Lattice Monte Carlo Determination of Harrison Kinetics Regimes for Grain Boundary Diffusion In Materials with Inhomogeneous Grain Structures

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Talk outline:

1. Introduction
2. Parallel slab model:
   a) homogeneous grain structure
   b) inhomogeneous grain structure
3. Closed (cubic) grains model
   a) homogeneous grain structure
   b) inhomogeneous grain structure
4. Summary

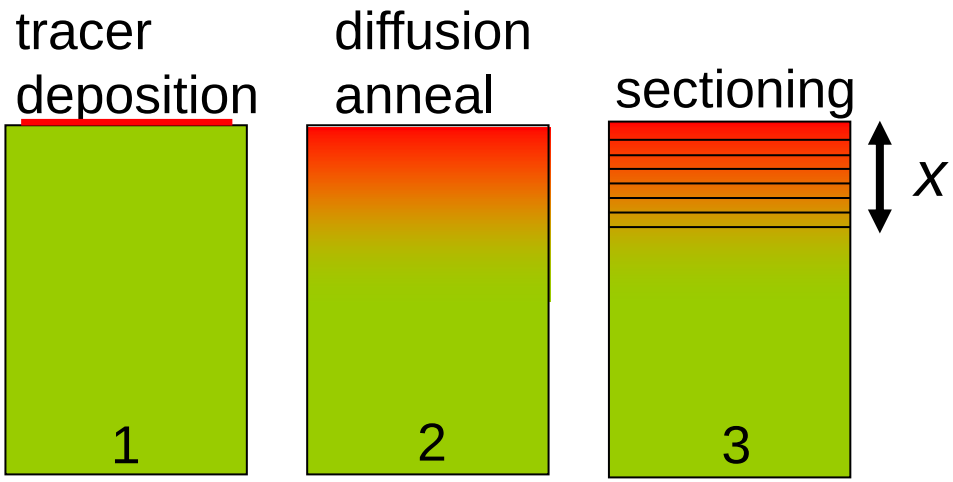
Diffusion experiment: Radiotracer method (some details)

Advantages:

- direct method
- element selective
- e.g. ^{59}Fe ($t_{1/2}$ = 45.1 d), ^{57}Co (271 d), ^{65}Zn (244 d), ^{63}Ni (100 y), ^{71}Ge (14 d), ^{31}Si (2.6 h), and many other suitable isotopes
- tiny amount of tracer atoms
  → no chemical gradient
  → no complications due to thermodynamic factors

However:

- time consuming, laborious



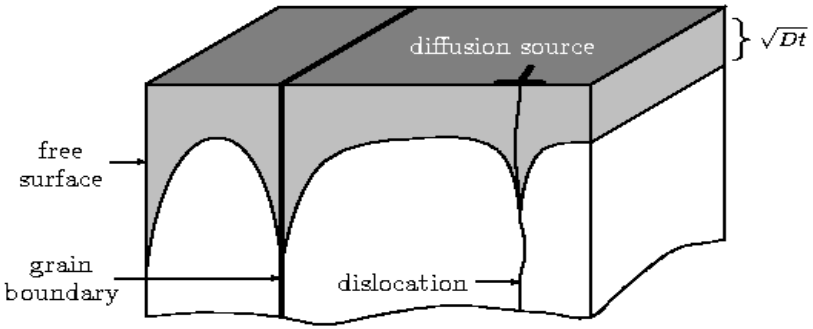
Grinder or microtome:

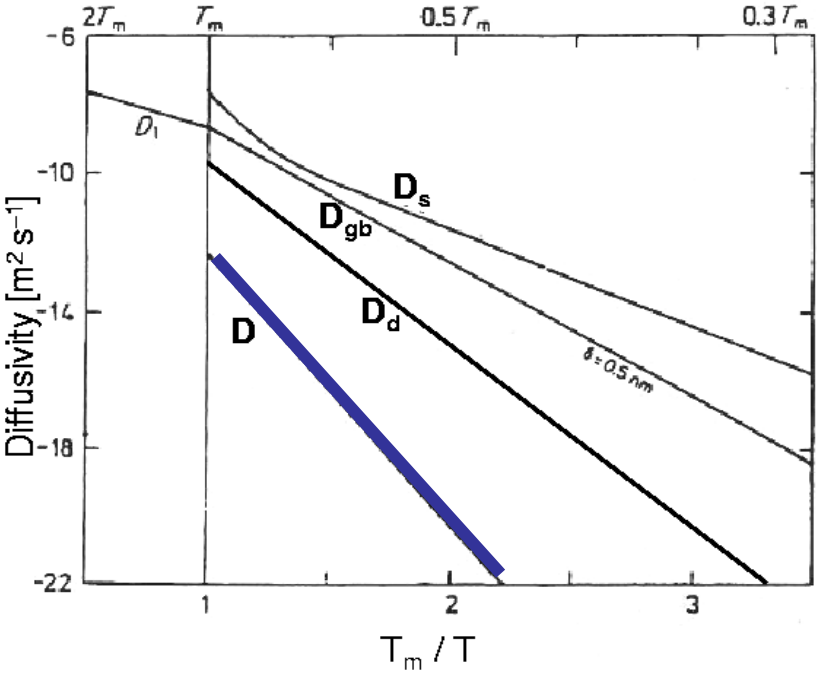
- penetration depths x > 20 µm

Ion-beam sputtering:

- penetration depths x < 10 µm

High-diffusivity paths (short circuits) in solids





High-diffusivity paths

Dislocations, Grain boundaries, Free surfaces

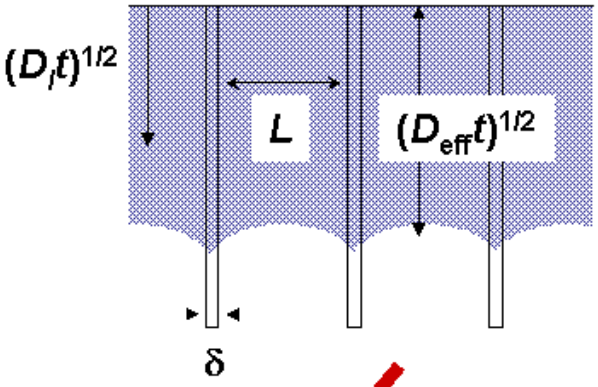
'Diffusion spectrum'

D(lattice) << D_d(dislocation)

< D_{gb}(grain boundaries) < D_s(surface)

The Harrison Type – A and B kinetics regimes for analysing tracer diffusion depth profiles from a thin-film source:

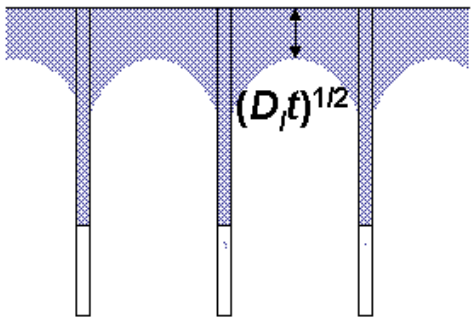
Type A



$(D_l t)^{1/2} >> L$

D_{eff}

Type B

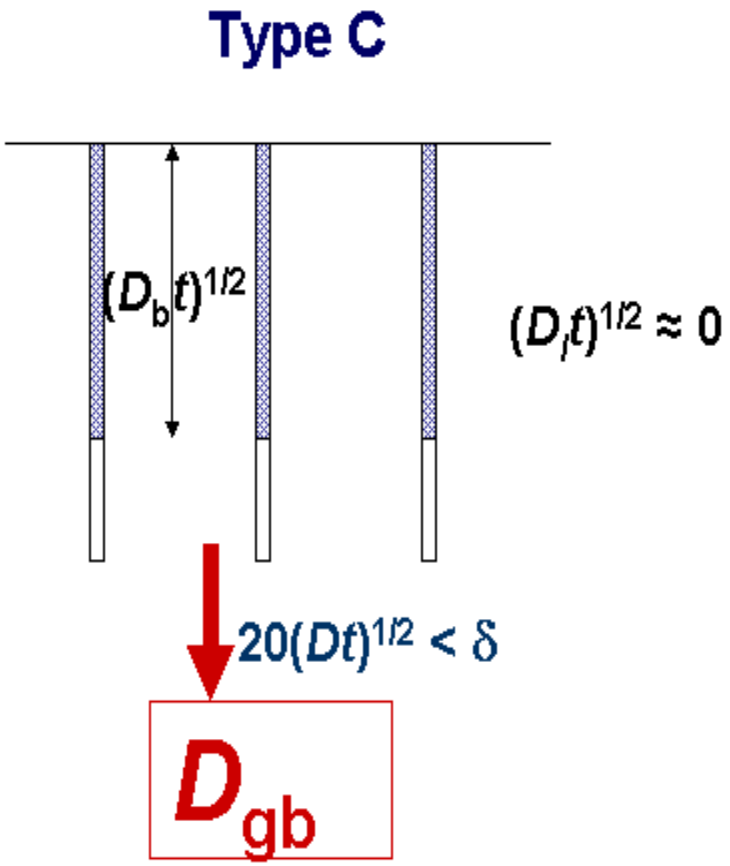


$100\delta < (D_l t)^{1/2} < L/20$

$\delta D_{gb} = P$

$+ \; D_l$?

The Harrison Type - C kinetics regime

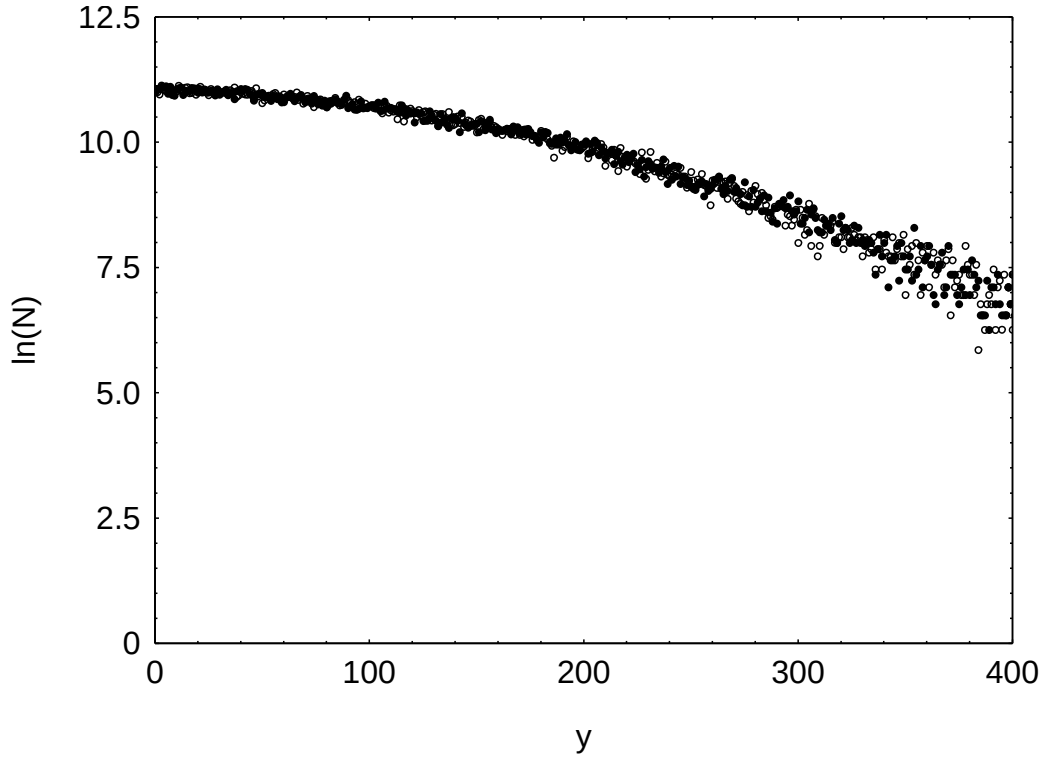


Analysis of diffusion profiles in the Harrison Type-C and Type-A kinetics regimes.

General equation for analysis of the Type-C kinetics regime:

$$D_{gb} = \frac{1}{4t}\left(-\frac{\partial \ln c}{dy^{2.0}}\right)^{-1}$$

α = 10; $\beta = 10^3$; Λ = 22



Gaussian solution, equation is similar to the Type-A kinetics analysis.

Analysis of the diffusion in the Harrison Type-B kinetics regimes .

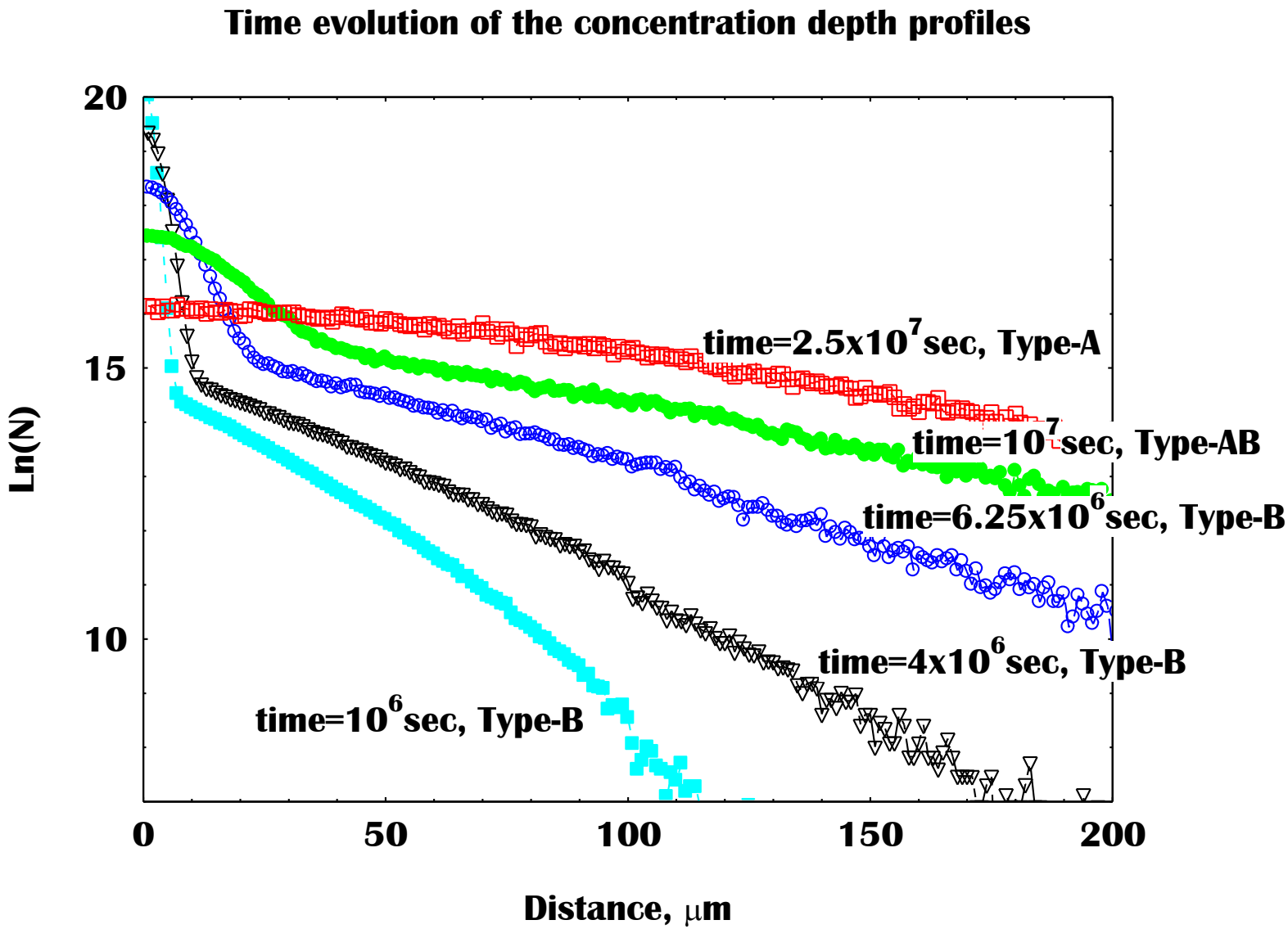
General equation for analysis of the Type-B kinetics regime (tail section of the profile):

$$\delta D_{gb} = g \frac{D_l^r}{t^q} \left(- \frac{\partial \ln c}{dy^{1.2}} \right)^{-w}$$

t **is time;**

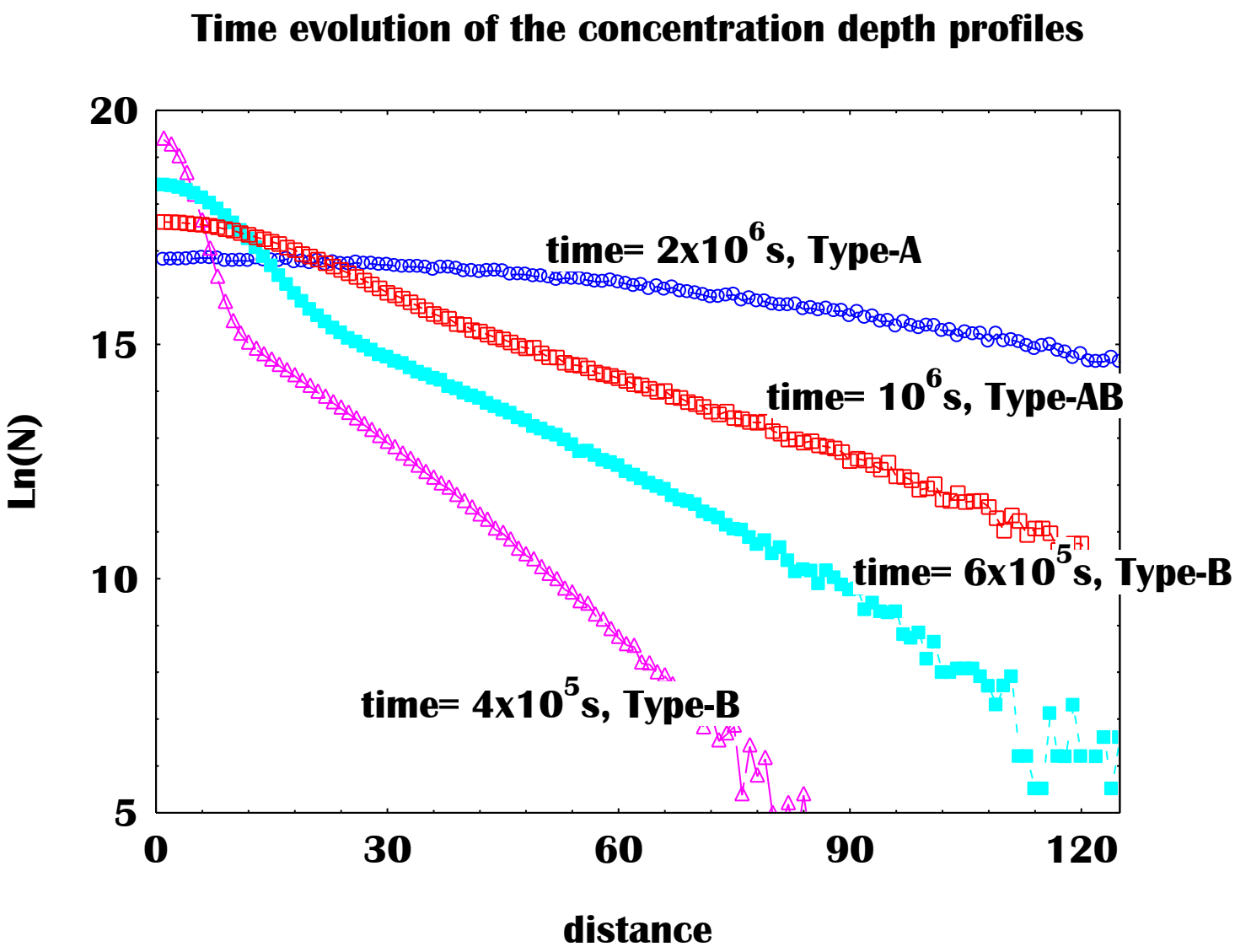
g, r, q, w **– constants, solution dependent**

Examples of (LMC) simulated concentration depth profiles



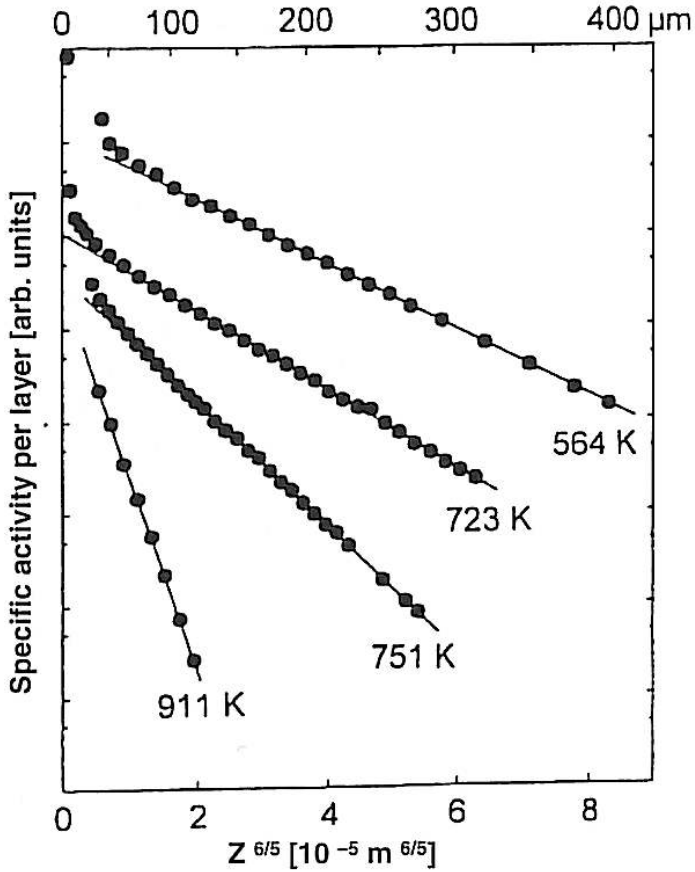
Grain size is about 100μm

Examples of concentration depth profiles



Grain size is about 20μm

Examples of experimentally obtained diffusion profiles:



Type-B kinetics depth profiles for self-diffusion in Ag polycrystals according to Sommer and Herzig (J. Appl. Phys., 14, 351,1992)

Parallel Slab Model

It is extremely important to know when a diffusion depth profile is in the Type-A, Type-B or Type-C kinetics regimes.

For homogeneous materials (not much spread in grain size) and for self-diffusion, the transition points have been identified for the parallel slab geometry (Belova and Murch Phil. Mag. 2009):

Regime C – $\alpha > 5.0$;

Transition Regime BC – $0.1 > \alpha > 5.0$;

Regime B – $\{\Lambda > 3\} \cap \{\alpha < 0.1\}$;

Transition Regime AB – $0.4 < \Lambda < 3$;

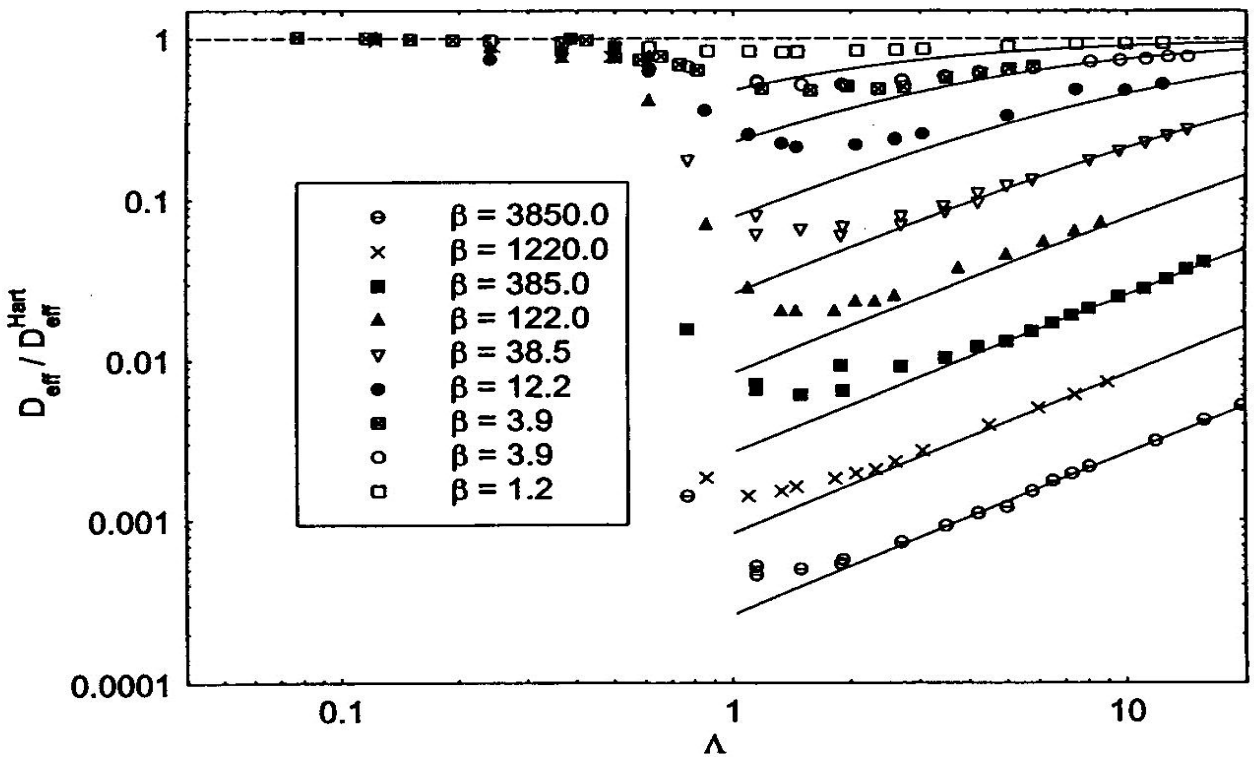
Regime A – $\Lambda < 0.4$

$$\Lambda = \frac{L}{\sqrt{D_l t}}$$

$$\alpha = \frac{\delta}{2\sqrt{D_l t}}$$

Parallel Slab Model

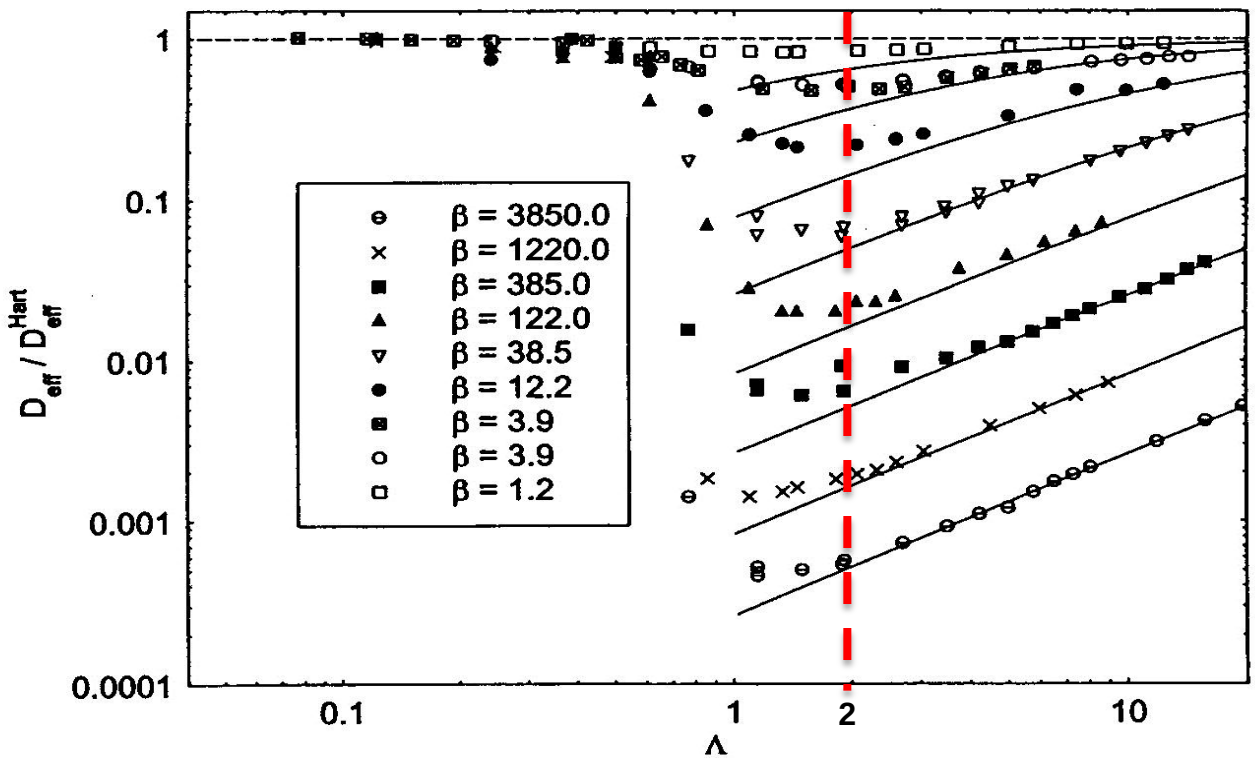
Type-A regime ▼ Type-B regime



D_{eff}/D_{eff}^{Hart} as a function of Λ (= $L/(D_l\, t)^{1/2}$ for various values of β (slow surface diffusion model). Solid lines correspond to the Harrison Type-B kinetics condition (D_l/D_{eff}^{Hart}).

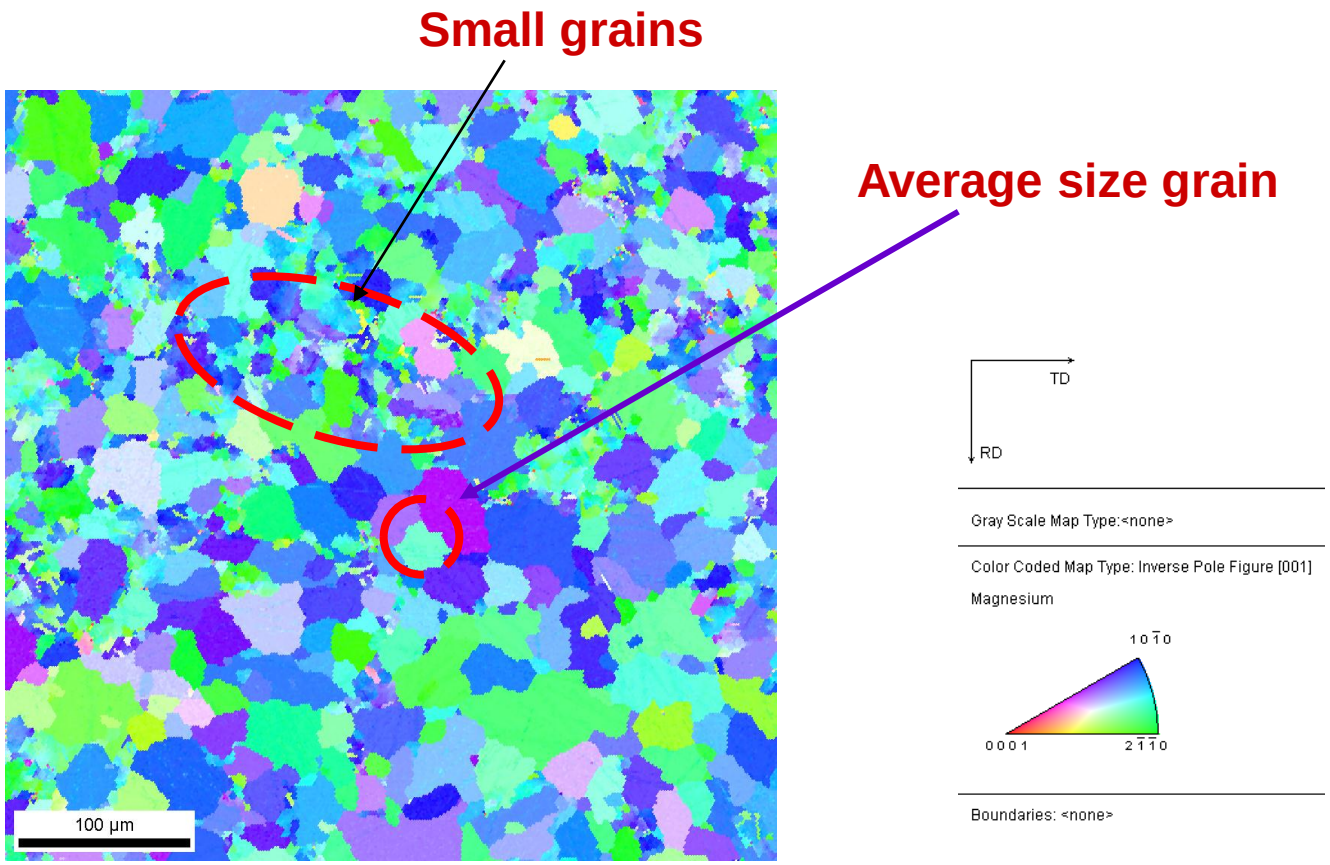
<u>The transition occurs at $\Lambda \approx 0.4$</u> and depends slightly on the β or 'Le Claire' parameter = $\delta D_{gb}/2D_l \sqrt{D_l\, t}$. (Belova and Murch, Phil Mag 2001).

Parallel Slab Model



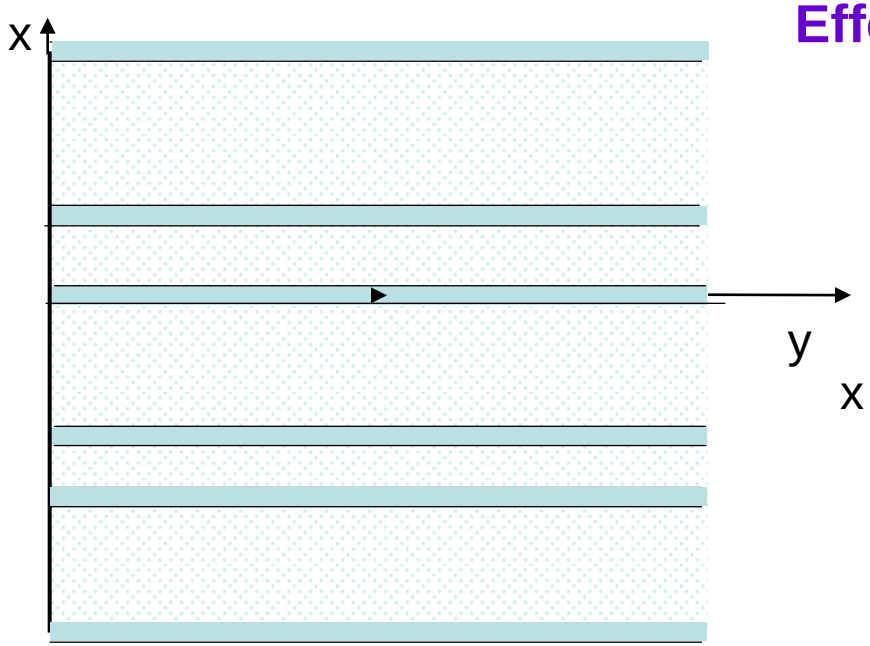
It was not noticed previously that the critical value of Λ is about 2.0 for the Type-B kinetics regime analysis for the *first section of the profiles (Gaussian)* to obtain D_I.

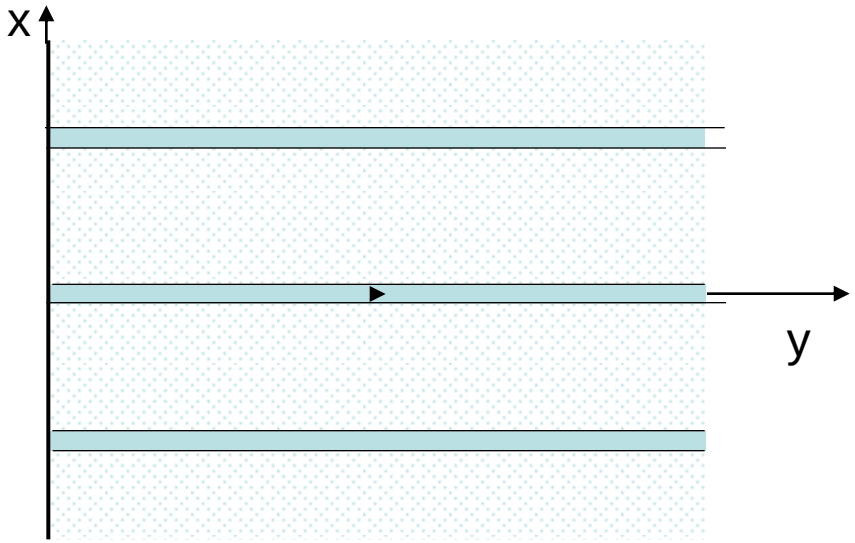
Example of experimentally observed grain structure (Mg polycrystalline)



Parallel Slab Model

Effect of inhomogeneous grain sizes?



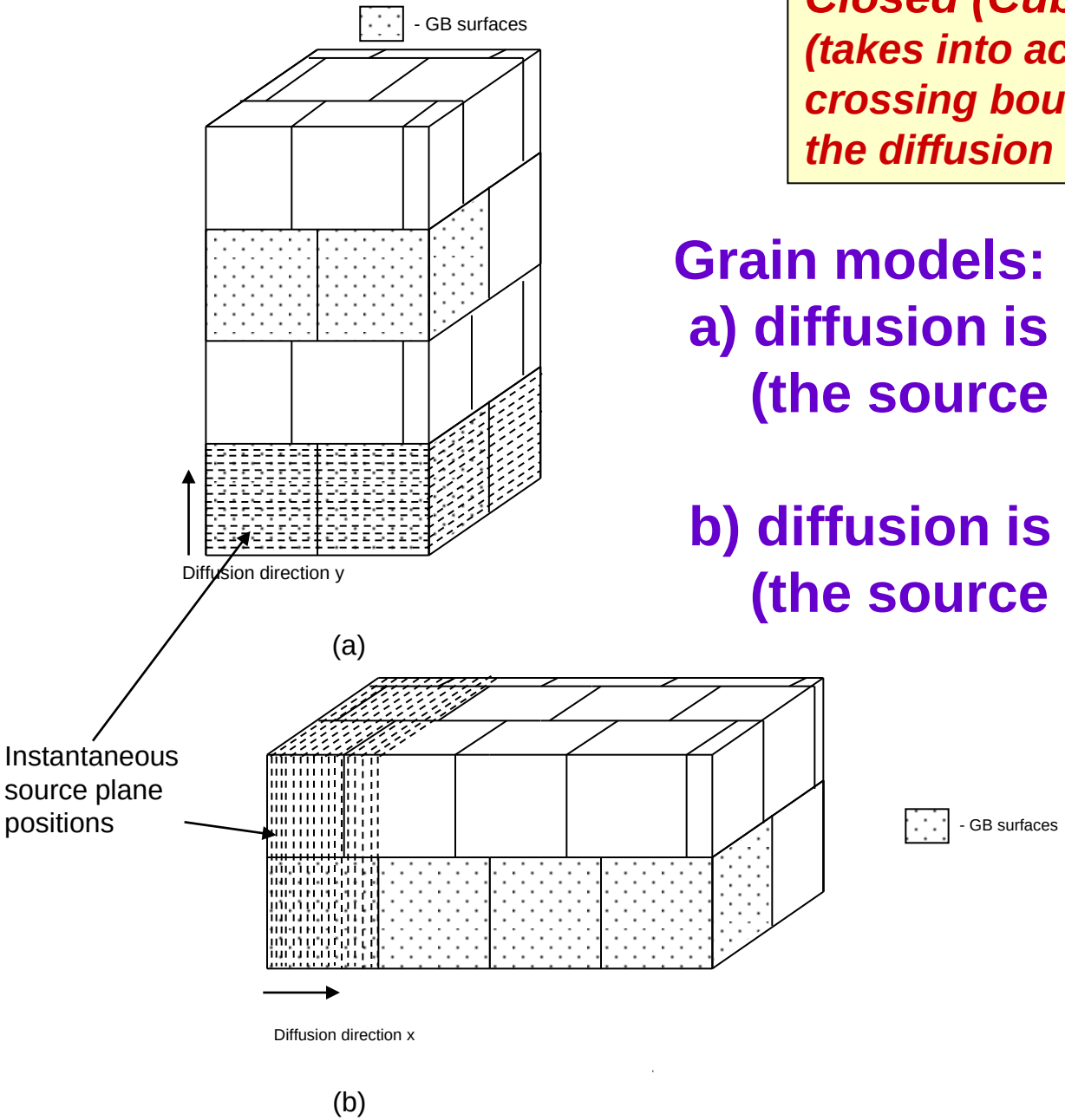


Condition: the volume fraction of the grain boundary region is the same.

It turns out that for the Parallel Slab Model there are NO differences in the resulting depth profiles!

(Provided that all other diffusion parameters are the same.)

Closed (Cubic) Grain model (takes into account the tracers crossing boundaries normal to the diffusion direction).



Grain models:

a) diffusion is in the y direction, (the source plane is at y = 0).

b) diffusion is in the x direction (the source plane is at x = 0).

Closed (Cubic) Grain model

Regime C – $\alpha > 5.0$;

Transition Regime BC – $0.5 > \alpha > 5.0$;

Regime B – $\{\Lambda > 5\} \cap \{\alpha < 0.5\}$;

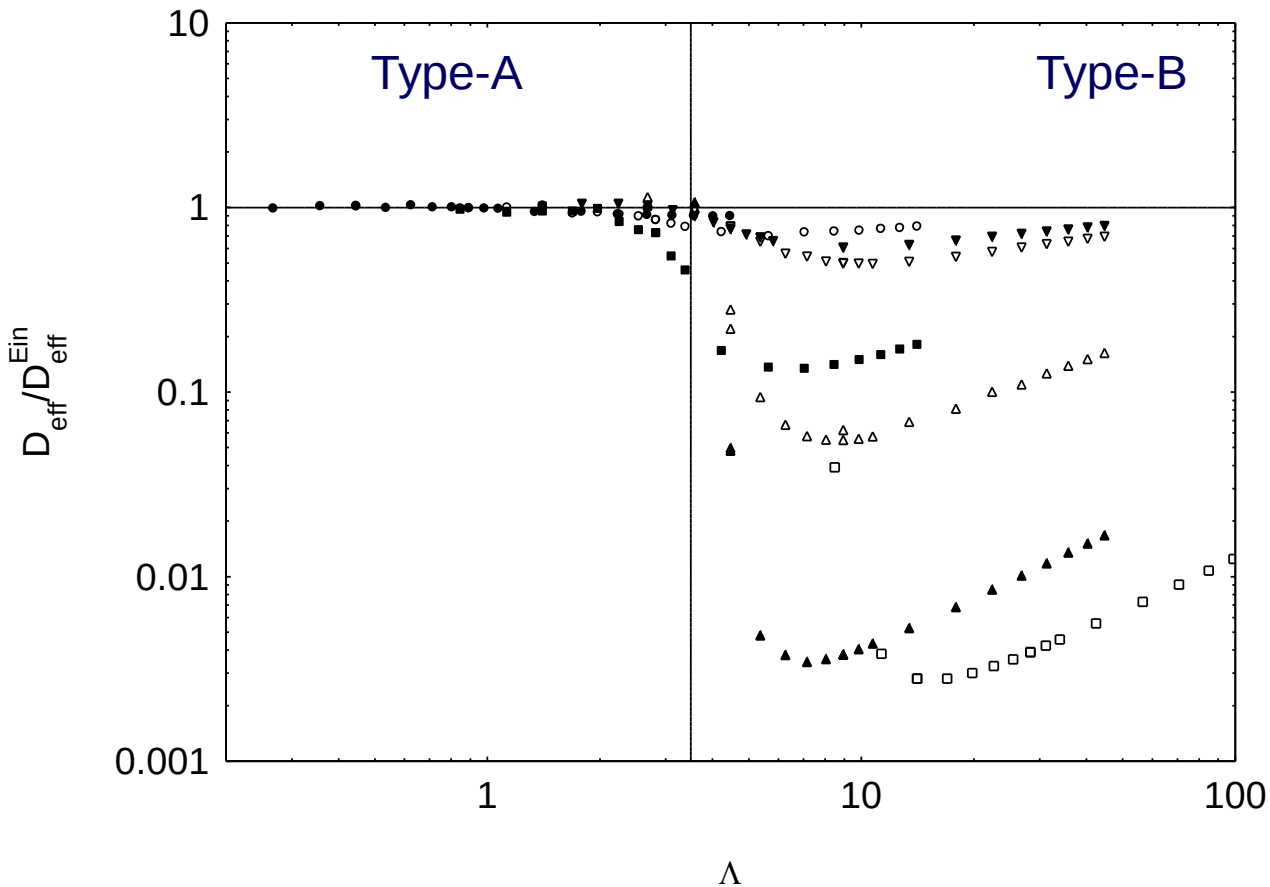
Transition Regime AB – $3 < \Lambda < 5$;

Regime A – $\Lambda < 3$

$$\Lambda = \frac{L}{\sqrt{D_l t}}$$

$$\alpha = \frac{\delta}{2\sqrt{D_l t}}$$

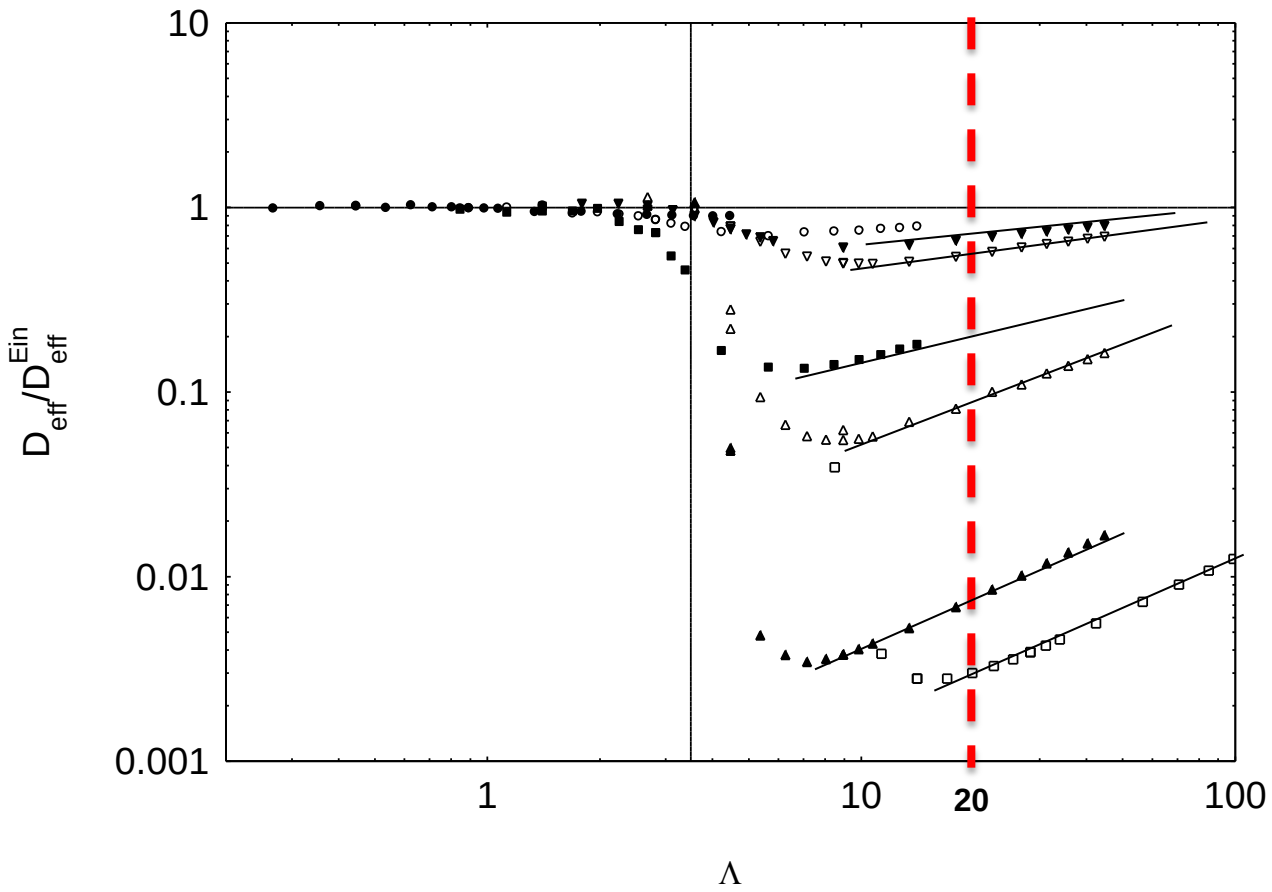
Closed (Cubic) Grain model



***D_{eff}/D_{eff}^{Ein}* as a function of Λ for various values of *β* for the case of cubic grains.**

<u>The transition between Type-A and the next regime now occurs at $\Lambda \approx 3.0$</u>

Closed (Cubic) Grain model

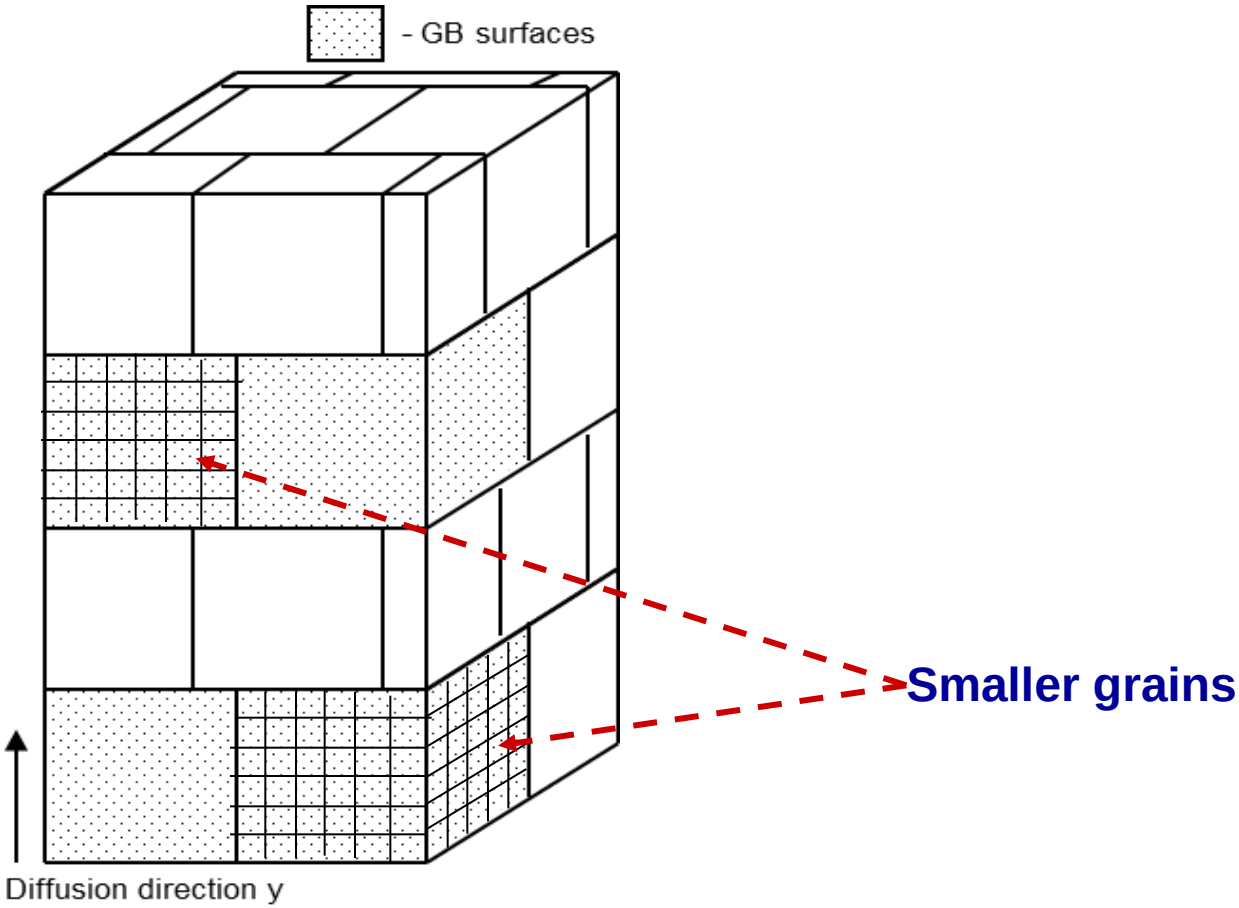


Again, it was not noticed previously that the critical value of Λ is about 20.0 (!) and is applicable for the Type-B kinetics regime analysis of the *first section of the profiles* to obtain D_I.
(Possibly another parameter (Δ) influences this transition point.)

Closed (Cubic) Grain model

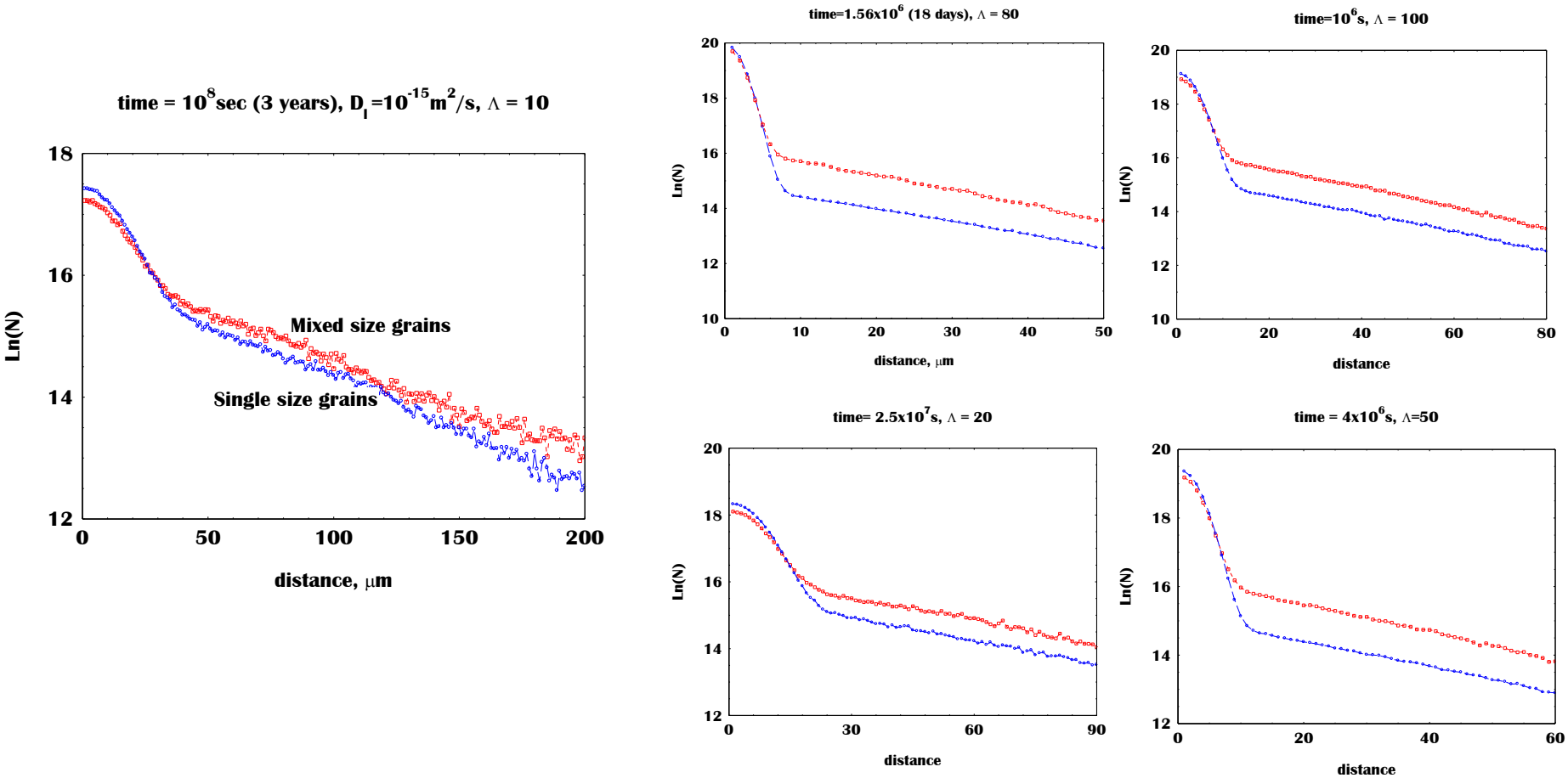
Effect of inhomogeneous grain sizes?

Numerical approach



Condition: the volume fraction of the grain region is the same.

Closed (Cubic) Grain model



- **First section of the profile**: mixed size grains will result in the determined lattice diffusivity (D_l) being about 5-10% greater than the real value.
- **Tail section of the profile**: the difference will result in the double product ($D_{gb}\delta$) being about 10-15% smaller than the real value.

Summary:

1.The effect of the inhomogeneous grain sizes was analysed making use of Lattice Monte Carlo mesoscale numerical method.

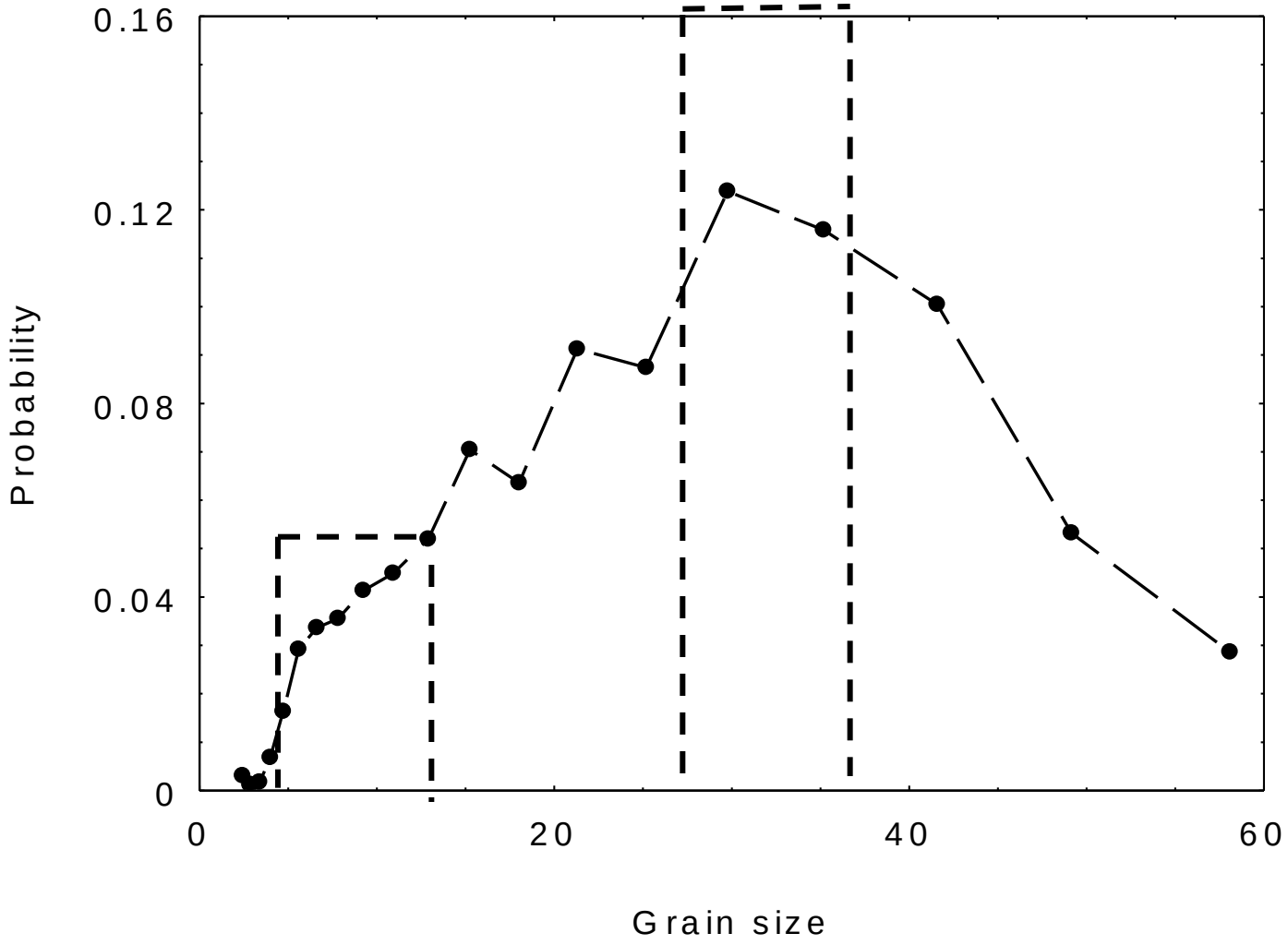
2. Results depend on the geometry of the model considered:

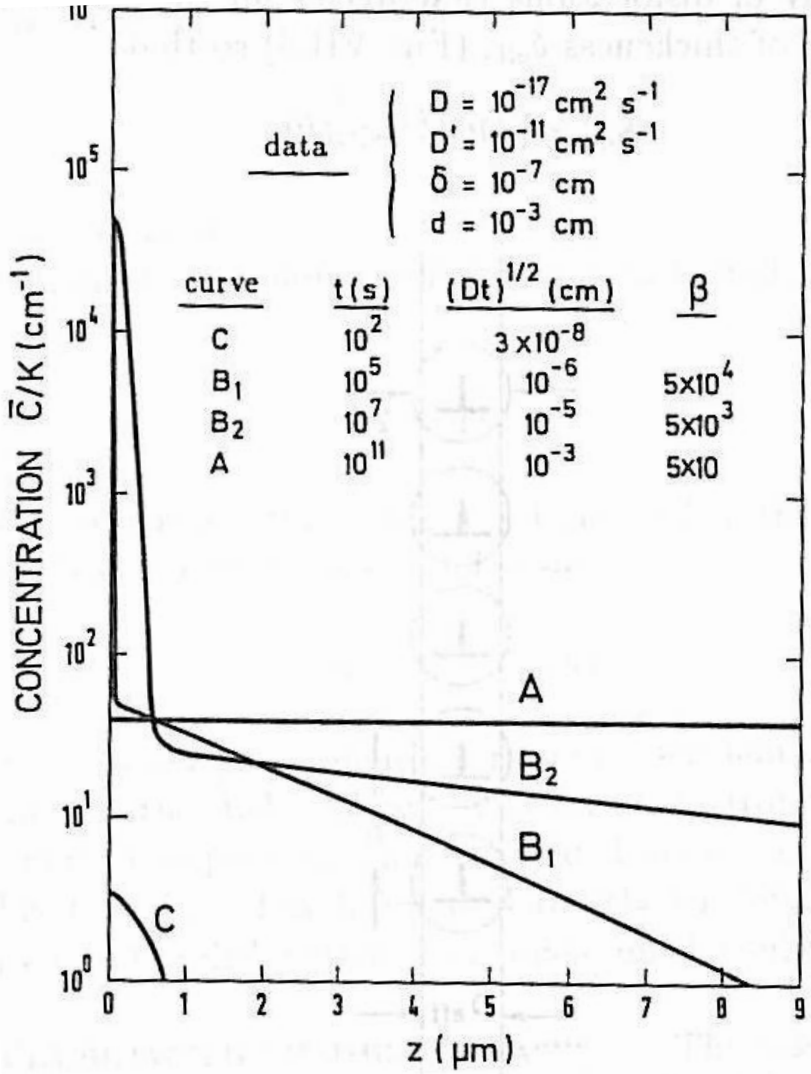
3. The usually considered parallel slab model does not show a difference between the equally spaced slabs and randomly (inhomogeneously) spaced slabs.

4. For the closed grain model (cubic shape) results are:

- First part of the profile: the mixed size grains will result in the lattice diffusivities about 5-10% greater than the real value.
- Tail part of the profile: the difference will result in the double product ($D_{gb}\delta$) about 10-15% smaller than the real value.

Thank you!


0.16
0.12
0.08
0.04
0
Probability
0
20
40
60
Grain size

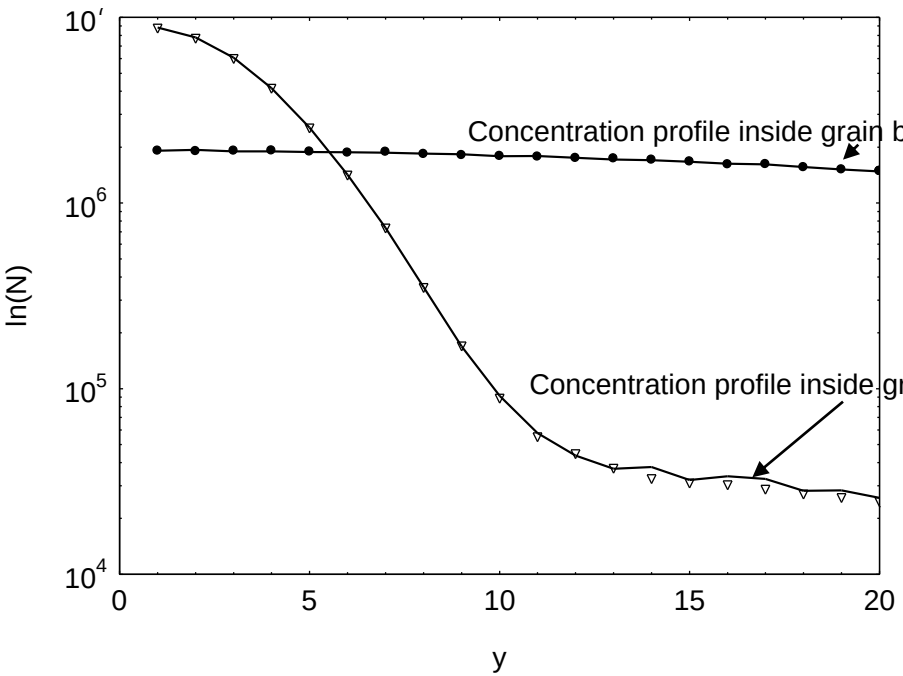


Calculated diffusion profiles (according to the analytical Suzuoka solution) for a polycrystalline material with grain size of 10 μm for different diffusion times. (Atkinson, Solid State Ionics, 12 309, 1984)

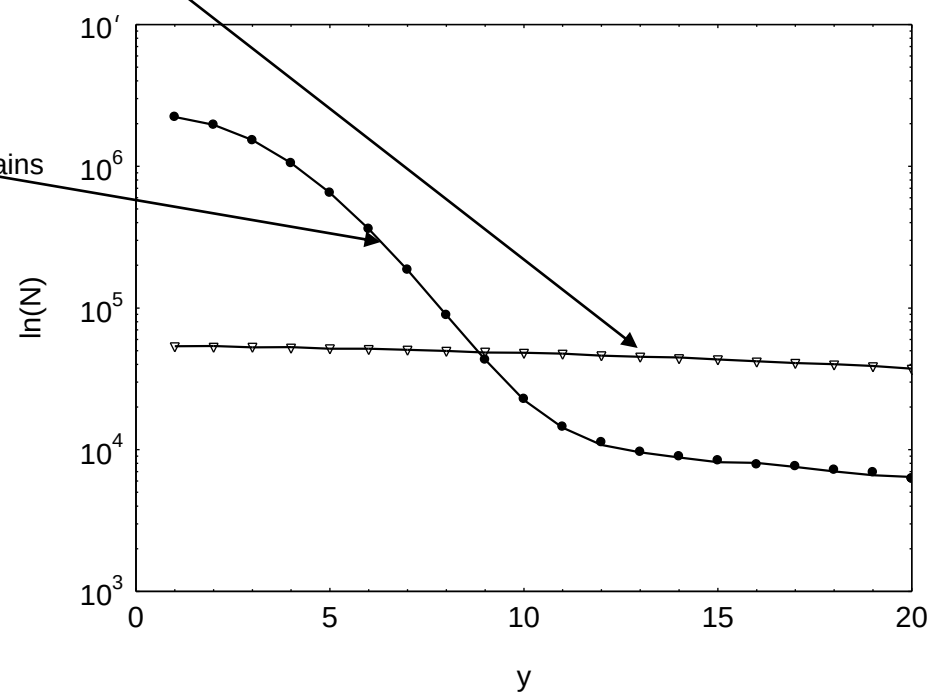
Tests for *separate* contributions to the concentration profiles – atoms from the grains only and from the grain boundaries only, Type-B regime

LMC results

$d = 10^2\delta$



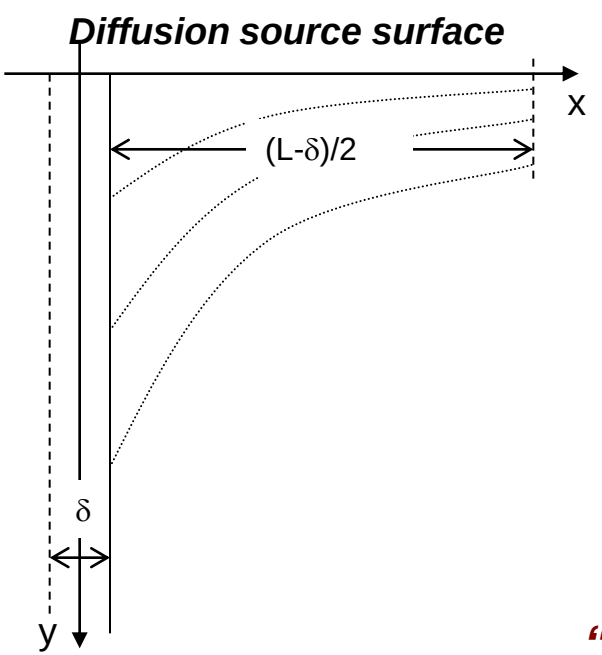
$d = 10^4\delta$



Definition of the segregation factor for the purposes of the computer simulation (LMC).

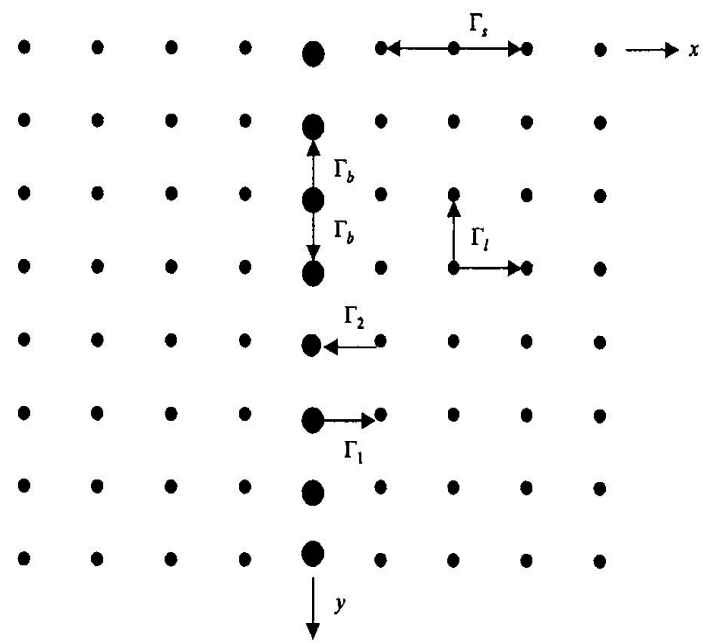
The usual definition of the segregation factor for the dilute regime of solute solution (Henry's isotherm/law) as was used in the boundary conditions:

$$c_b(y,t)_{x=\delta/2} = sc_g(y,t)_{x=\delta/2}$$



For computer simulations we need the following form of the same:

$$s = \Gamma_2 / \Gamma_1 = \exp(-Q_{bind} / kT)$$

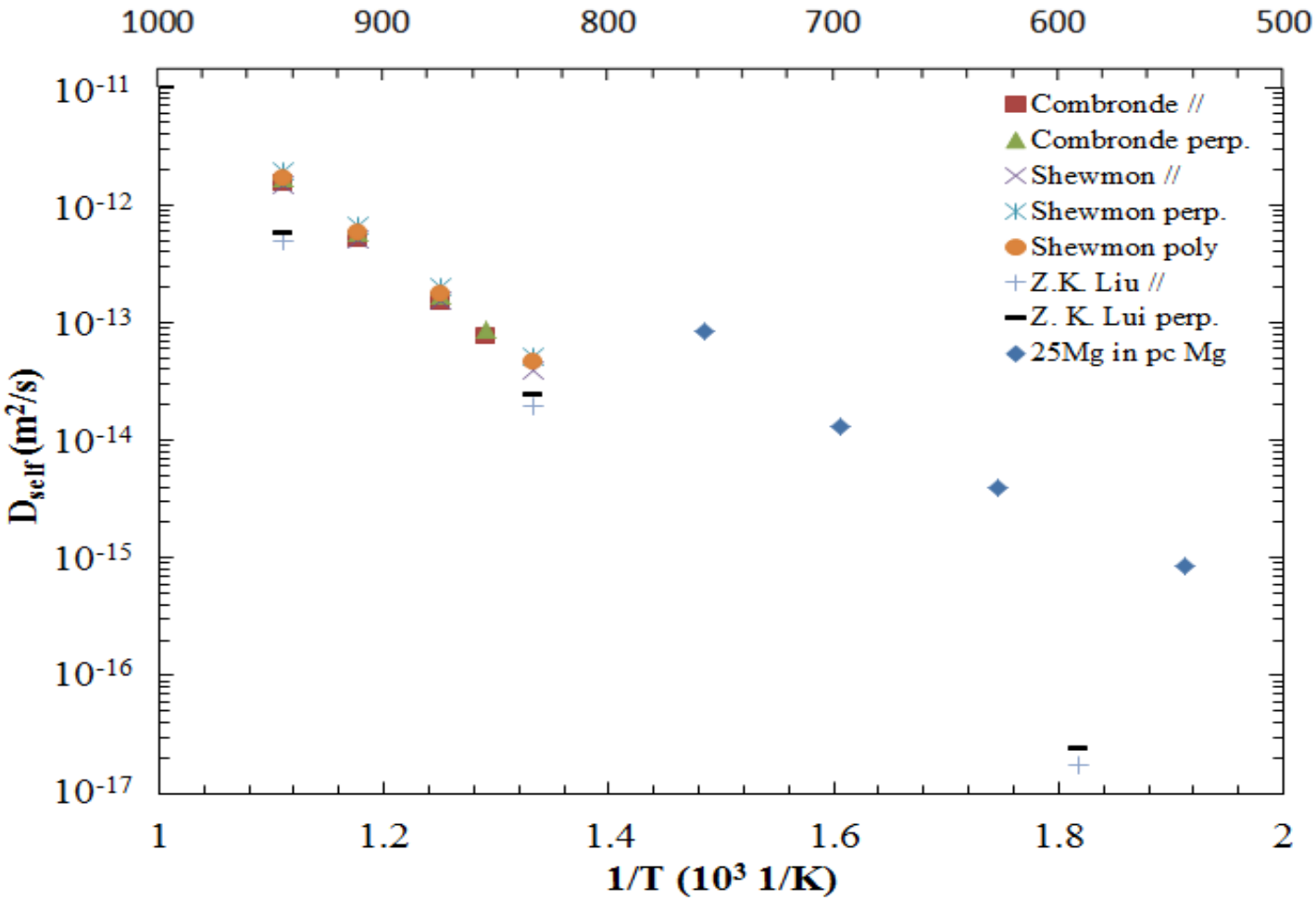


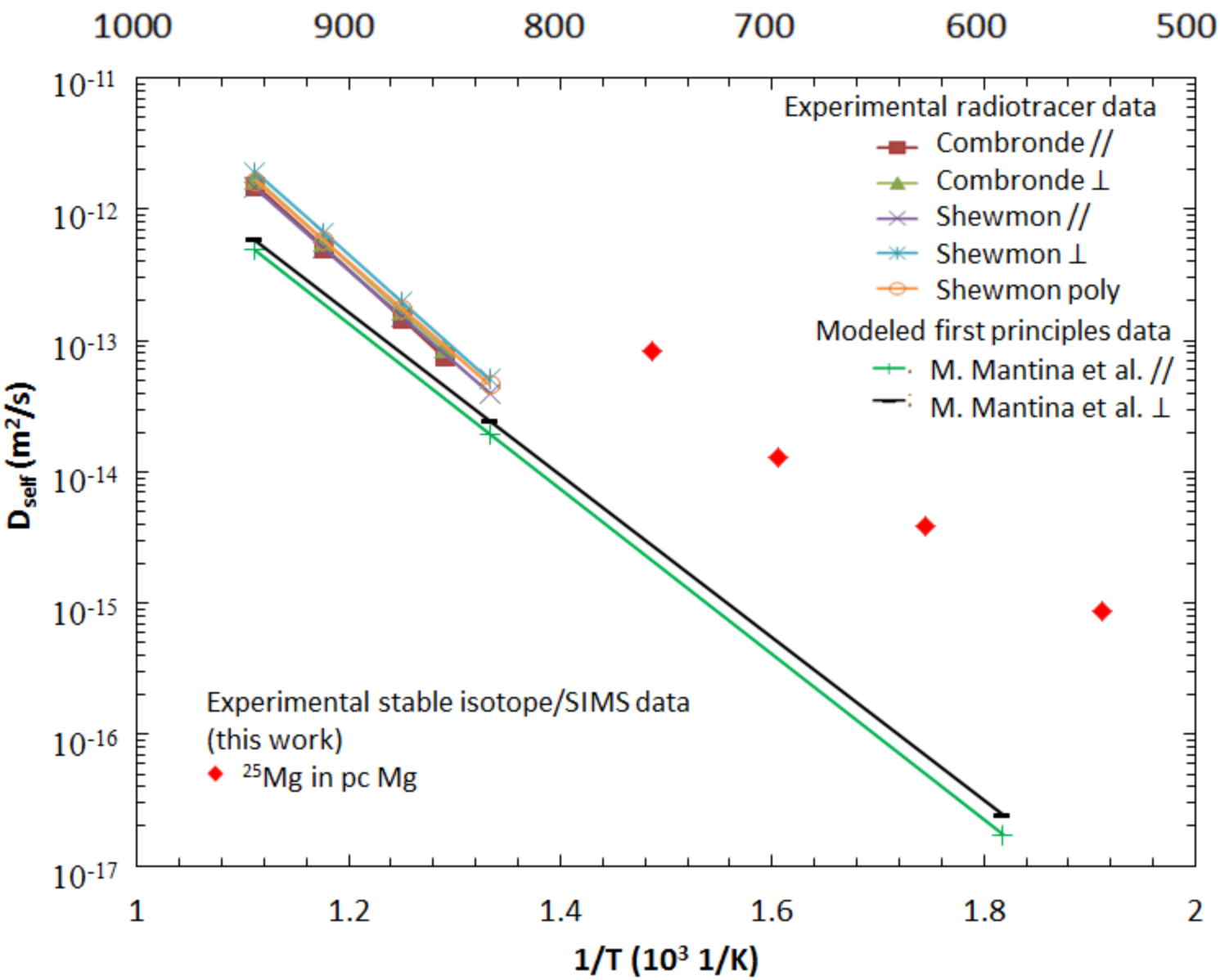
2D lattice model of the grain boundary diffusion

"Local" definitions

^{25}Mg on Poly Mg SIMS

(10kV, no flood)




1000
900
800
700
600
500
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
D_{self} (m^2/s)
1
1.2
1.4
1.6
1.8
2
1/T (10^3 1/K)
Experimental radiotracer data
Combronde //
Combronde ⊥
Shewmon //
Shewmon ⊥
Shewmon poly
Modeled first principles data
M. Mantina et al. //
M. Mantina et al. ⊥
Experimental stable isotope/SIMS data
(this work)
^{25}Mg in pc Mg

Calculations from the SIMS data

Specimen	Dself (m²/s)
250°C 12 hrs	8.65×10^{-16}
300°C 4 hrs	3.90×10^{-15}
350°C 1 hr	1.30×10^{-14}
400°C 30 min	8.37×10^{-14}

Specimen	Λ
250°C 12 hrs	5.0
300°C 4 hrs	4.0
350°C 1 hr	4.0
400°C 30 min	2.5