Diffusion in Solids and the Kirkendall-Effect

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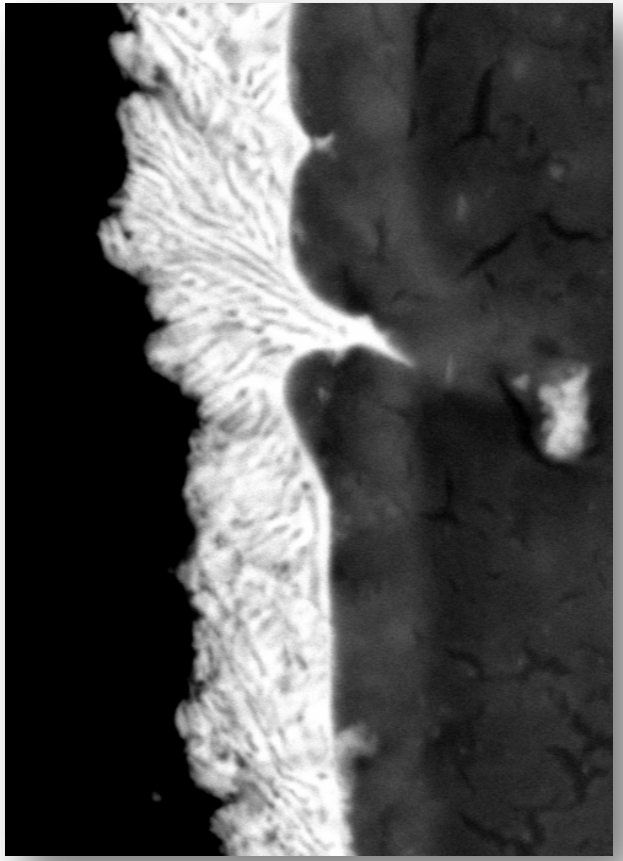
Hypereutectic thermal treatment

- Heterogeneous
- Difficult to control
- Patterns forming during solidification



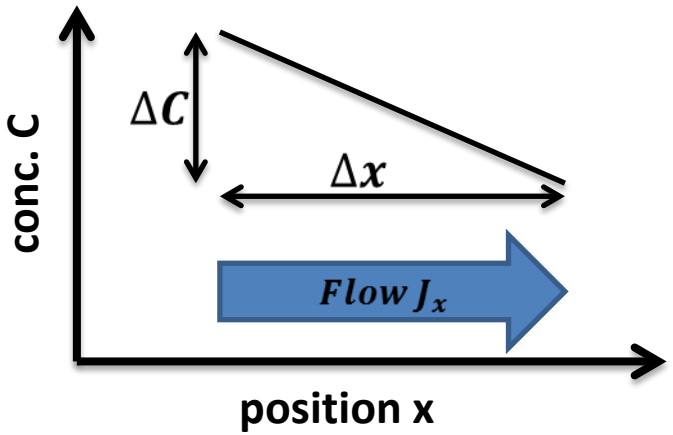
Fick‘s First Law

$$J_x = -D \frac{\partial C}{\partial x}$$

J_x = diffusion flux

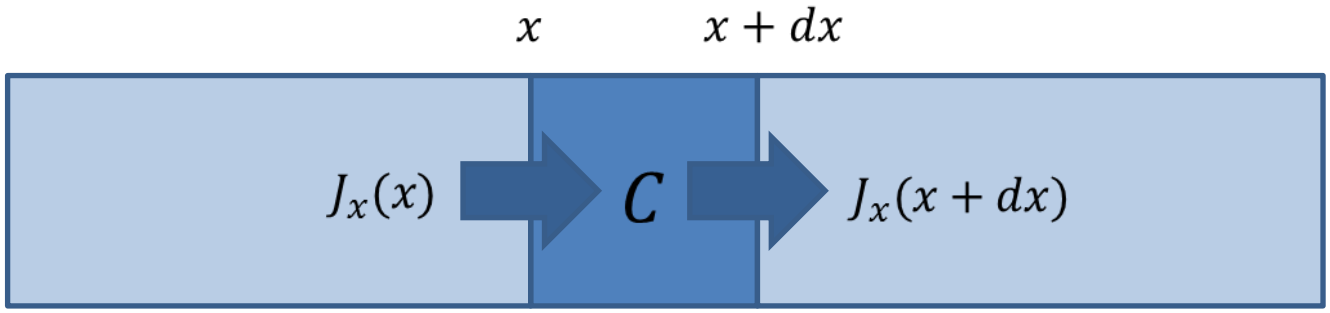
D = diffusion coefficient

C = concentration



Equation of Continuity

- Time dependency?



$$-\frac{\partial J_x}{\partial x} = \frac{\partial C}{\partial t}$$

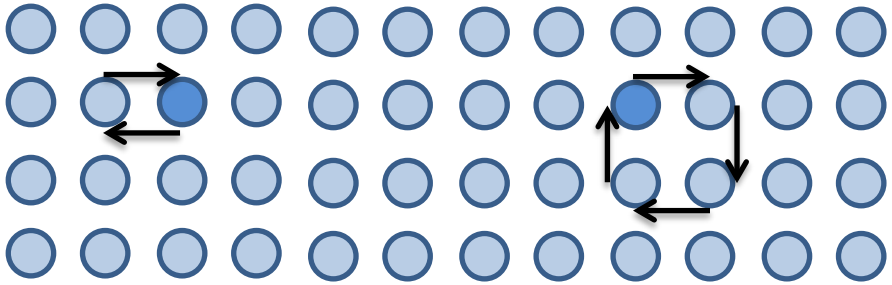
Fick‘s Second Law

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right)$$

If D is independant of x:

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2}$$

Atomic Jump Process

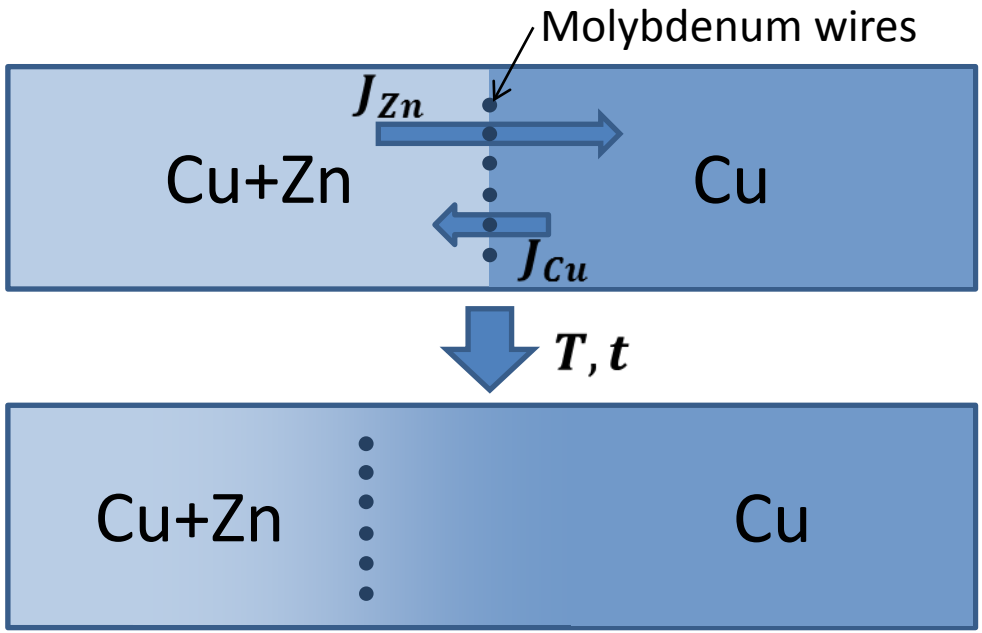


Direct exchange? Ring exchange?

- Direct exchange requires a large distortion of the lattice and therefore has a high activation enthalpy
- Ring exchange requires less activation enthalpy but an unlikely collective motion

→ Those processes barely contribute to diffusion

Kirkendall Effect

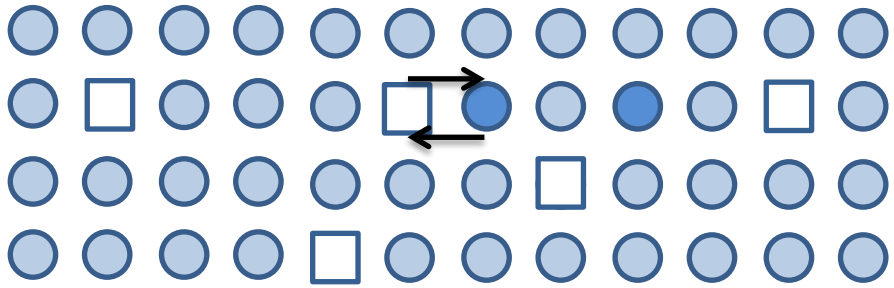


$J_{Zn} \neq J_{Cu}$ but direct or ring exchange would imply $J_{Zn} = J_{Cu}$

Another process must be responsible

The Vacancy Mechanism

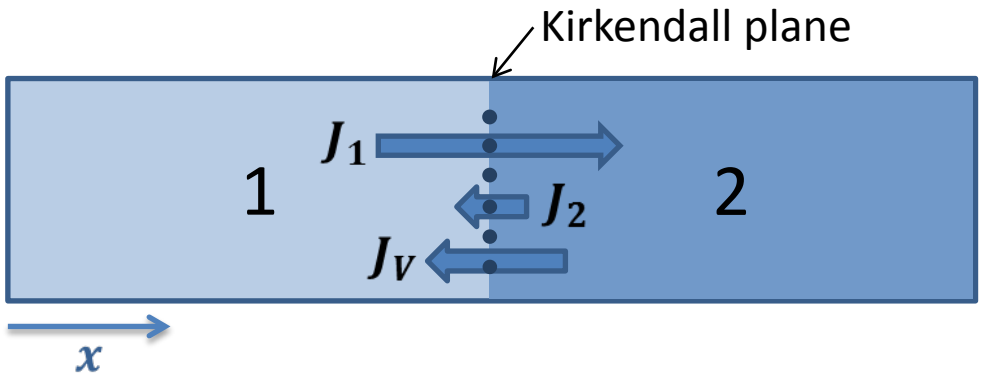
- Site fraction of vacancies lie around 10^{-3} and 10^{-4} near T_S



Vacancy Exchange

- Under normal conditions vacancy exchange is the main mechanism of diffusion

Kirkendall Voids



$J_1 > J_2$ ➡ Net flow of metal atoms in x-direction

➡ Vacancy flow J_V in negative x-direction

Kirkendall Voids (example)

$J_{Cu} > J_{Ni}$ → Vacancy flow into original copper domain

(Choi, Matlock and Olson)

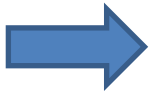
14 min

1000°C

(Choi, Matlock and Olson)

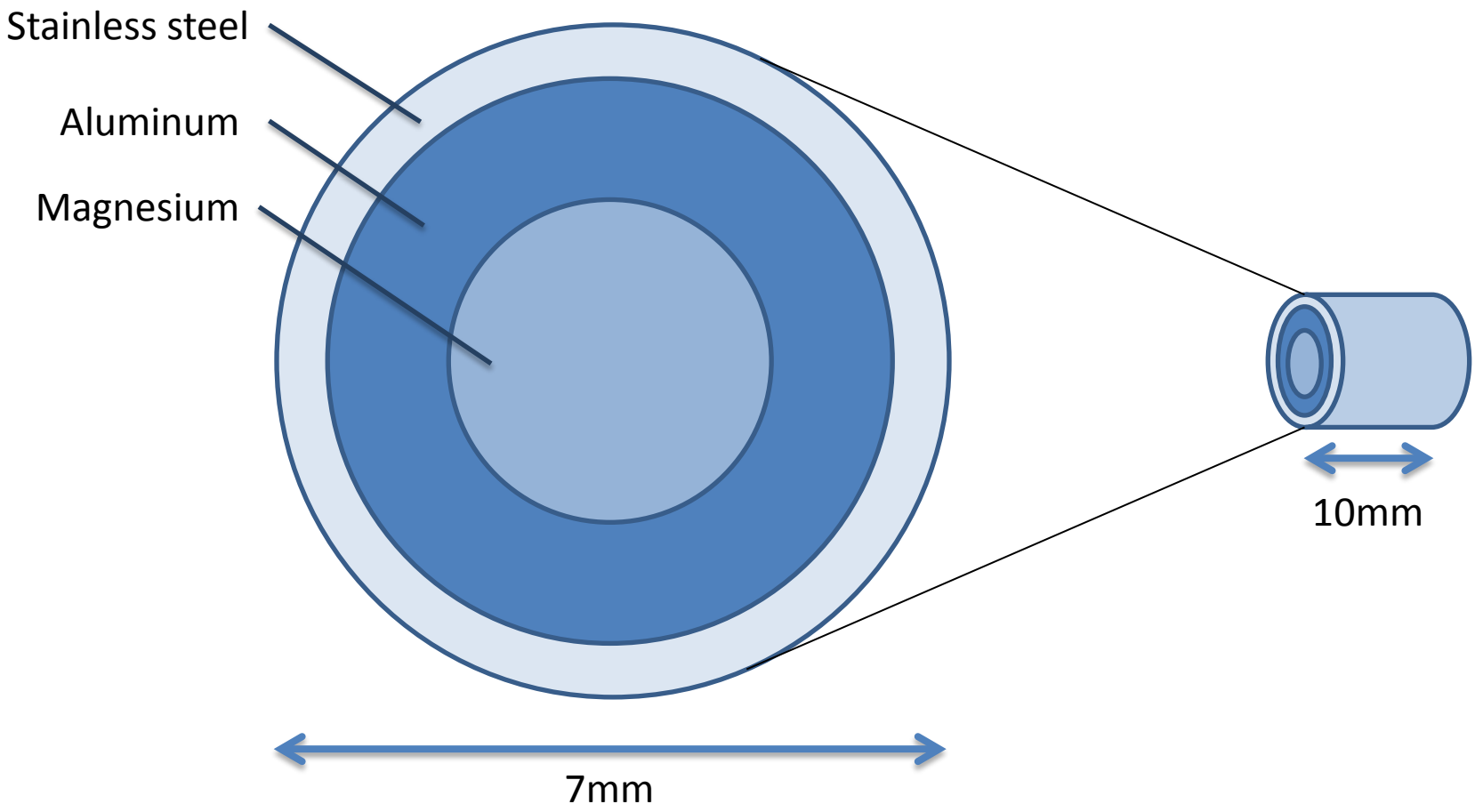
Aluminum-Magnesium binary alloy

- Better understanding of Al-Mg interdiffusion
- Measurement of the interdiffusion coefficient



Infinite reservoir experiments

Experimental Setup

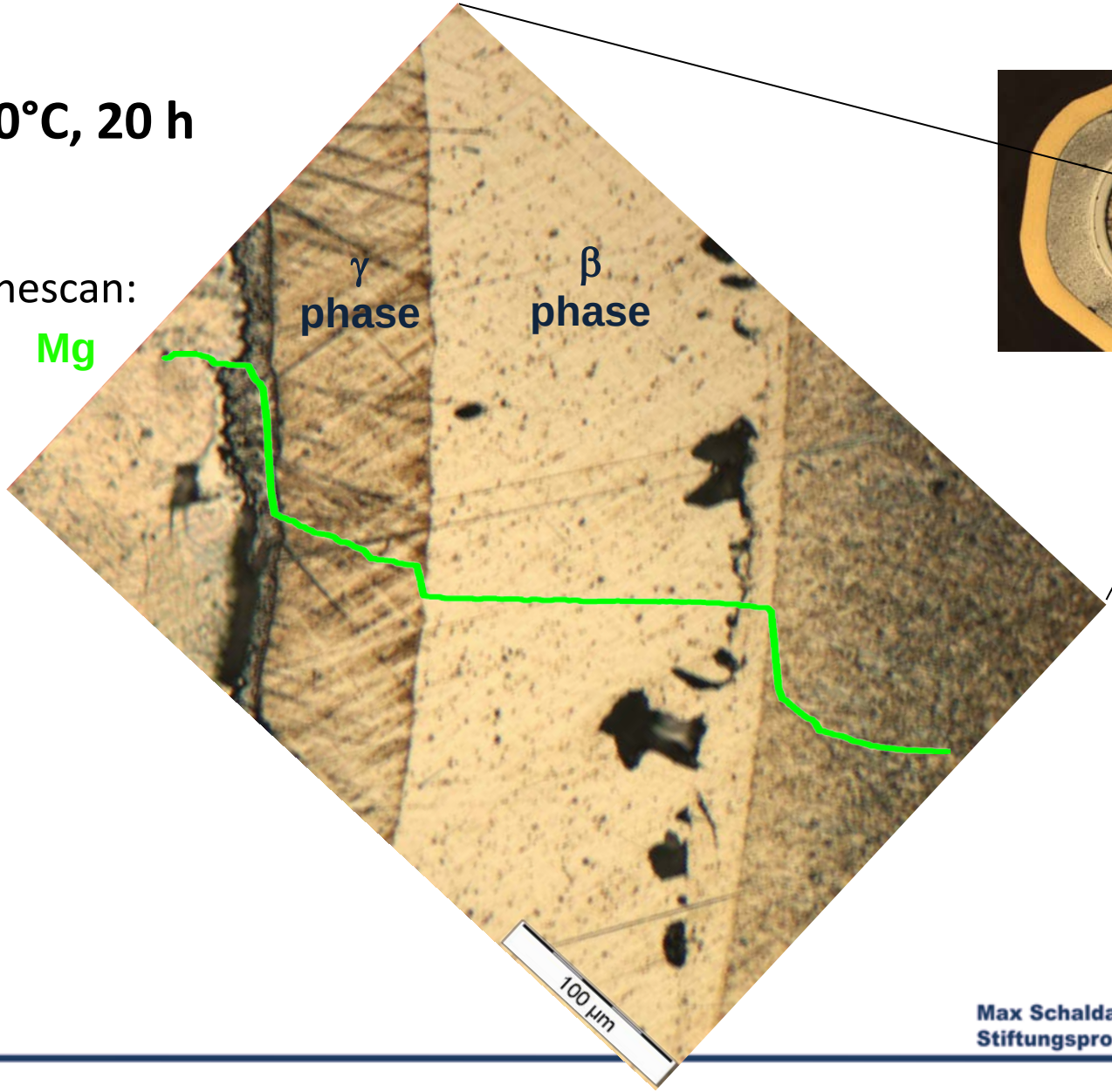


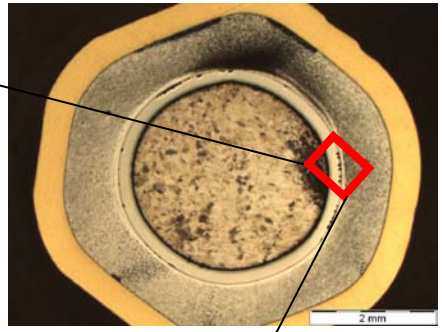
Measurements

420°C, 20 h

EDX-Linescan:

Mg



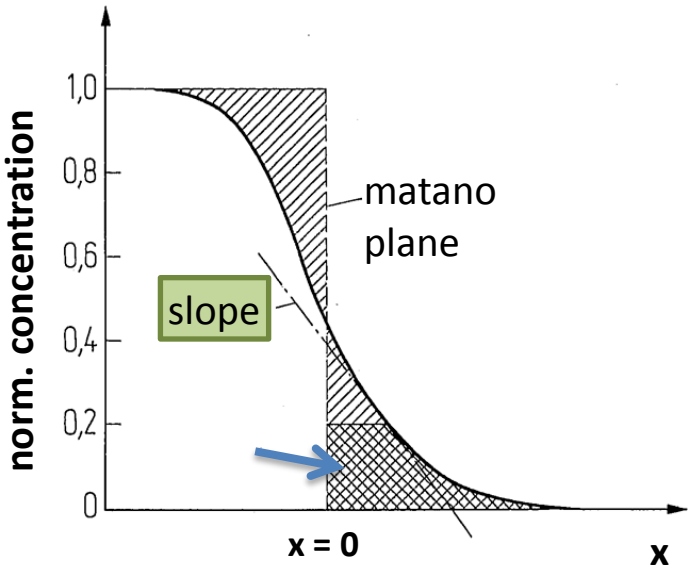


Boltzmann-Matano Method

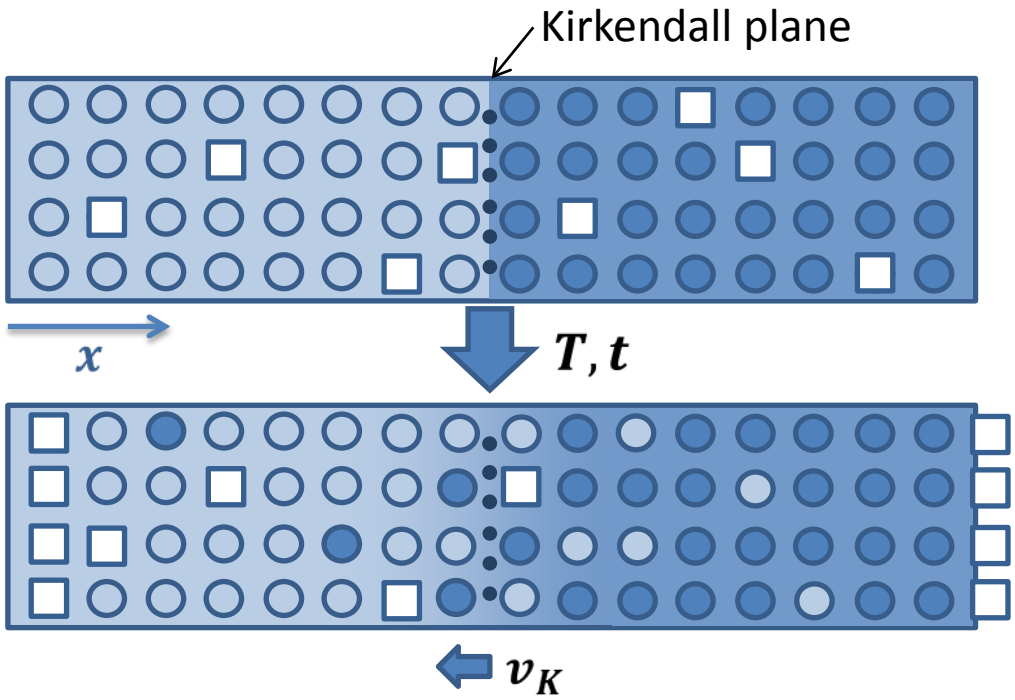
- Determination of interdiff. coeff. $\widetilde{\boldsymbol{D}}(C)$
- EDX-Linescans yield $\boldsymbol{C}(x)$

- Matano plane: $\int_0^1 x \, dc' = 0$

$$\tilde{D}(c) = -\frac{1}{2t}\left(\frac{dx}{dc}\right)_c \int_0^c x \, dc'$$



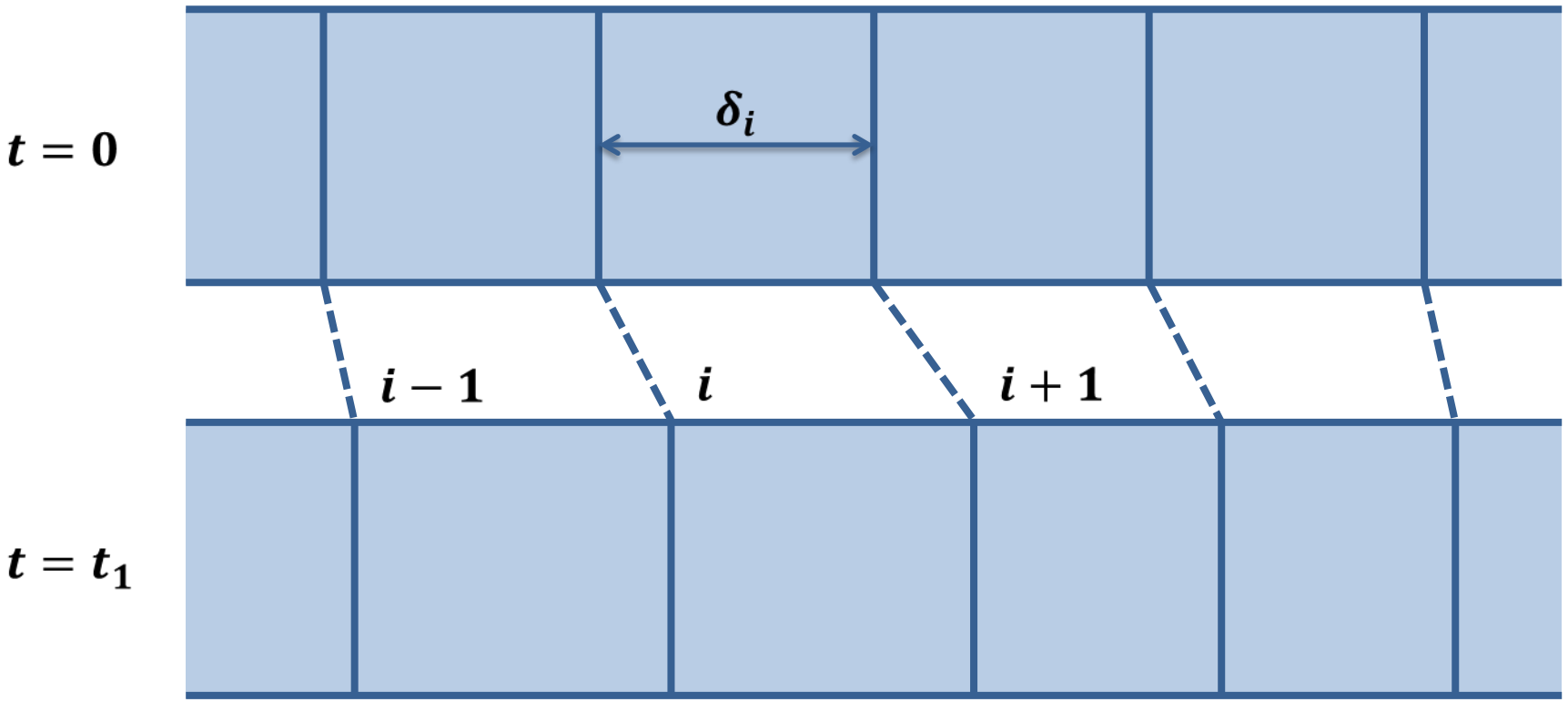
Darken Equation



$$J_x = -D\frac{\partial C}{\partial x} \pm v_K C \qquad v_K = \tilde{V}(D_1 - D_2)\frac{\partial C}{\partial x}$$

$$J_x = -\tilde{D}\frac{\partial C}{\partial x} \quad \text{with} \quad \tilde{D} = X_1 D_2 + X_2 D_1$$

Simulation - Setup



Indices:

i = position

k = component

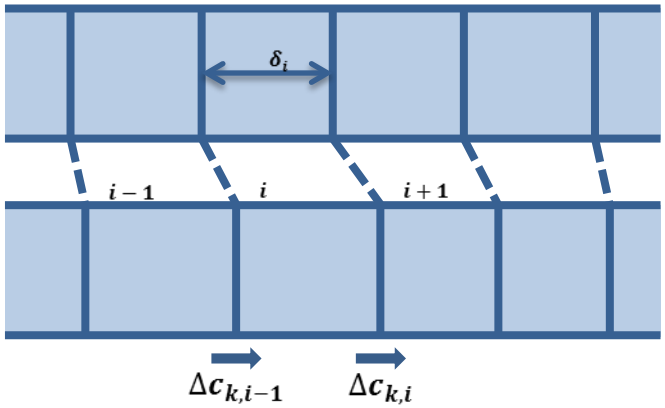
Simulation - Parameters

Parameters:

$\boldsymbol{D_{k,i}} =$ effective diffusion coefficient

$\boldsymbol{c_{k,i}} =$ concentration

$\boldsymbol{X_{k,i}} =$ mole fraction



Indices:

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Simulation - Algorithm

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

finite difference method

$$\Delta c_{k,i} = -D_{k,i} \frac{c_{k,i+1} - c_{k,i}}{(x_{k,i+1} - x_{k,i})^2} \Delta t$$

~~$c_{k,i}(t + \Delta t) = c_{k,i}(t) + \Delta c_{k,i-1} - \Delta c_{k,i}$~~ not valid, as $\Delta c_{k,i}$ also changes δ_i

Therefore we use the relative amount of substance $n^*_{k,i}$

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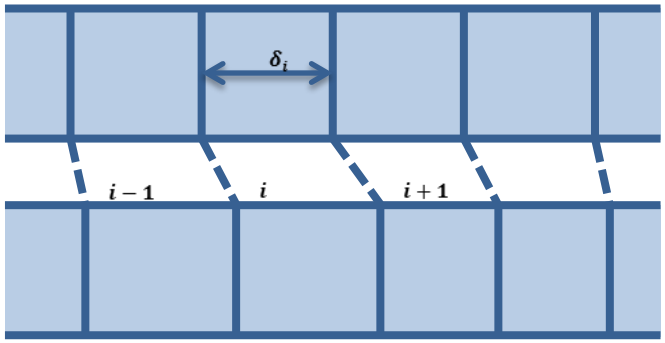
$\boldsymbol{X_{k,i}} =$ mole fraction

$$\widetilde{\boldsymbol{V}}_{\boldsymbol{i}} = \sum_{\boldsymbol{k}} \boldsymbol{X_{k,i}} \cdot \widetilde{\boldsymbol{V}}_{\boldsymbol{k}} = \text{molar volume}$$

$$\boldsymbol{n_i} = \frac{\boldsymbol{V_i}}{\widetilde{\boldsymbol{V}}_{\boldsymbol{i}}} = \text{amount of substance}$$

$$\left.\begin{aligned} \boldsymbol{n_i^*} &= \frac{\boldsymbol{\delta_i}}{\widetilde{\boldsymbol{V}}_{\boldsymbol{i}}} \\ \boldsymbol{n_{k,i}^*} &= \boldsymbol{\delta_i} \cdot \boldsymbol{c_{k,i}} \end{aligned}\right\} = \text{relative amount of substance}$$



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Therefore we use the relative amount of substance $n^*_{k,i}$

$$n^*_{k,i}(t + \Delta t) = n^*_{k,i}(t) + \Delta c_{k,i-1} \cdot \delta_{i-1}(t + \Delta t) - \Delta c_{k,i} \cdot \delta_i(t + \Delta t)$$

$n^*_{k,i}; \delta_{i-1}; \Delta c_{k,i-1}$ Known from previous steps

$\delta_i(t + \Delta t)$ Dependent on $n^*_i(t + \Delta t)$

Simulation - Algorithm

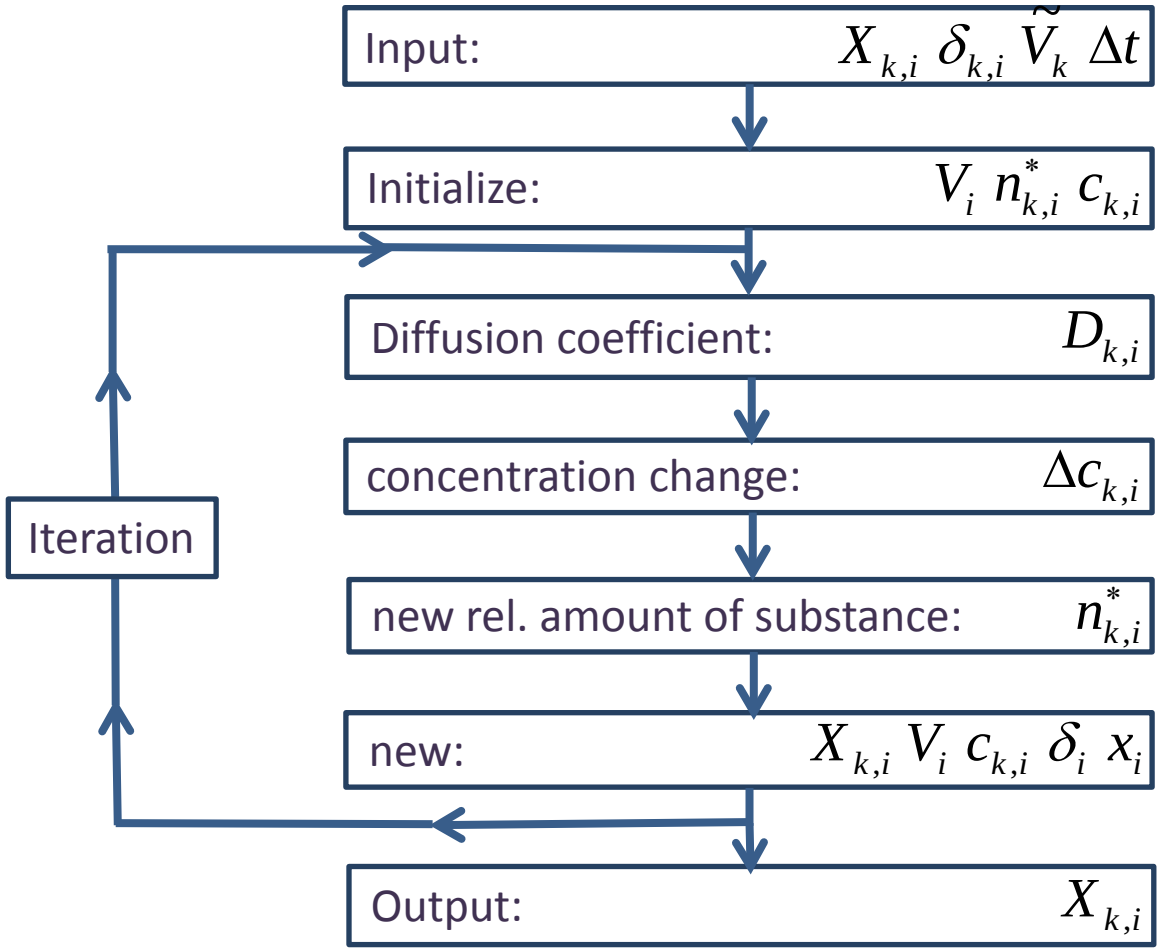
… a few calculations later …

$$n^{*}_{A,i} = \frac{n^{re}_{A,i}\,(1+\Delta c_{B,i}\,\tilde{V}_B) - n^{re}_{B,i}\,\Delta c_{A,i}\,\tilde{V}_B}{1+\Delta c_{A,i}\,\tilde{V}_A + \Delta c_{B,i}\,\tilde{V}_B}$$

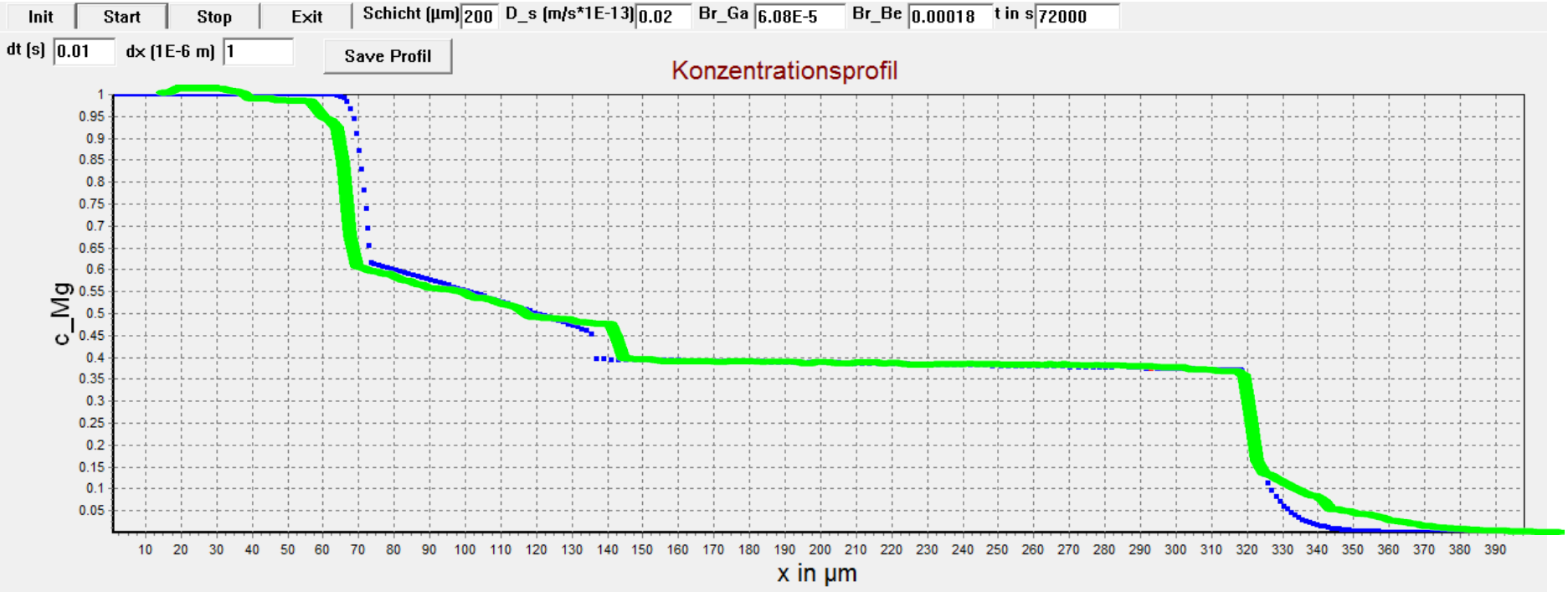
$$n^{*}_{B,i} = \frac{n^{re}_{B,i}\,(1+\Delta c_{A,i}\,\tilde{V}_A) - n^{re}_{A,i}\,\Delta c_{B,i}\,\tilde{V}_A}{1+\Delta c_{A,i}\,\tilde{V}_A + \Delta c_{B,i}\,\tilde{V}_B}$$

$$n^{re}_{k,i} = n^{*}_{k,i}(t') + \Delta c_{k,i-1}\,\delta_{i-1}(t' + \Delta t)$$

Simulation - Algorithm



Simulation vs. Measurement



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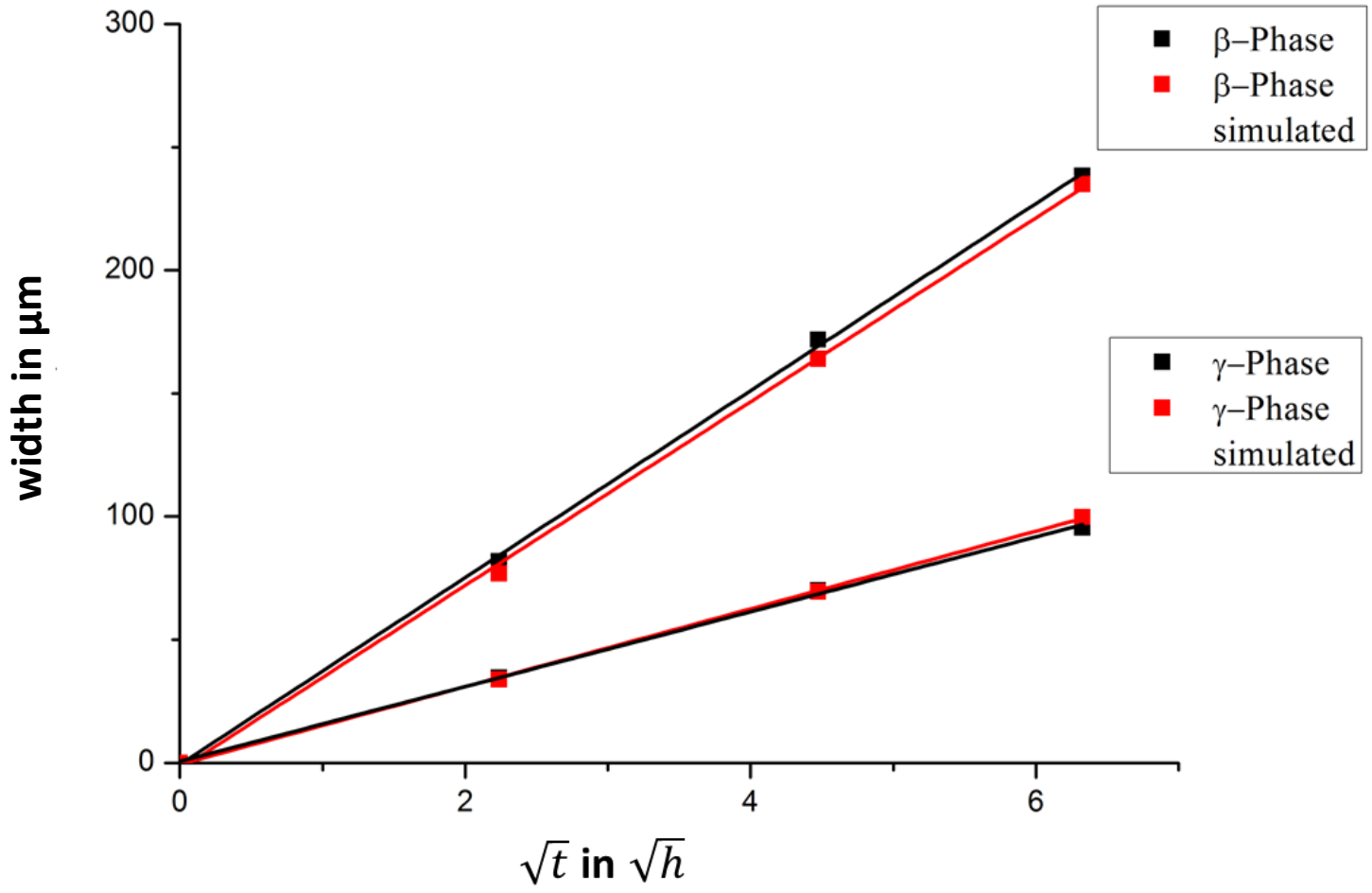
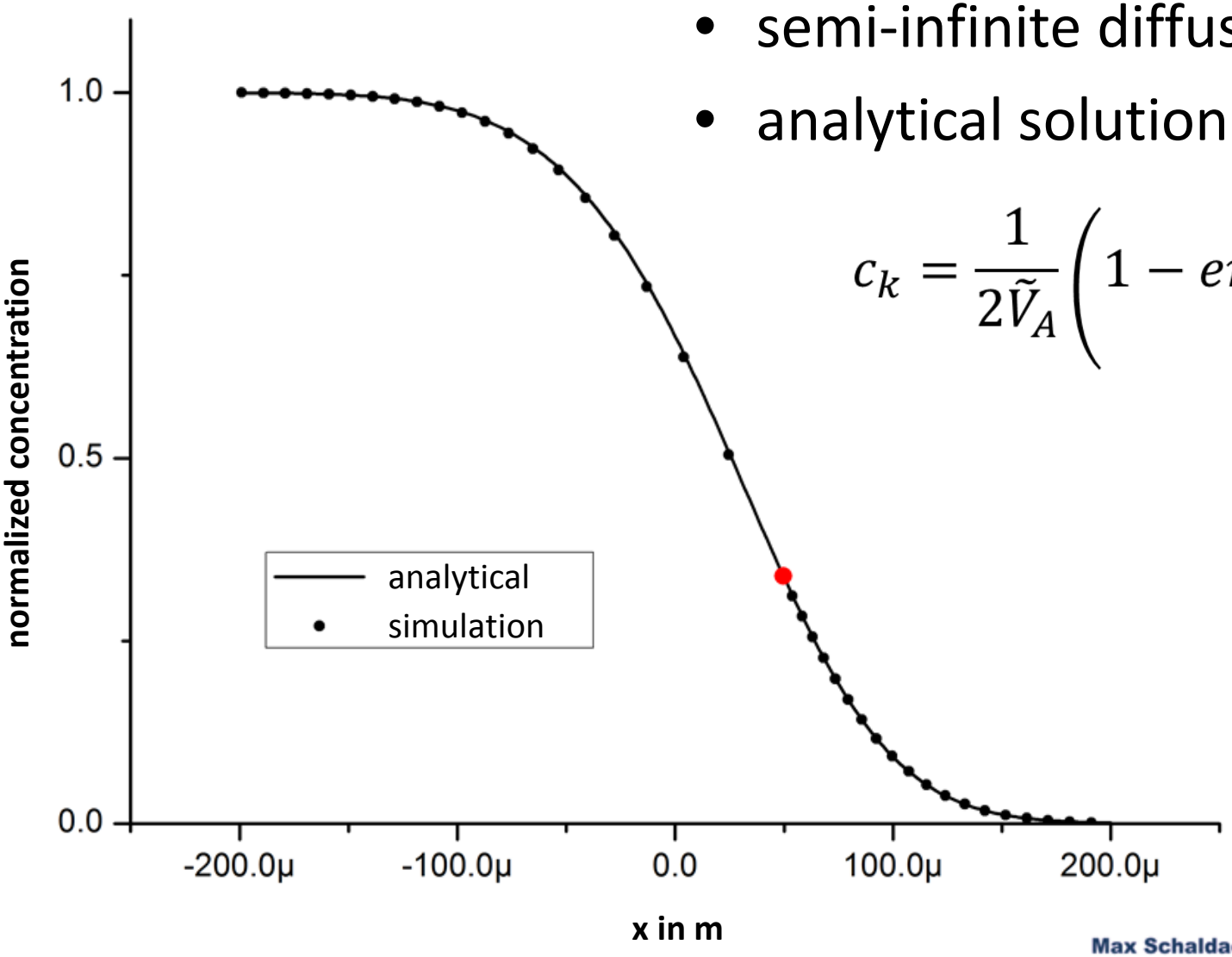


Simulation vs. Analytical Solution

- semi-infinite diffusion couple
- analytical solution:

$$c_k = \frac{1}{2\tilde{V}_A}\left(1 - erf\left(\frac{x}{2\sqrt{\widetilde{Dt}}}\right)\right)$$



Demonstration, Questions and Discussion

Thank you for your attention

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