Non-linear Effects in Diffusion on Nanoscale

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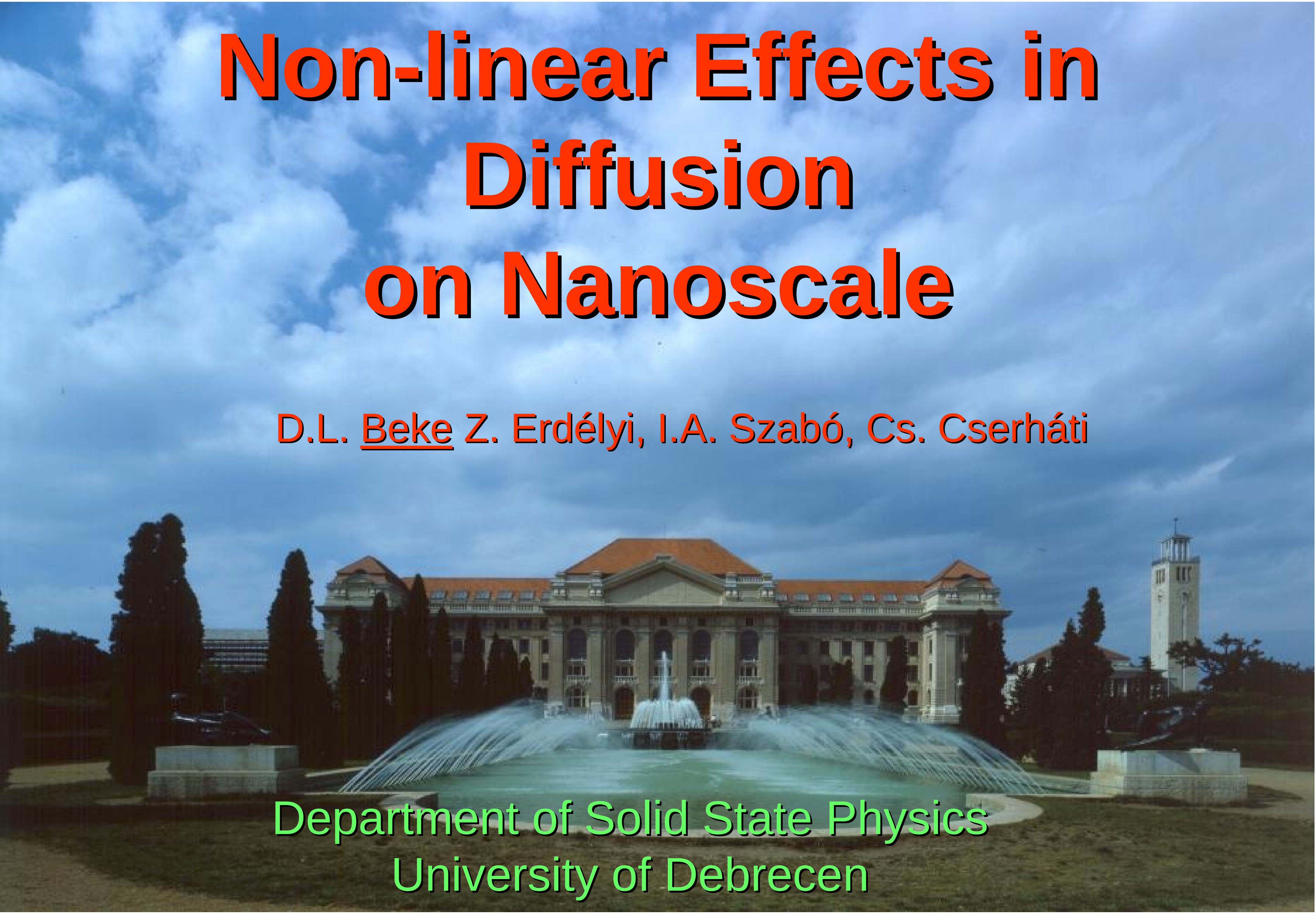


Diffusion in nanomaterials

Two important features

- High numbers of grain- or phase boundaries (GB or PB) and dislocations

  - fast diffusion and solid st. reactions, segregation, etc.

b) Principal problems (very short distances and preferably no structural defects)

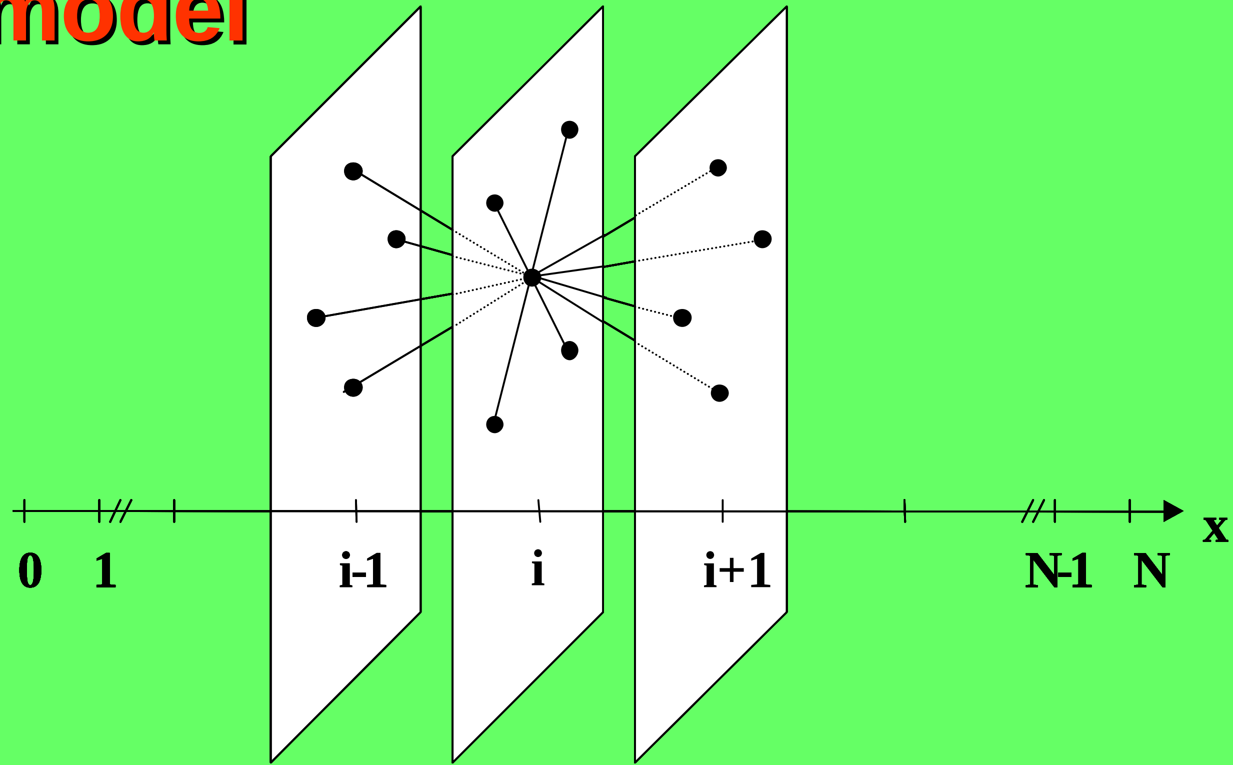
Principal difficulties:

-Short diffusion distances L $\simeq$ d
(continuum description fails)

- Gradient energy corrections

- Stress effects

Discrete (Martin's) model



$$dc_i/dt = -z_v[c_i(1-c_{i-1})\Gamma_{i,i-1} - (1-c_i)c_{i-1}\Gamma_{i-1,i} + $$
$$+ c_i(1-c_{i+1})\Gamma_{i,i+1} - c_{i+1}(1-c_i)\,\Gamma_{i+1,i}]. \qquad \Gamma_{i,i+1}=\nu\exp(-E_{i,i+1}/kT)$$

„Classical" Fick I.-II.

$$j_{i,i+1} = -D_i(\partial c/\partial x)/\Omega \qquad \partial c_i/\partial t = \partial[D_i(\partial c/\partial x)/\Omega]/\,\partial x$$

$E_{i,i+1} = E^o - \alpha_i + \varepsilon_i$ and $E_{i+1,i} = E^o - \alpha_i - \varepsilon_i$,

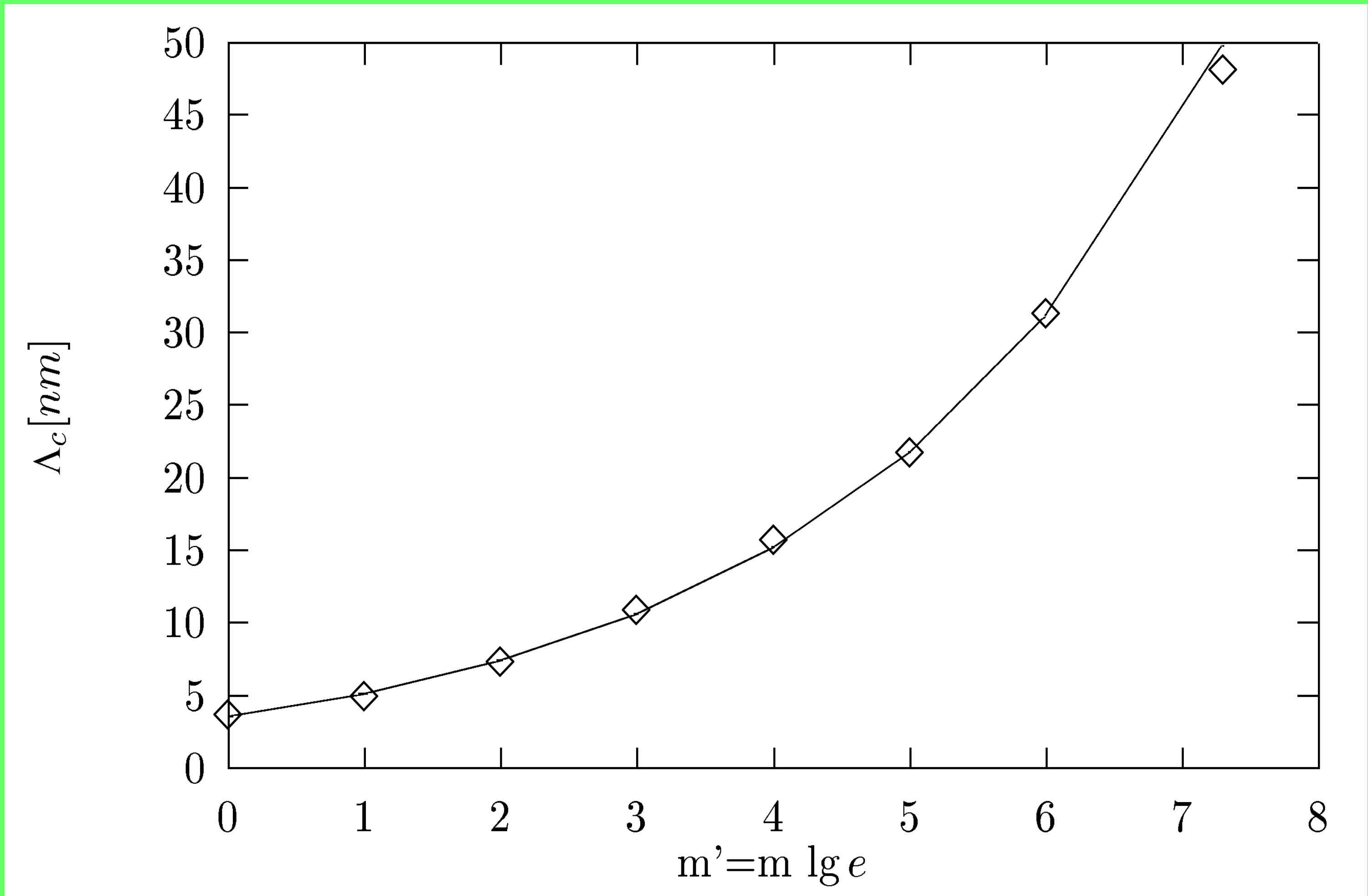
$V = V_{AB} - (V_{AA} + V_{BB})/2$

$\alpha_i = [z_v(c_{i-1} + c_{i+1} + c_i + c_{i+2}) + z_l(c_i + c_{i+1})](V_{AA} - V_{BB})/2$

$\varepsilon_i \propto V.$

Input parameters: z_v, z_l, $V_{AA} - V_{BB}$, V, T $(Z = 2z_v + z_l)$

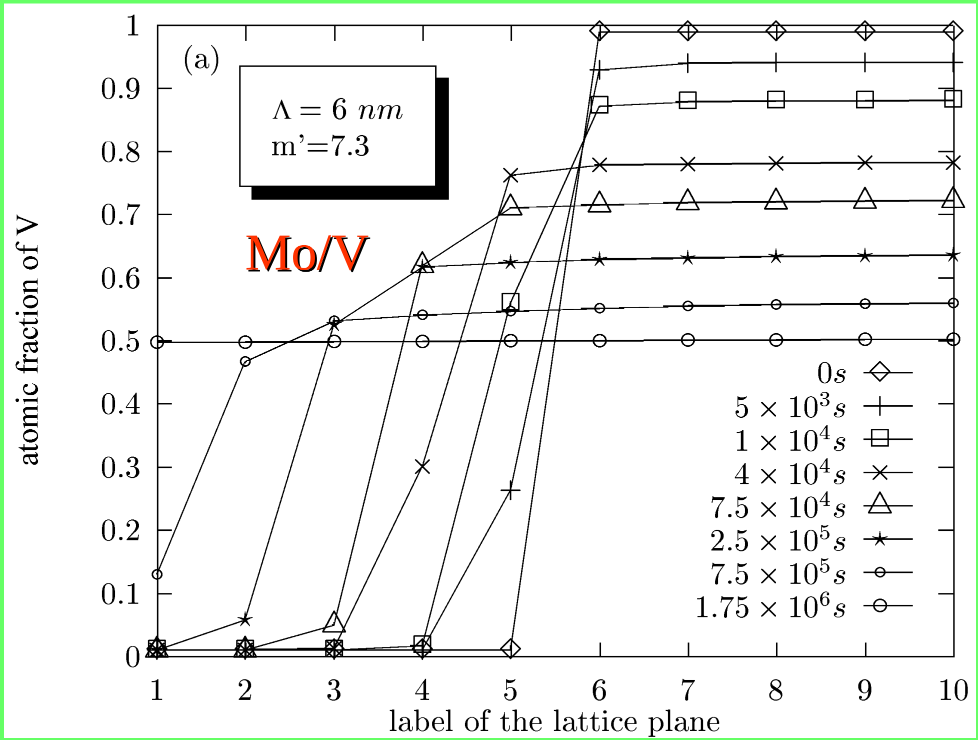
-validity limit

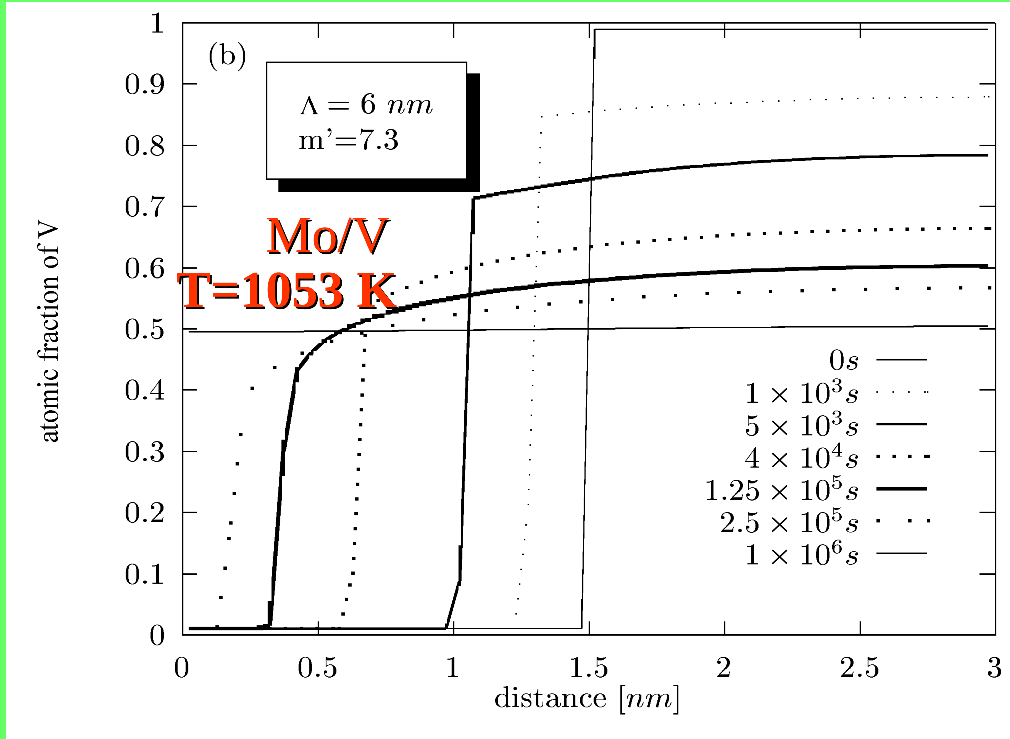


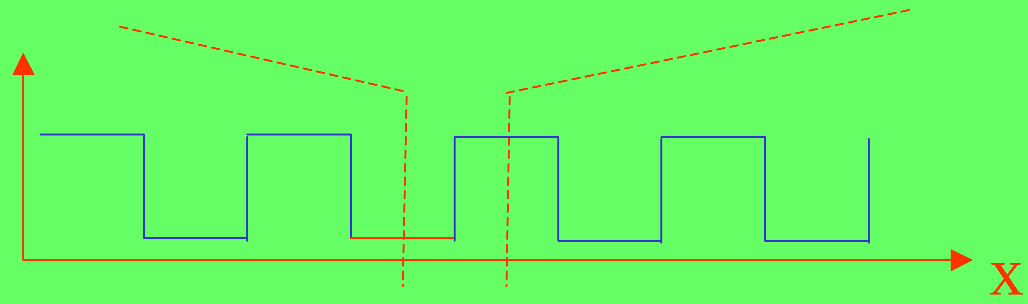
$$D_i^h = D(0)\exp(mc)$$

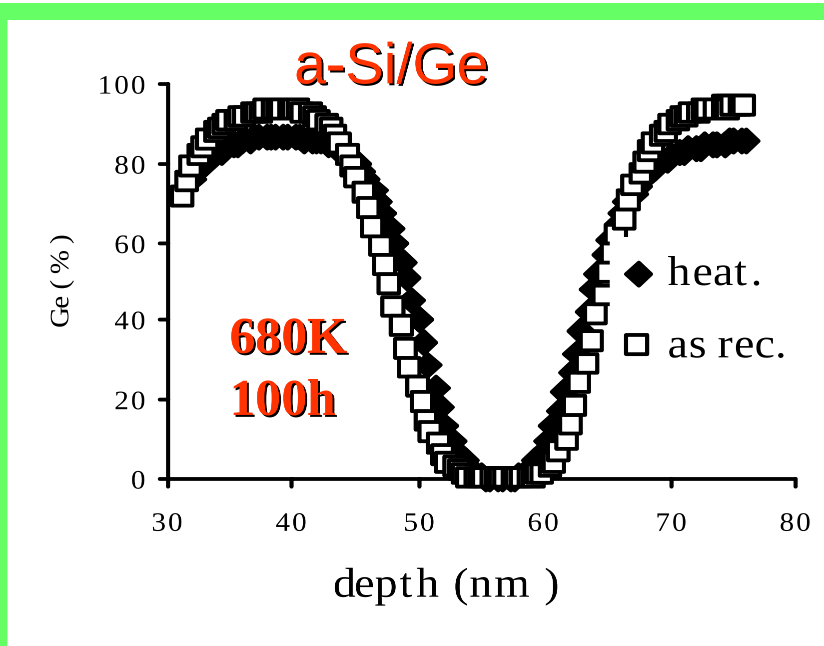
$$m = Z(V_{AA} - V_{BB})/kT$$

Effect of the strong concentration dependence of D



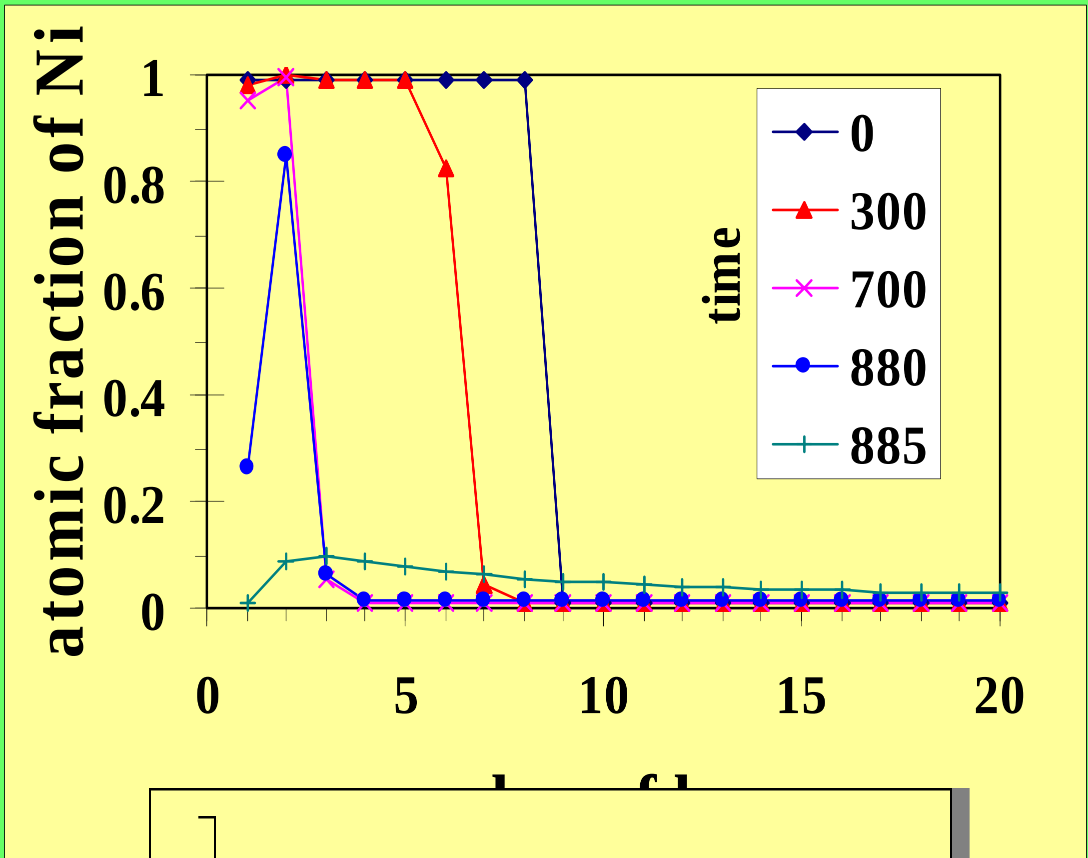


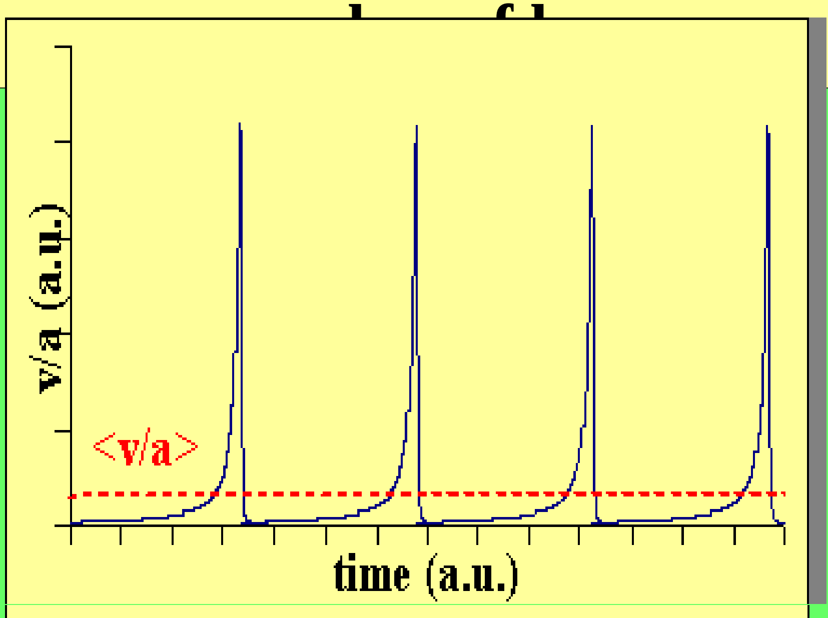


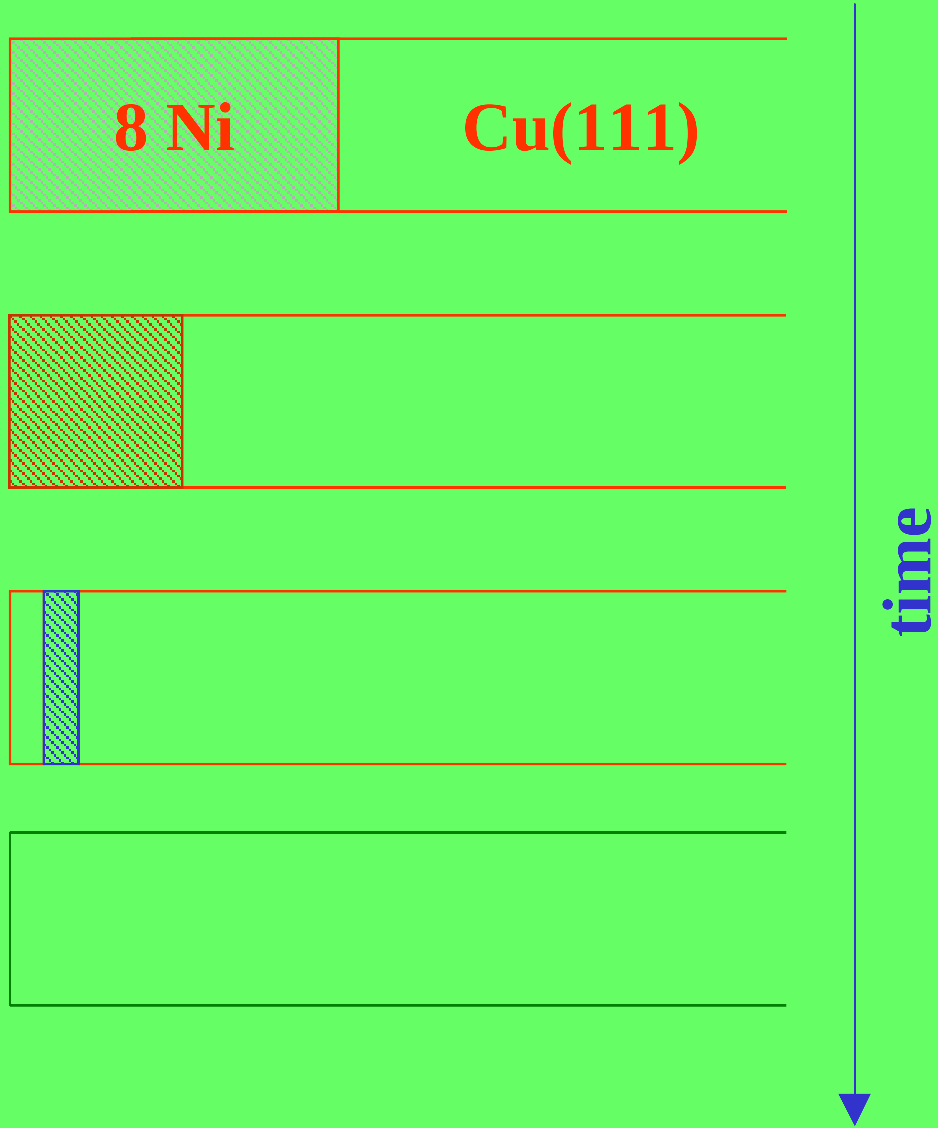


The interface reamins sharp and shifts!

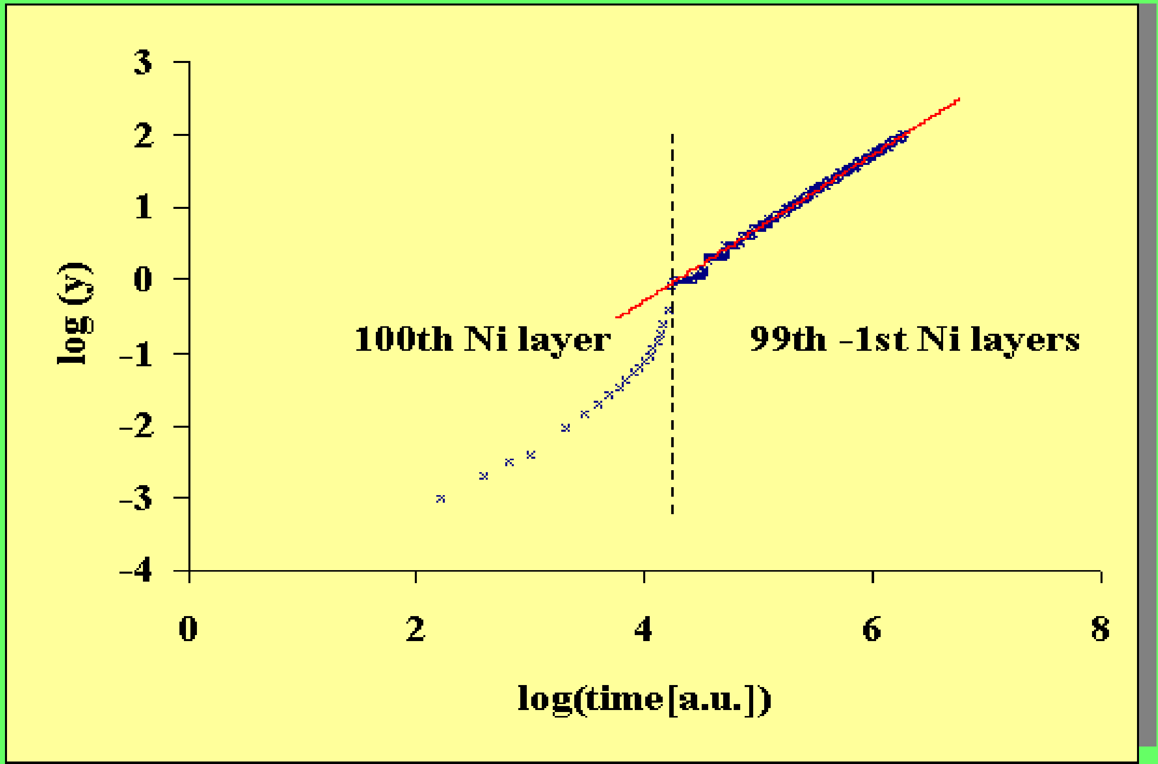
Dissolution in ideal systems: Ni into Cu





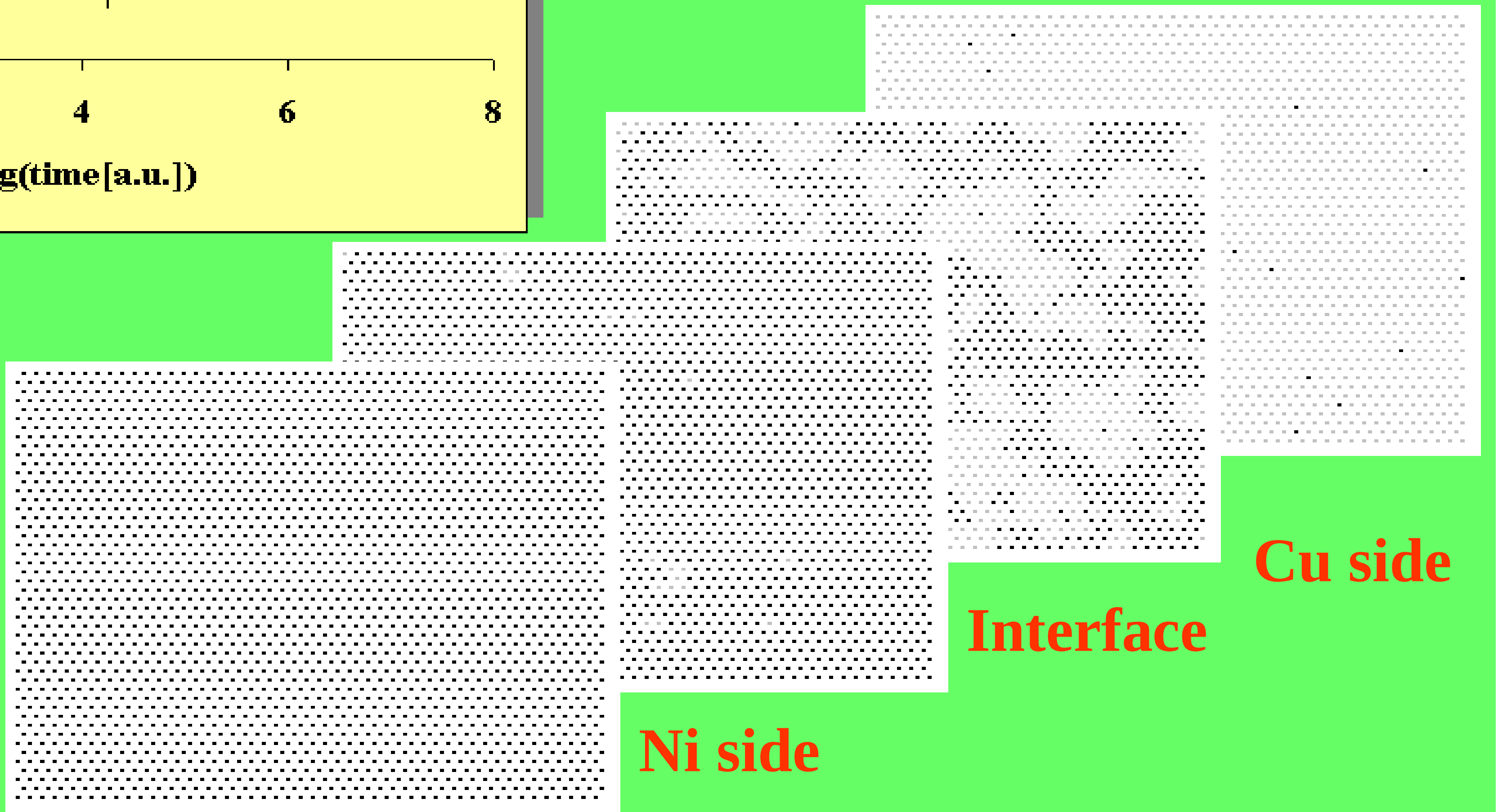


***D*(in Ni)<<*D*(in Cu)**



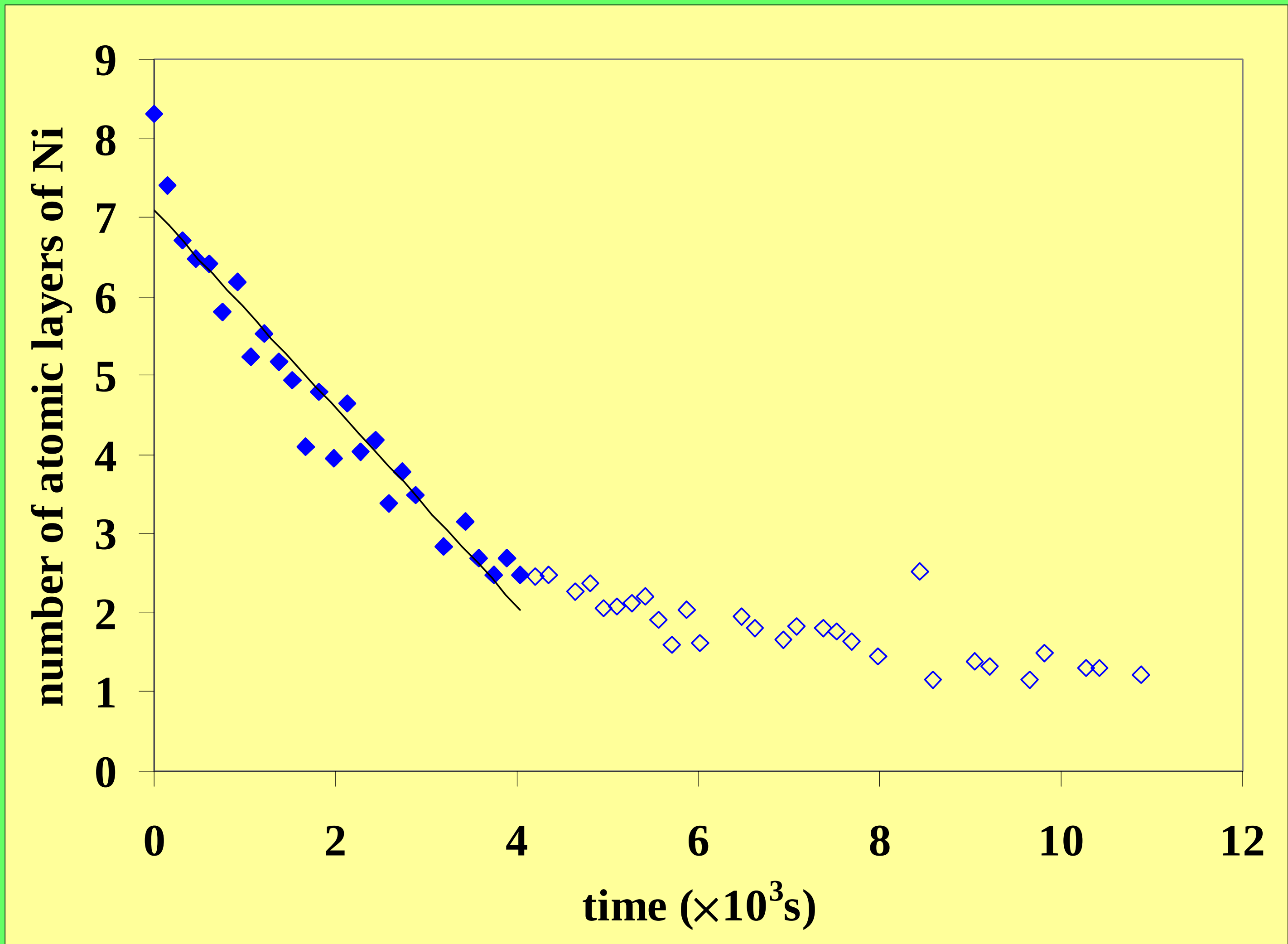
Linear kinetics !!!

Monte Carlo

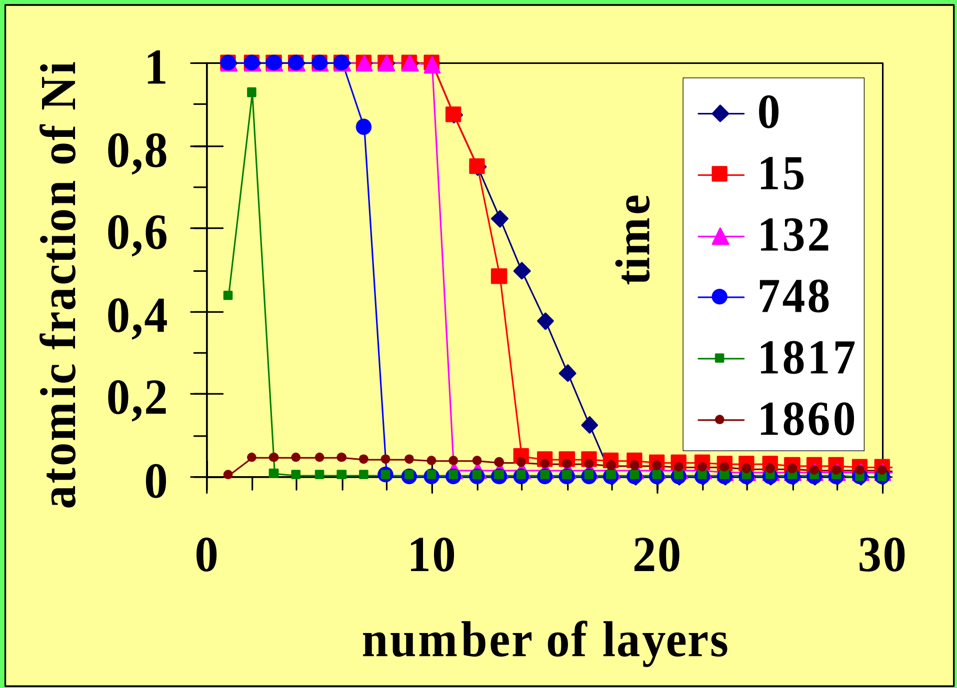


Experiment: AES from the top of Ni on Cu(111)

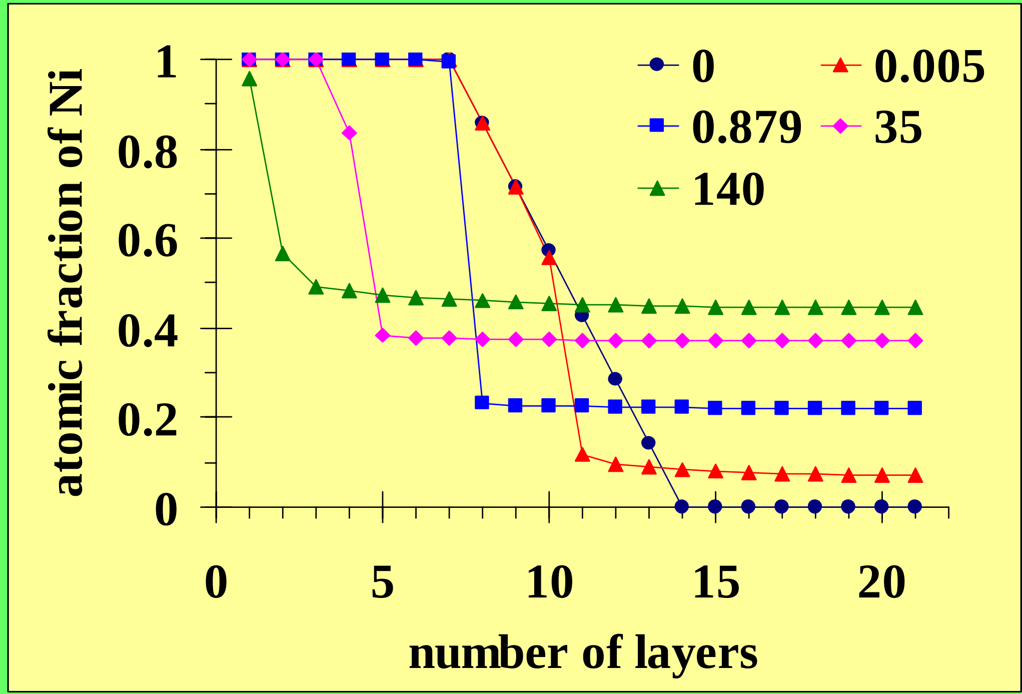
T=679K

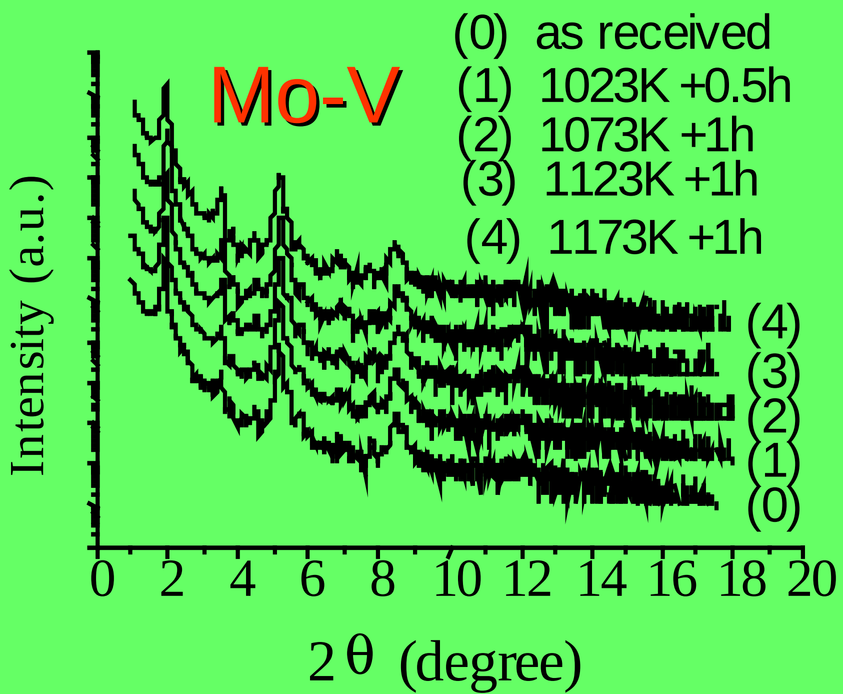


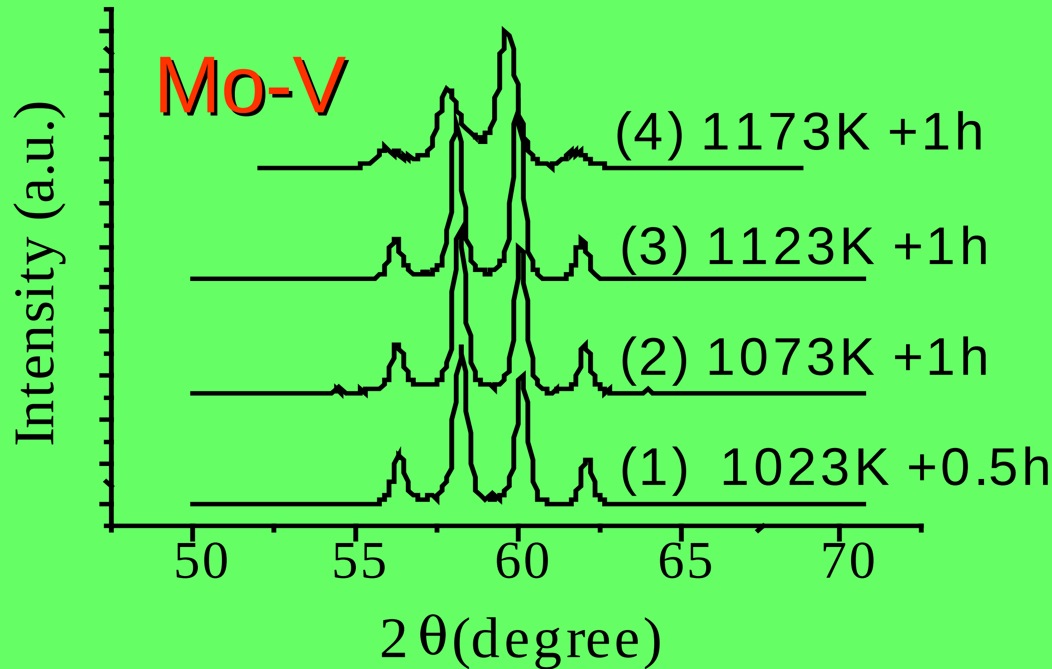
Sharpening of a wide interface (T=1000K, m'=9)



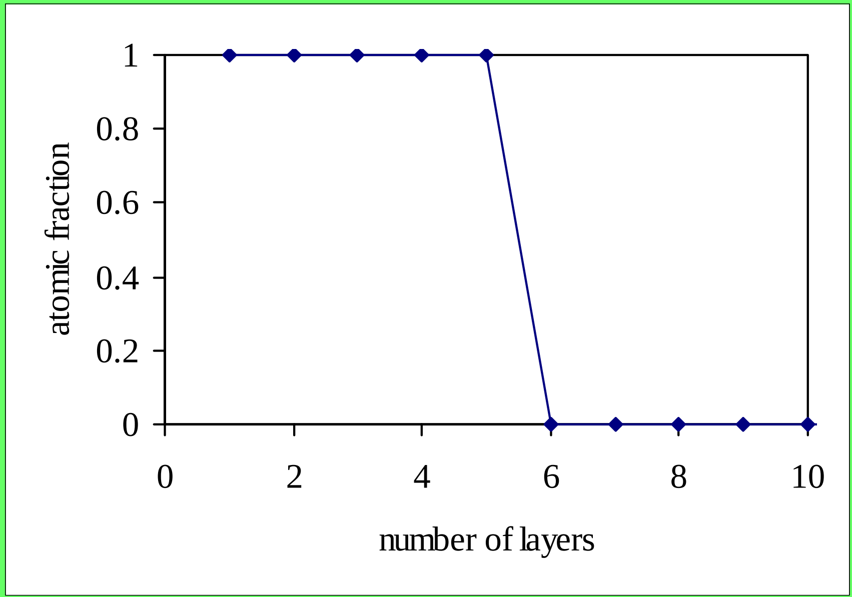
Ni-Cu

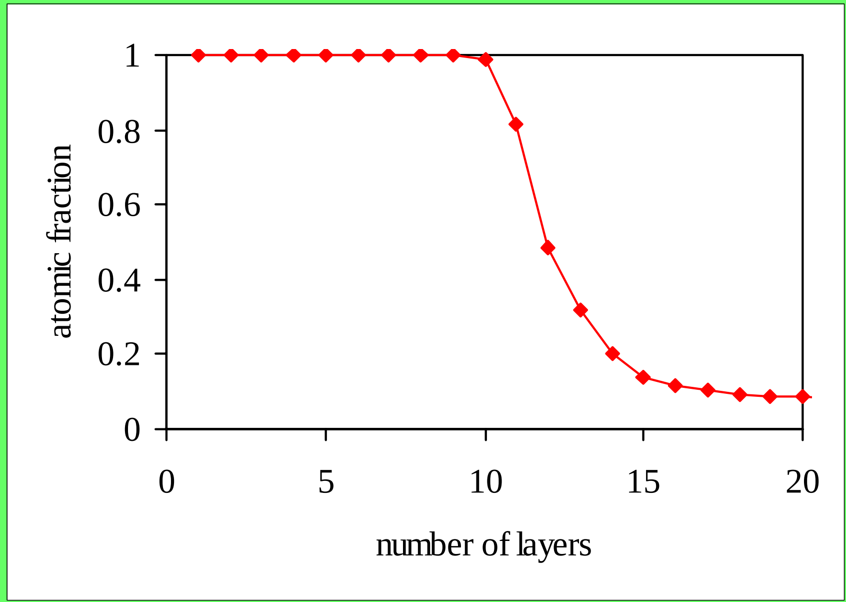


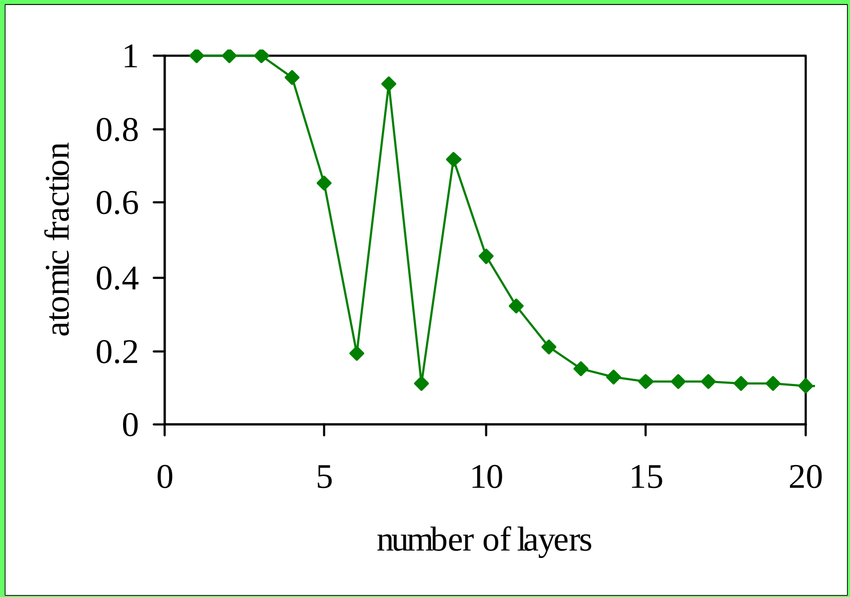


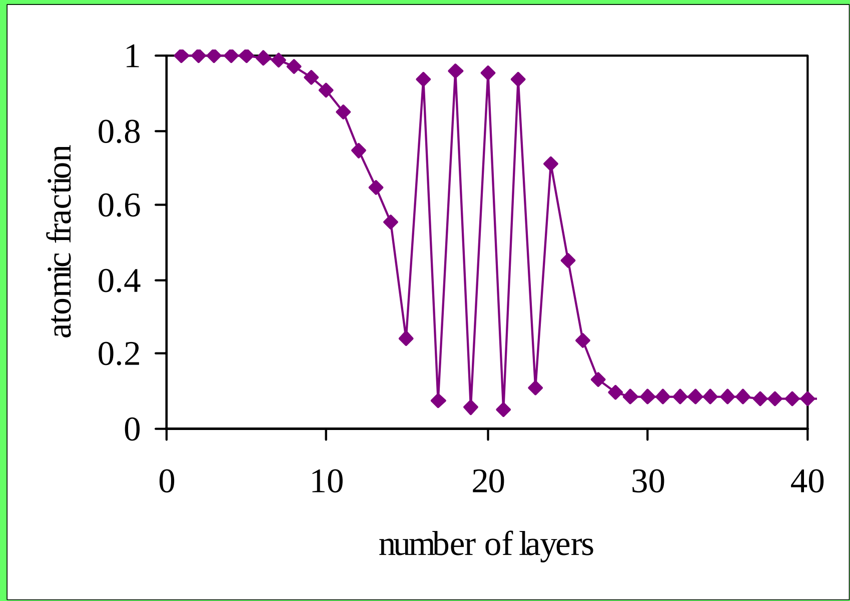


Growth of intermetallid layer:

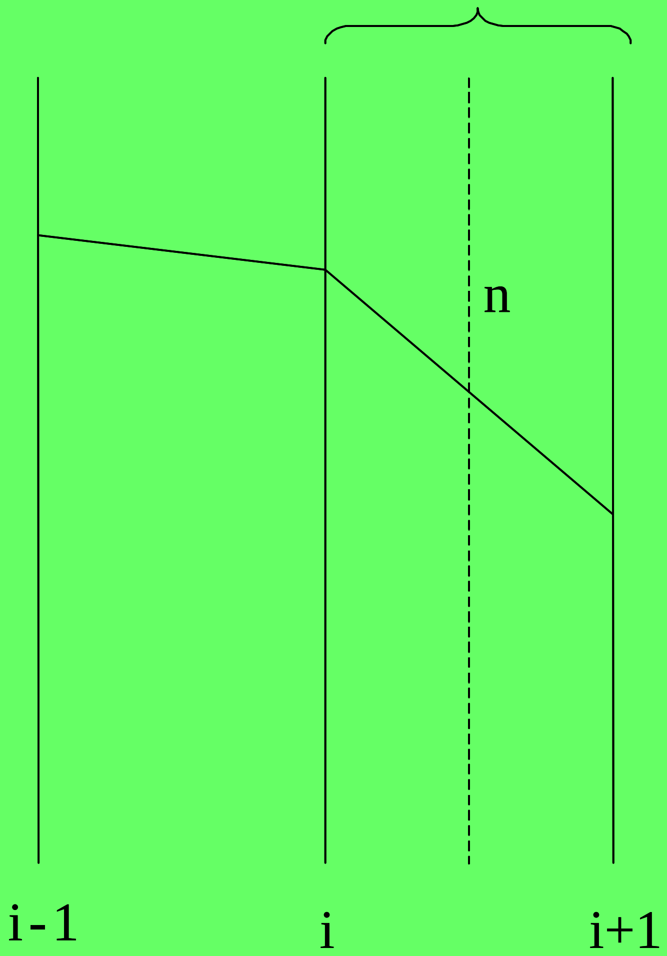








$$nd = \rho = c/\Omega$$



$$n_i = n - \frac{d}{2}\frac{\partial n}{\partial x} + \frac{(d/2)^2}{2!}\frac{\partial^2 n}{\partial x^2} - \frac{(d/2)^3}{3!}\frac{\partial^3 n}{\partial x^3} + \dots$$

$$\frac{\partial c}{\partial x} = \frac{c_{i+1} - c_i}{d}$$

$$\frac{\partial^2 c}{\partial x^2} = \frac{\frac{c_{i+1} - c_i}{d} - \frac{c_i - c_{i-1}}{d}}{d}$$

e.g. $\alpha_i = (V_{AA}-V_{BB})\{cZ + (z_v+Z/4)d^2\partial^2 c/\partial x^2 + \ldots\} = cZ(V_{AA}-V_{BB}) + \alpha_i' + \ldots$

Introducing $\Gamma_{i,} = \nu \exp[-(E^o-\alpha_i)/kT] = \Gamma_i^h \exp[\alpha_i'/kT]$.

and if $\varepsilon_i/kT \ll 1$ (i.e. $\exp[\varepsilon_i/kT] \cong 1 + \varepsilon_i/kT$

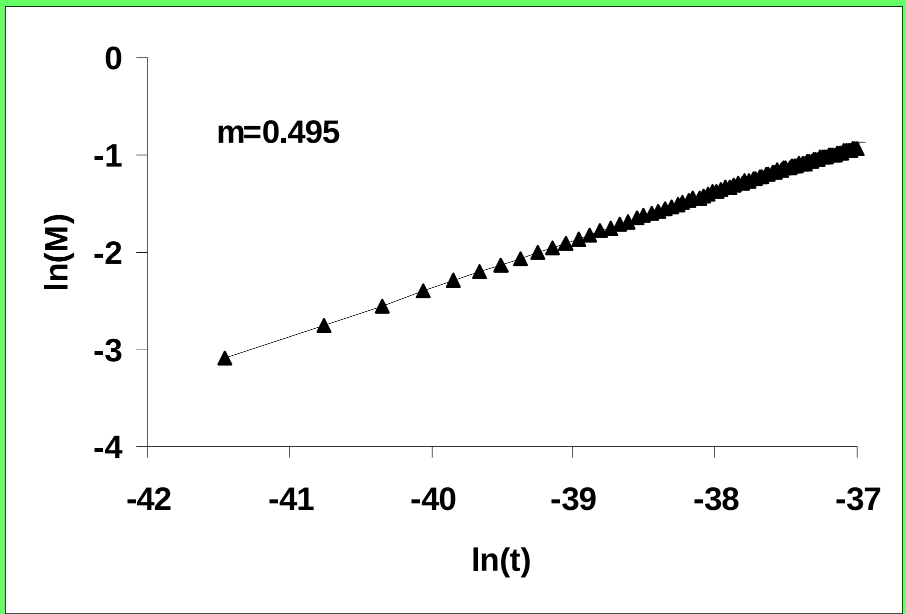
$$j_{i,i+1} = J_{i,i+1}/q = J_{i,i+1} d/\Omega = -D_i(\partial c/\partial x)/\Omega + $$
$$+ D_i[2\kappa/f_o'' - d^2/24](\partial^3 c/\partial x^3)/\Omega + \ldots$$

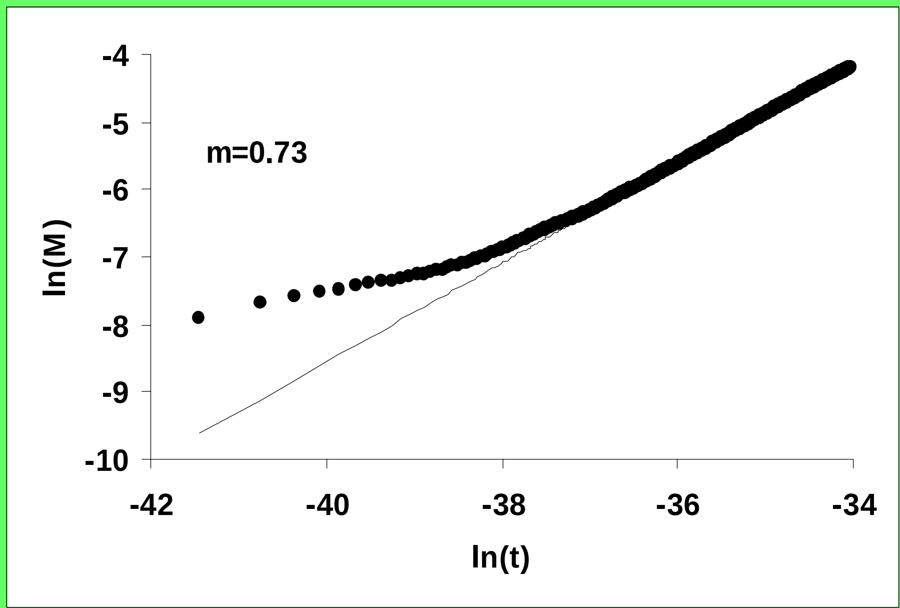
$D_i = z_v d^2 \Gamma_i \theta$ $\kappa \sim V$ Fick I.

Amorphous systems?, Stress effects…

Constant concentration at the surface:

$$D(c) = D(0)\,e^{m'c}$$





Conclusions (ideal systems):

- At short distances the continuum descriptions fails and this strongly depends on the concentration dependence of D (non-linearity)
- Non-linearity leads to ***shift of a sharp*** interface
- The non-linearity leads to
  - ***a linear*** shift of a sharp interface
  - ***sharpening*** of an originally wide interface
- Gradient energy corrections are important not only in the currents but also in the mobilities

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