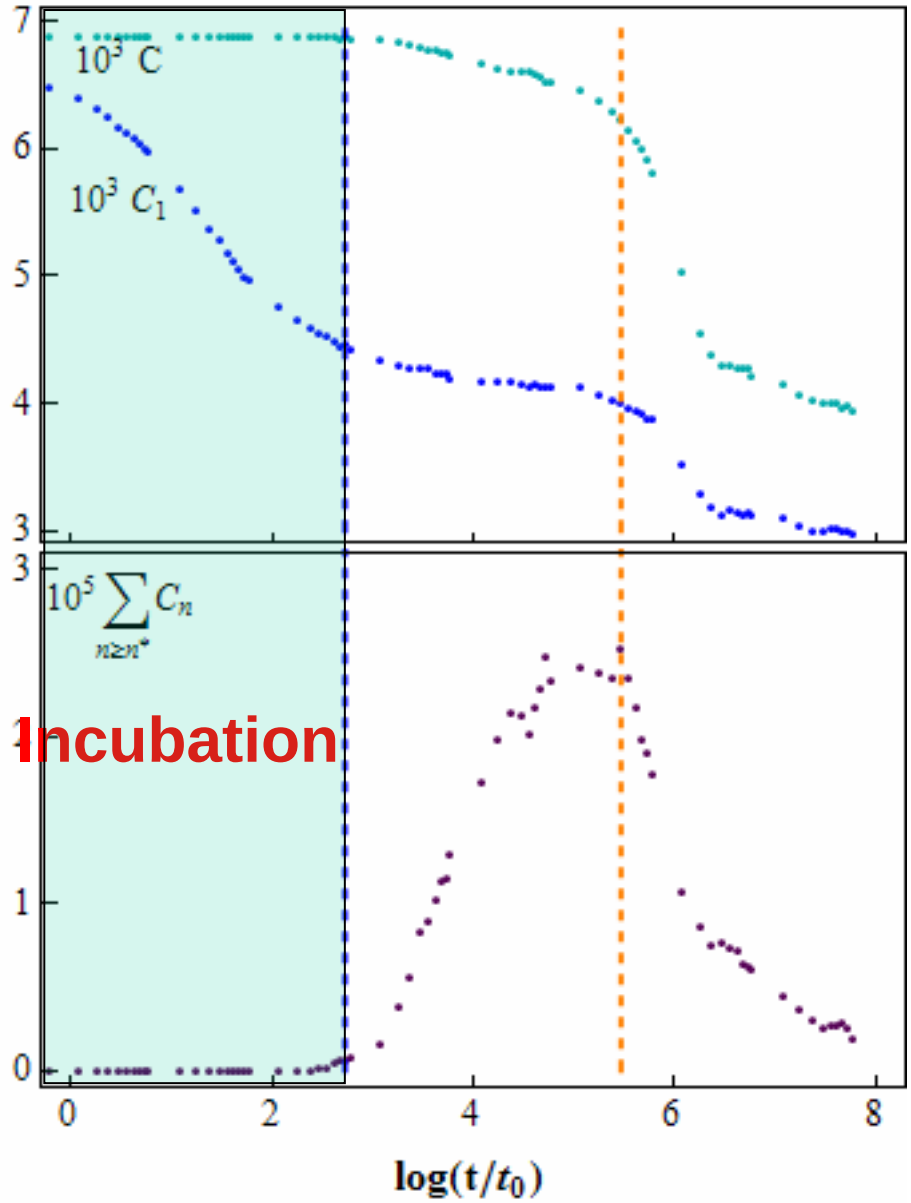
$T / T_c = 0.2$

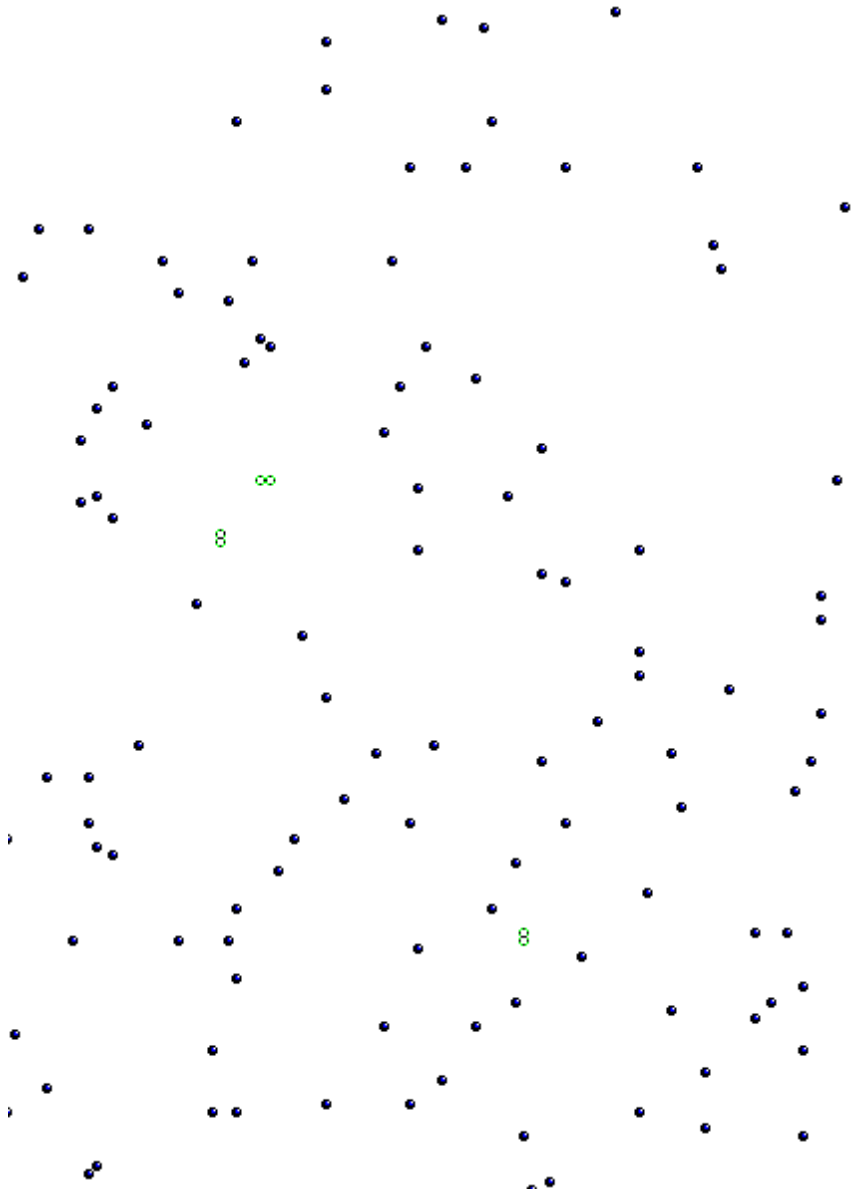
$N_i = 6900$

$N_s = 10^6$

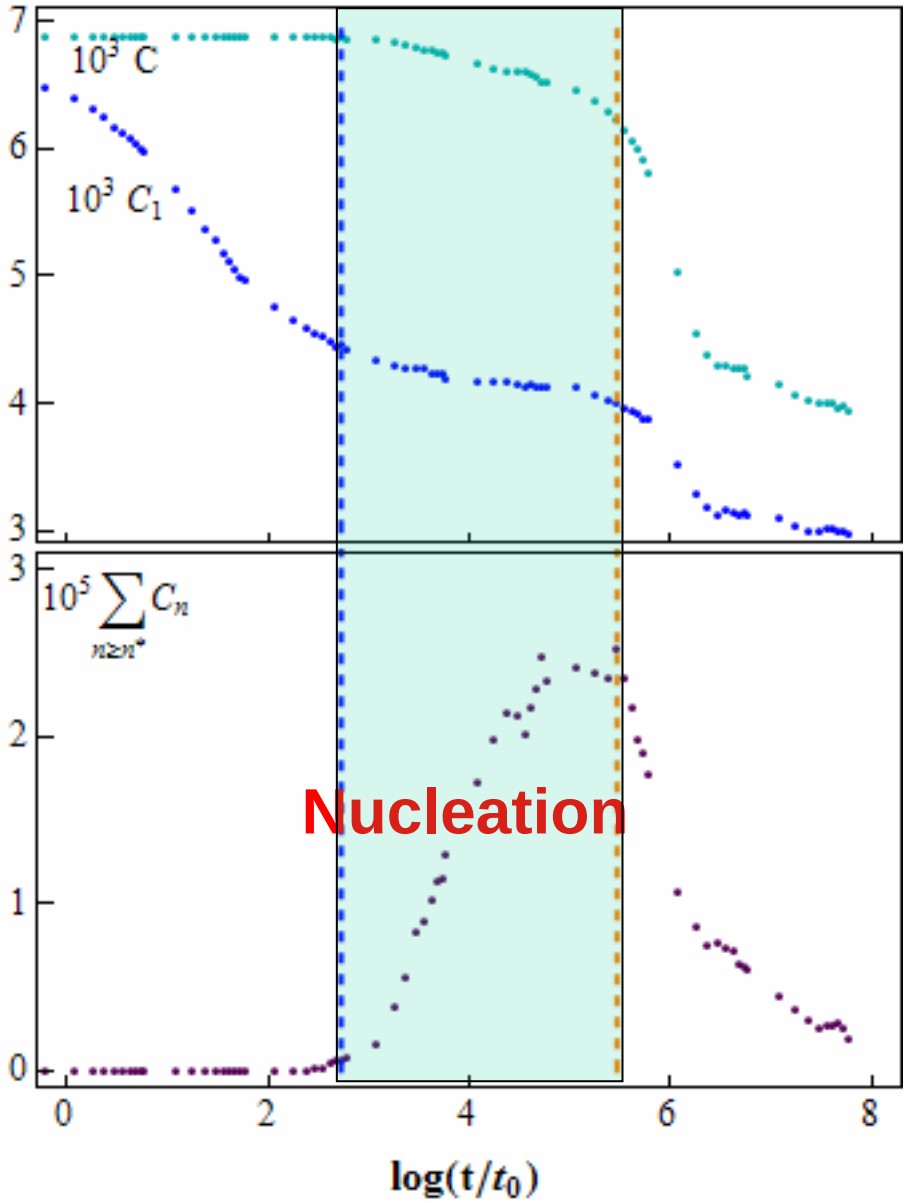
$n^* = 9$

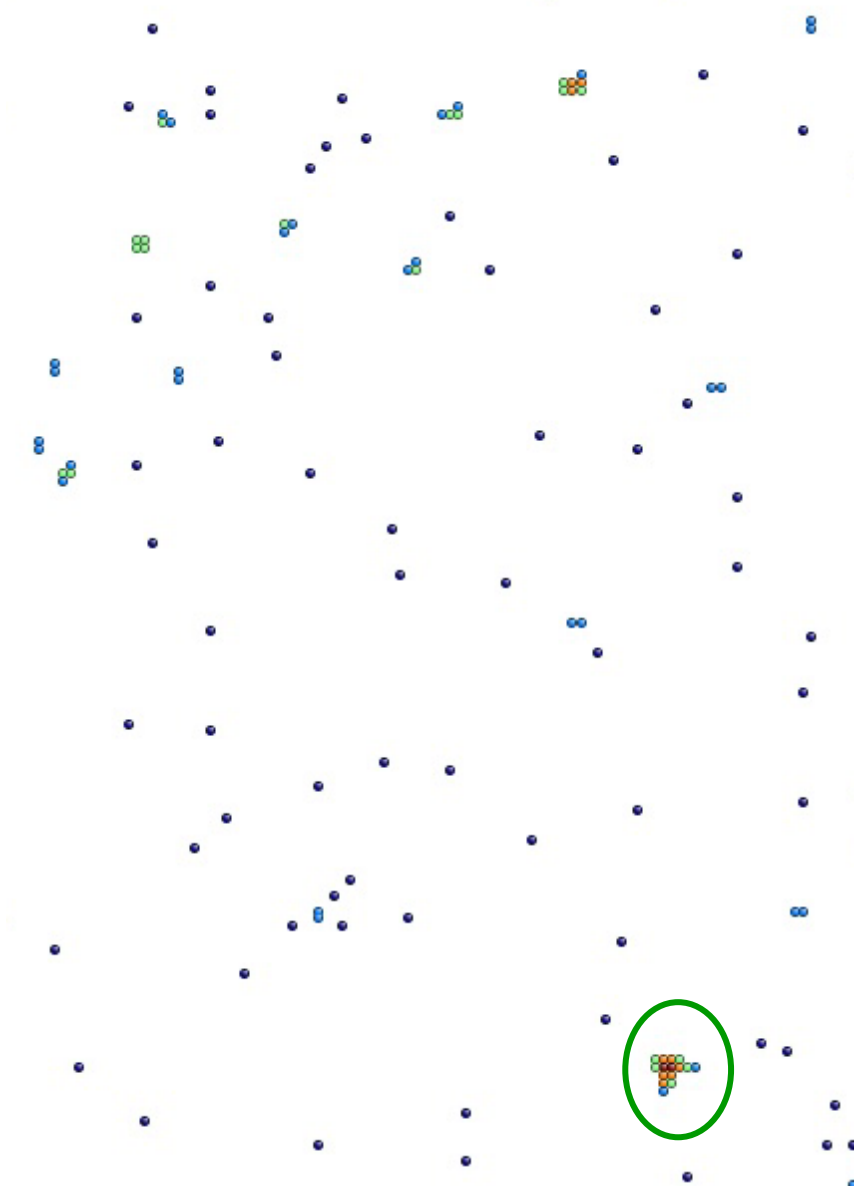
Monte Carlo Kinetics



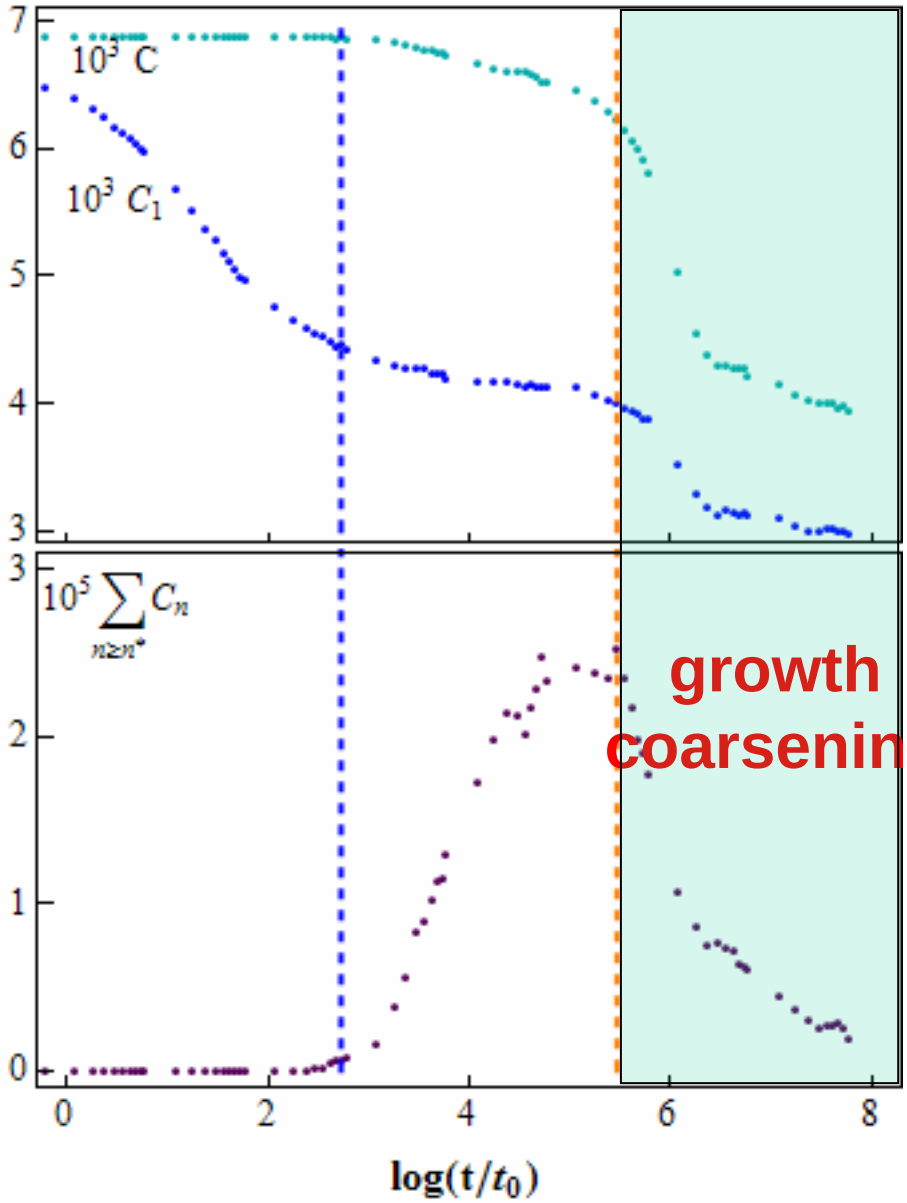


Monte Carlo Kinetics





Monte Carlo Kinetics



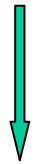
very time consuming…

Mesoscopic modelling : Cluster Dynamics (CD)

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

$n = 1,\ldots, ?$

$C_n(t) \rightarrow C(x,t)$ (Fokker-Planck type equation)

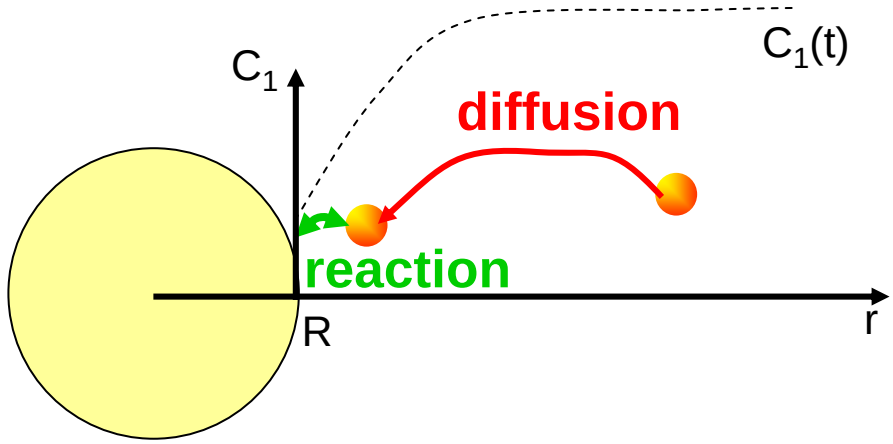


$x \rightarrow n + \Delta x$

$\beta_n, \alpha_n = ?$

Mesoscopic modelling : Cluster Dynamics (CD)

$$\beta_n, \alpha_n = ?$$



$$C_I = 0$$

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

mesoscopic description

$$C_I = C_1$$

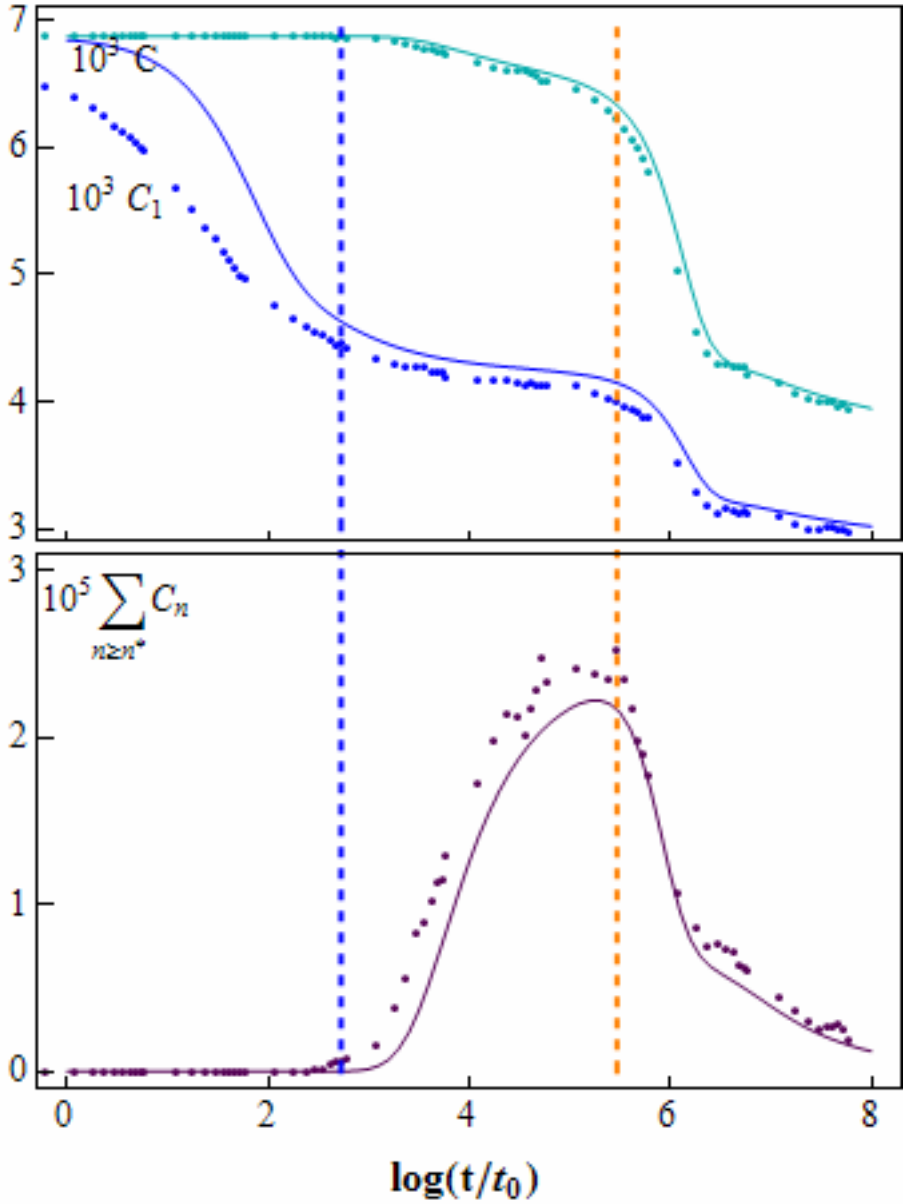
$$\frac{dn}{dt} = \beta_n C_I - \alpha_n\left(1 - C_I\right)$$

atomistic description

Kinetics controlled by the diffusion

$$\beta_n \propto DC_1$$

$$\alpha_{n+1} \propto \frac{C_n^{eq}}{C_{n+1}^{eq}} DC_1^{eq}$$



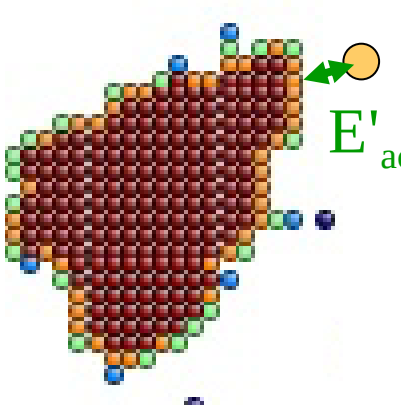
KMC

CD

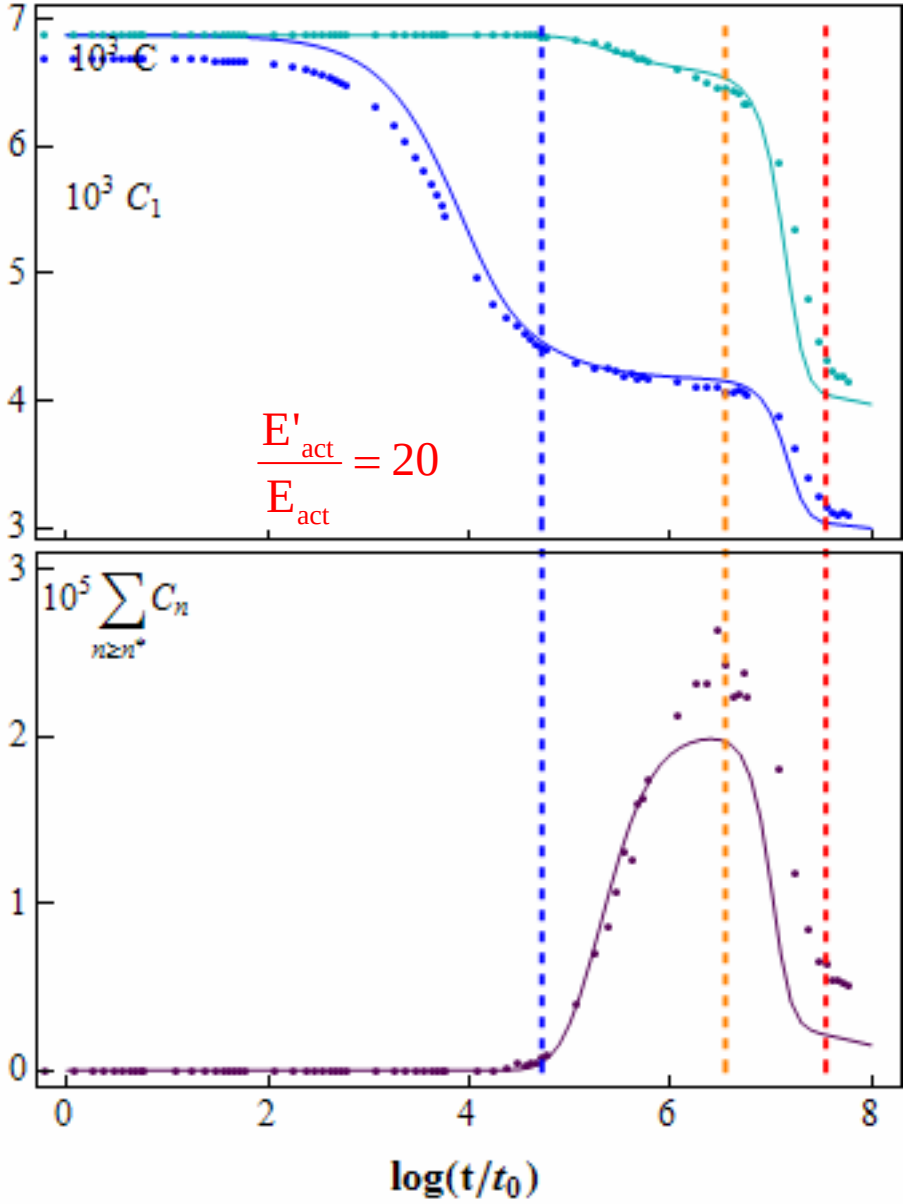
Kinetics controlled by the reaction

$$\beta_n \propto C_1 \exp\left(-\frac{E'_{act}}{kT}\right)\sum_i N_n^{iB,+} \exp\left(-\frac{n_i V}{kT}\right)$$

$$\alpha_n \propto \exp\left(-\frac{E'_{act}}{kT}\right)\sum_i N_n^{iB,-} \exp\left(\frac{n_i V}{kT}\right)$$

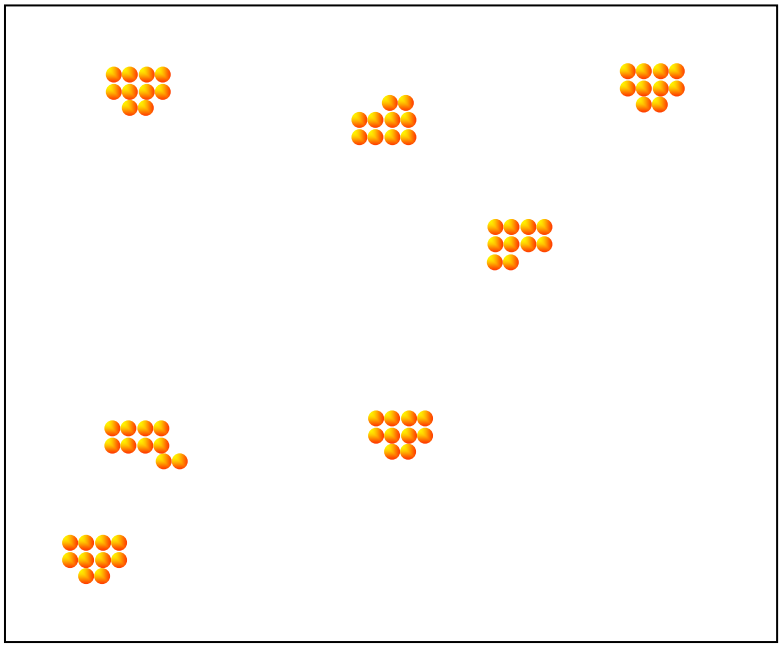


$E'_{act} >> E_{act}$

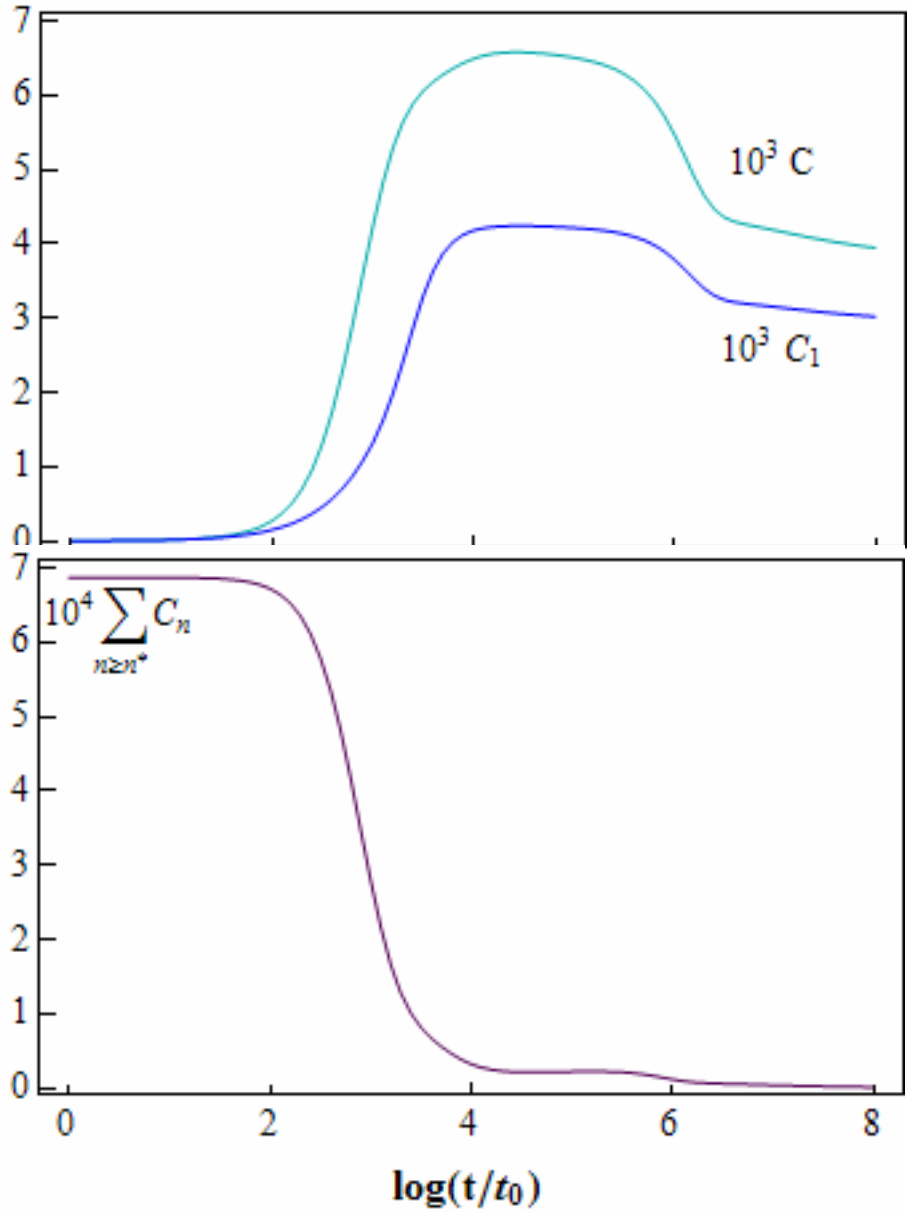


Application of CD

stability of homogeneous clusters

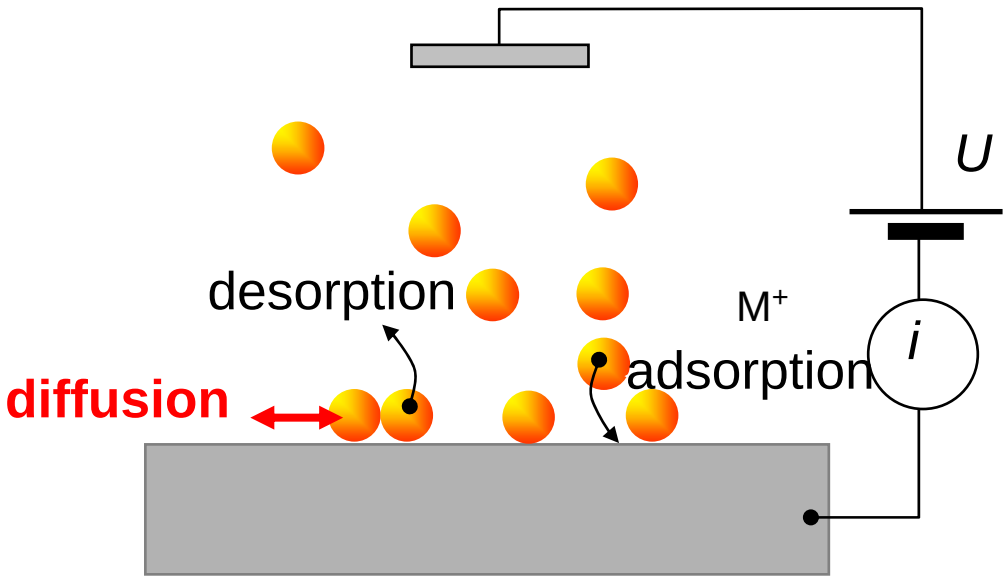


less than 1 s !



Perspectives

Coherent formalisms : KMC / CD / Avrami's law



adsorption/desorption and superficial diffusion

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