Equilibrium and Time-Dependent Solute Segregation at Grain Boundaries: Systematic Monte Carlo Studies

Irina V. Belova, Graeme E. Murch and Thomas Fiedler

University Centre for Mass and Thermal Transport in Engineering Materials,

Priority Research Center for Geotechnical and Materials Modeling,
School of Engineering, The University of Newcastle,
Callaghan, NSW 2308,
AUSTRALIA

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Talk outline:

1. Introduction

2. Investigation of the equilibrium solute segregation effect in grain boundary diffusion

3. Summary I

4. Investigation of the time-dependent solute segregation in grain boundary diffusion

5. Summary II

Introduction

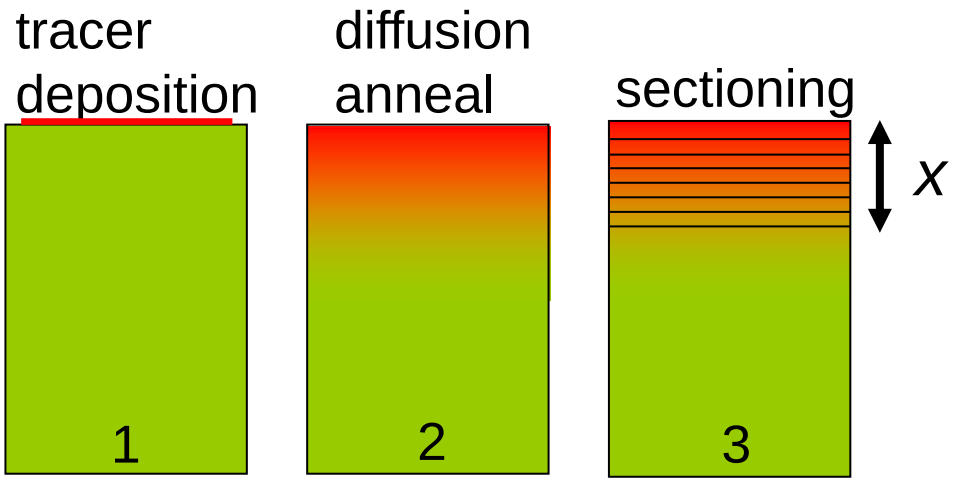
Diffusion experiment: Radiotracer method (some details)

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

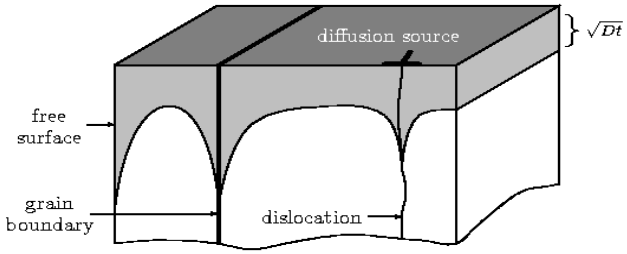
Ion-beam sputtering:

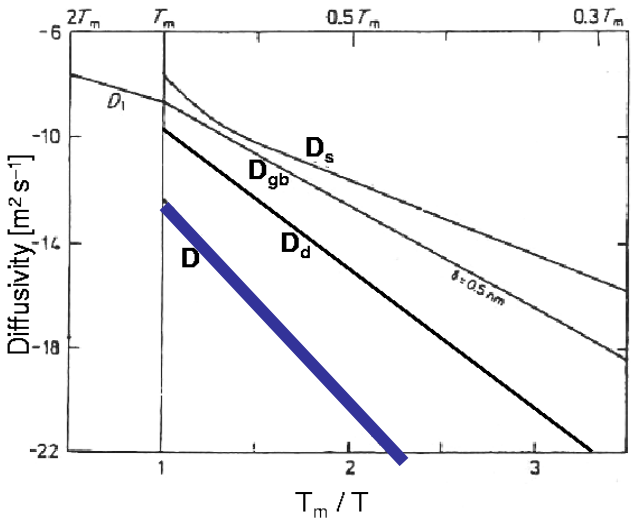
- penetration depths x < 10 µm

Then diffusion quantities are extracted from the penetration profiles using existing solutions to the Fick's laws

Introduction

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)

Introduction

Grain boundary diffusion measurements provide a way of determining the degree of binding of a solute to a grain boundary.

How do grain boundary diffusion measurements work?

Since a grain boundary diffusion measurement is really a time-dependent measurement, is there a potential problem when measuring an ‘equilibrium property’ like grain boundary segregation?

I. Investigation of the *equilibrium* solute segregation effect in grain boundary diffusion:

- **Harrison Type - A,B and C kinetics regimes for tracer diffusion from a thin-film tracer source of solute at the surface.**

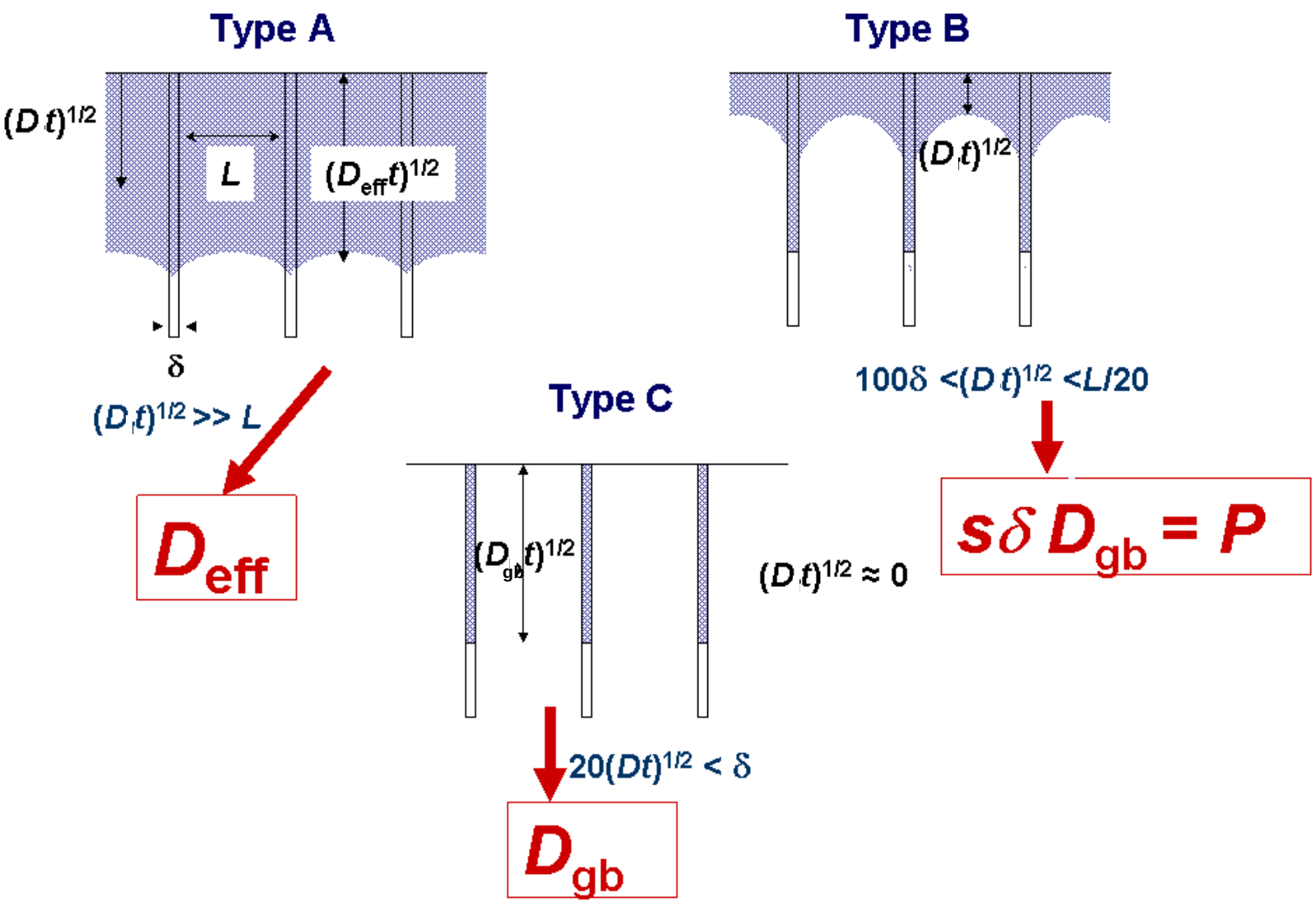
- **Examples of experimentally determined solute segregation factors**

- **Fisher's approach/model for addressing phenomenological diffusion problems.**

- **Equivalence of the two models in the parallel slab approach (Fisher's approach).**

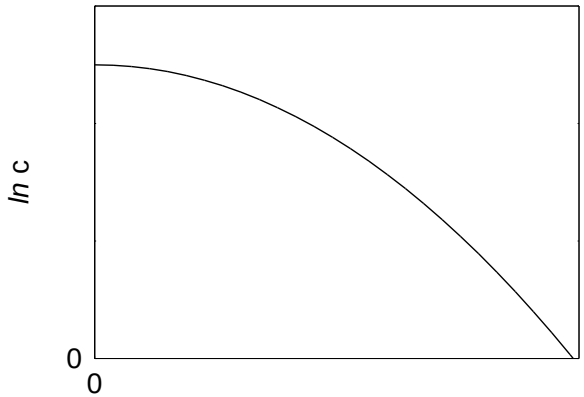
3. Summary I.

The Harrison Type - A,B and C kinetics regimes for tracer diffusion from a thin-film source at the surface into a medium containing grain boundaries:

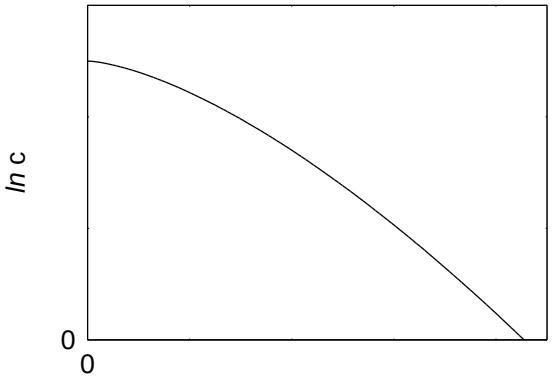


Logarithm of Concentration vs Depth for the kinetics regimes

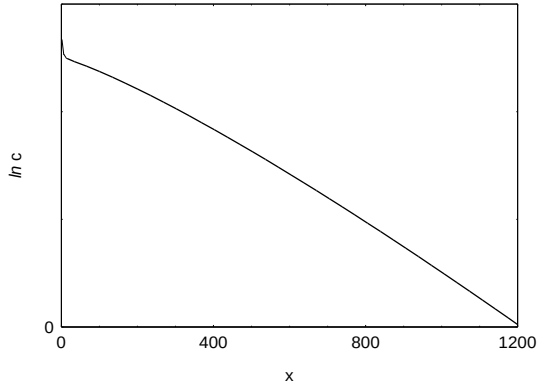
Type A –
2.0 exponent - Gaussian



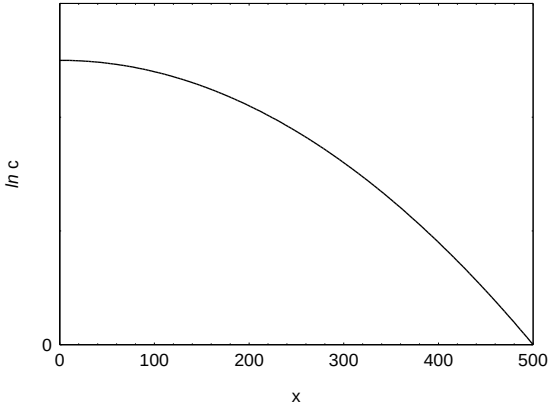
Type AB –
1.5 exponent (tail region)



Type B –
1.2 exponent (tail region)



Type C –
2.0 exponent - Gaussian



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

A. In the Harrison Type-A kinetics regime, a Gaussian analysis of the profile gives D_{eff} (the critical parameter for identification of Type-A regime kinetics):

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

t is time;
L is grain size;
s is segregation factor
δ is grain width.

$$D_{eff} = \frac{s\delta D_{gb} + (L-\delta)D}{s\delta + L - \delta} \approx \begin{cases} D(1 + s\delta\Delta / L), \text{ if } s\delta << L \\ D_{gb}, \text{ if } s\delta >> L \end{cases}$$

self-diffusion

nano-grains, strong segregation

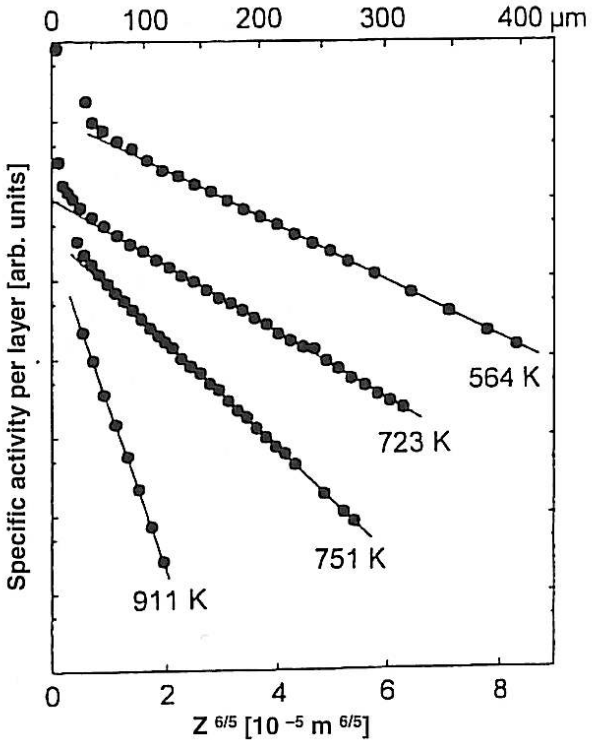
B. General equation for analysis of the Type-B kinetics regime:

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

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

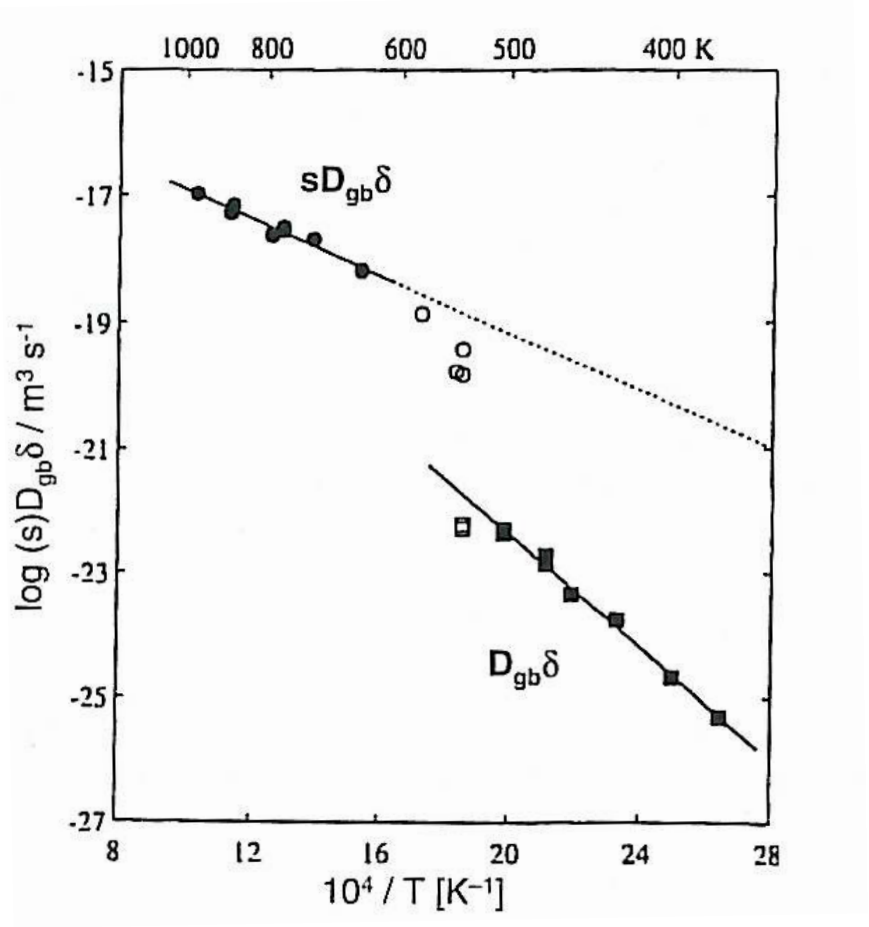
$$D_{gb} = \frac{1}{4t}\left(-\frac{\partial \ln c}{dy^{2.0}}\right)^{-1}$$

Examples of (experimentally obtained) diffusion profiles:



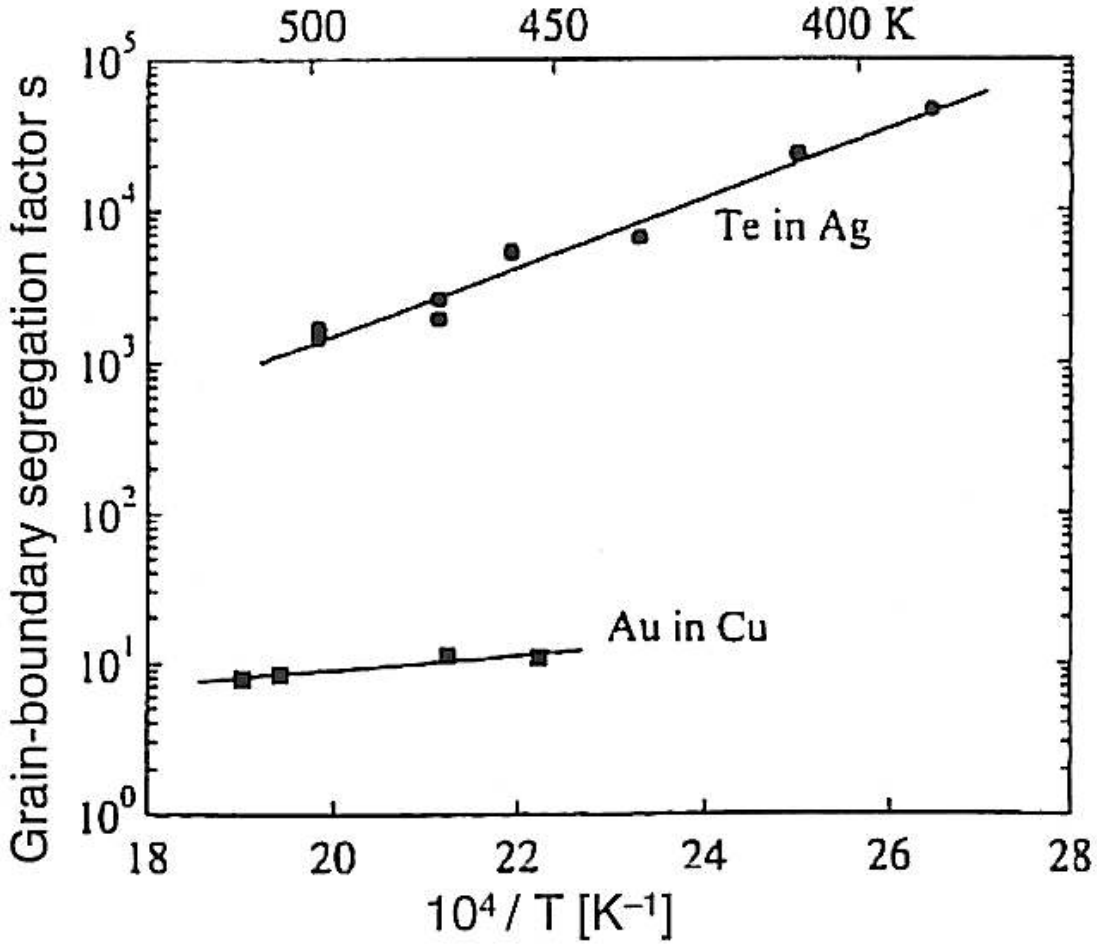
Type-B kinetics penetration profiles of self-diffusion in Ag polycrystals according to Sommer and Herzig (J. Appl. Phys., 14, 351,1992)

Further examples



Arrhenius diagram of the triple product $s\delta D_{gb}$ (measured in the Type-B regime) and of δD_{gb} (with D_{gb} measured in the Type-C regime) from Te diffusion along grain boundaries in Ag according to Herzig et al. (Acta Metall Mater., 41, 1683, 1993).

Type-B and C kinetics prevail above 600K and below 500K, respectively. The range 500-600K corresponds to a transition regime.



Grain boundary segregation factors for Te in Ag according to Herzig et al. (1993) and Au in Cu according to Surholt et al. (Phys. Rev. B, 50, 3577, 1994) determined from combined Type-B and Type-C measurements.

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

$\Rightarrow$ It is necessary to identify correctly the transition points marking the regimes.

For homogeneous materials (not much spread in grain sizes) and for self-diffusion (segregation factor = 1, no binding energy for the atoms to the grain boundary) transition points have been identified (Phil. Mag. 2009) as follows (2D geometry):

Regime C – $\alpha > 5.0$;

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

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

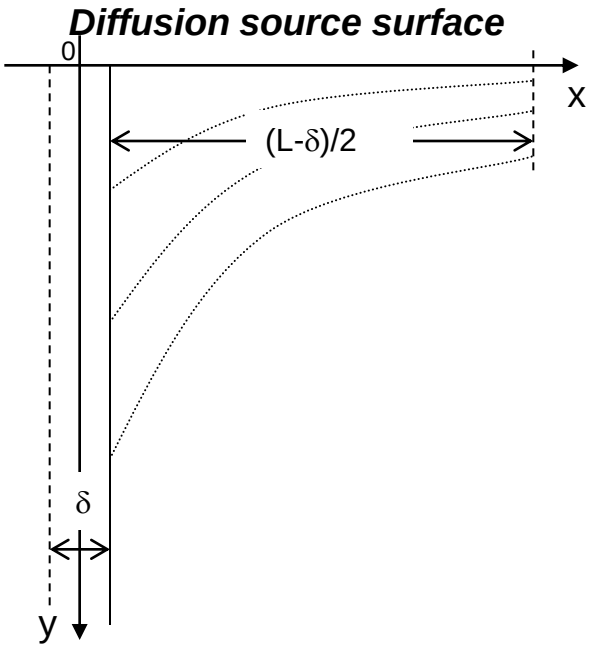
Transitional Regime AB – $0.4 < \Lambda < 3$;

Regime A – $\Lambda < 0.4$

$$\alpha = \frac{\delta}{2\sqrt{Dt}} \qquad \Lambda = \frac{L}{\sqrt{Dt}}$$

To be able to predict the same transition points for <u>solute</u> diffusion (where *s* is usually >> 1) we need to consider two equivalent problems as explained in the following:

Fisher's analytical Model I (segregation effect: Bokshtein et al., Phys Met Metallogr, 1958, Gibbs, Phys. Stat. Solidi a, 1966):



i Diffusion Equations to solve in the grain boundary ($0 \le x \le \delta/2$);
and in the grain ($\delta/2 \le x \le \infty$ (or $L/2$))

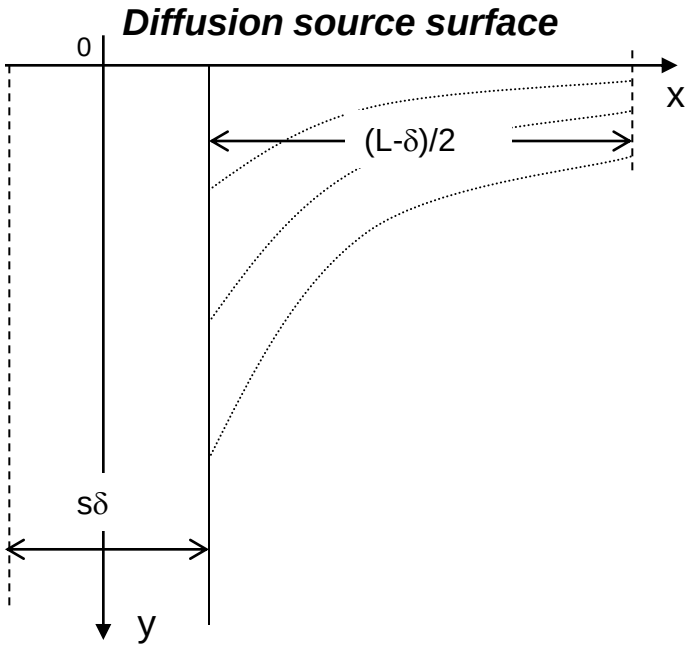
ii. Boundary conditions:

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

+ Continuity of the solute atomic fluxes at the $x = \delta/2$.

iii. Initial conditions: instantaneous source,
NOTE: partitioning at the plane y = 0 according to segregation (to preserve equilibrium segregation at all times, linear).

Fisher's analytical Model II:



i Diffusion Equations to solve in the grain boundary $(0 \le x \le s\delta/2)$;

and in the grain $(s\delta/2 \le x \le \infty$ (or $(L-\delta+s\,\delta)/2)$)

ii. Boundary conditions:

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

+ Continuity of the solute atomic fluxes at the $x = \delta/2$**.**

iii. Initial conditions: instantaneous source

Fisher's analytical model I and II: are they equivalent??

Jean Philibert (1991) pointed out that these two models for the 'infinite' grains are equivalent because of the reasonable assumption that the concentration in the GB is constant across the GB.

We have done extensive studies using computer simulations to validate this proposition for the case of finite size grains, but in the slab (effectively 2D) geometry only.

<u>Proposition</u>: Models I and II are *equivalent*. $\Rightarrow$ **We test this with Lattice Monte Carlo (LMC)**

This proposition has a very important consequence:
Harrison classification for Model I is *the same* as the Harrison classification for Model II where we should use:

$$\Lambda^* = \frac{L + (s-1)\delta}{\sqrt{Dt}}$$ **for the analysis of A, B and AB kinetic regimes;**

$$\alpha^* = \frac{s\delta}{2\sqrt{Dt}}$$ **for the analysis of B, C and BC kinetic regimes.**

Test:* *effective diffusivity in the Type-A kinetics regime:

Parallel slabs model

$\Downarrow$

$$D_{eff}^{par.sl.} = \frac{s\delta D_{gb} + (L-\delta)D}{s\delta + L - \delta}$$

Closed grains model

$\Downarrow$

$$D_{eff}^{cl.g.} = \frac{sD_{gb}}{g\,s + 1 - g}\left(1 + \frac{3(D - sD_{gb})(1-g)}{2sD_{gb} + D - (D - sD_{gb})(1-g)}\right)$$

$$g = 1 - (1 - \delta / L)^3$$

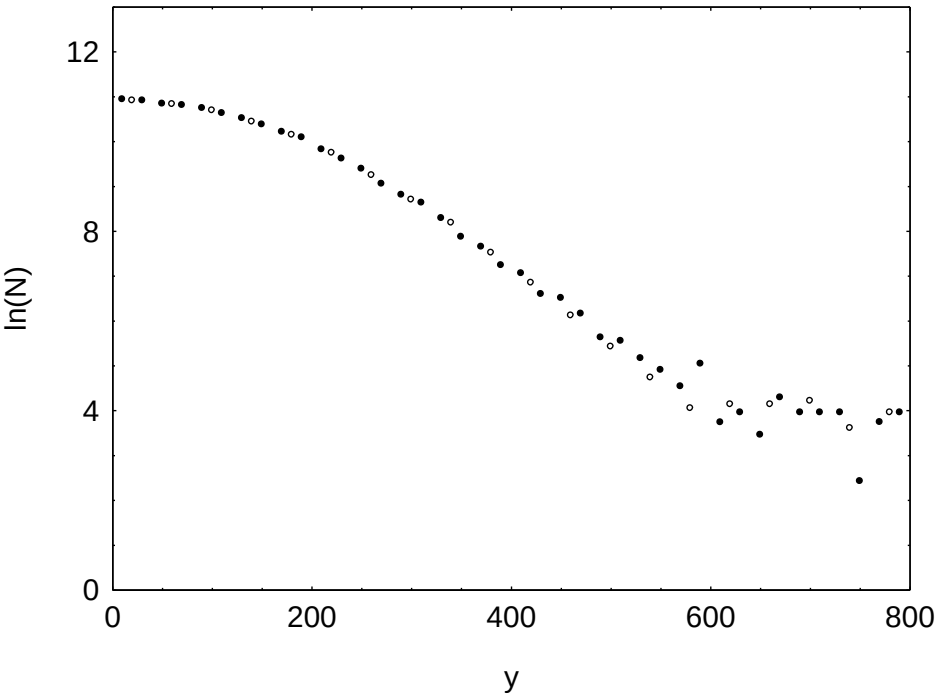
$\Rightarrow$ **This proposition can only be valid for the parallel slabs geometry!**

We analyze all regimes, but Type-B kinetics regime is of most interest

LMC results

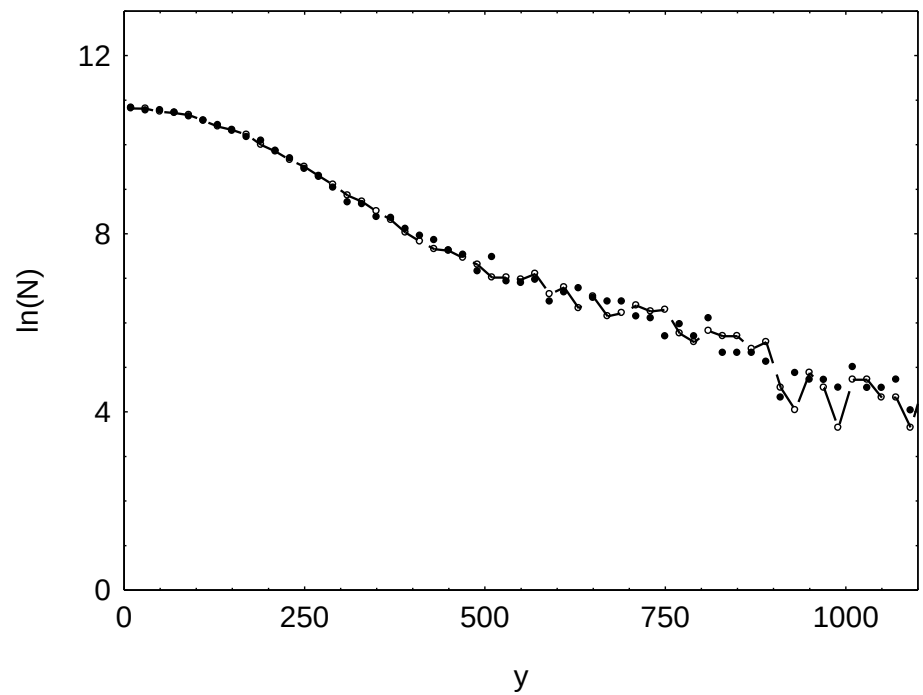
Type-B regime as an example

$\alpha^* = 0.05$; $\beta = 5$; $\Lambda^* = 10^2$; $s = 5$



Filled symbols: Model I
Open symbols: Model II

$\alpha^* = 0.05$; $\beta = 5$; $\Lambda^* = 10$; $s = 5$

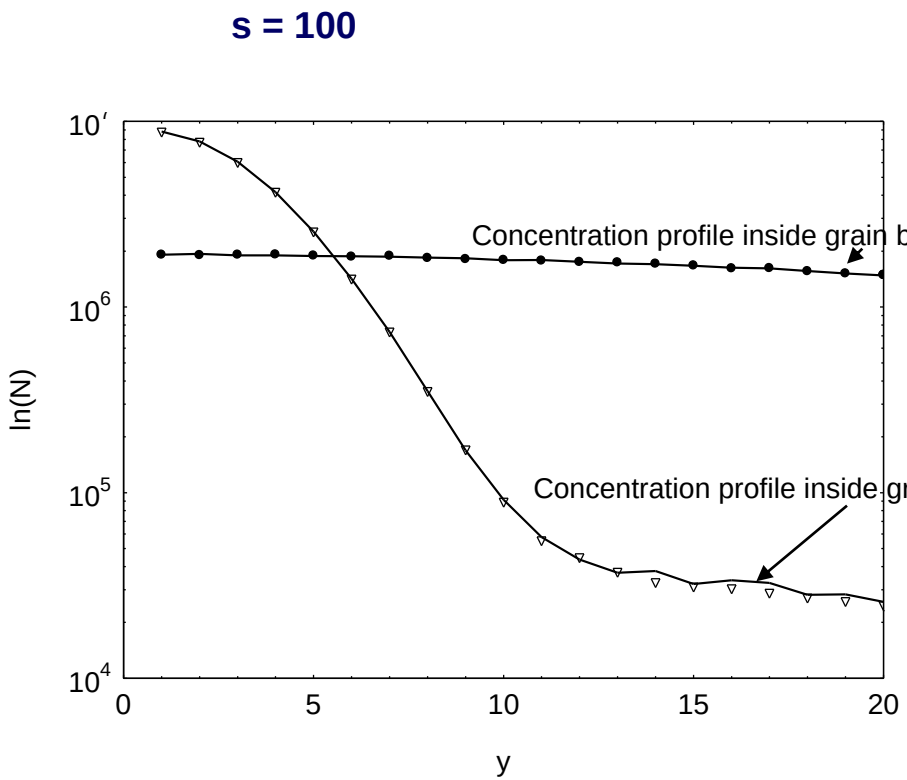


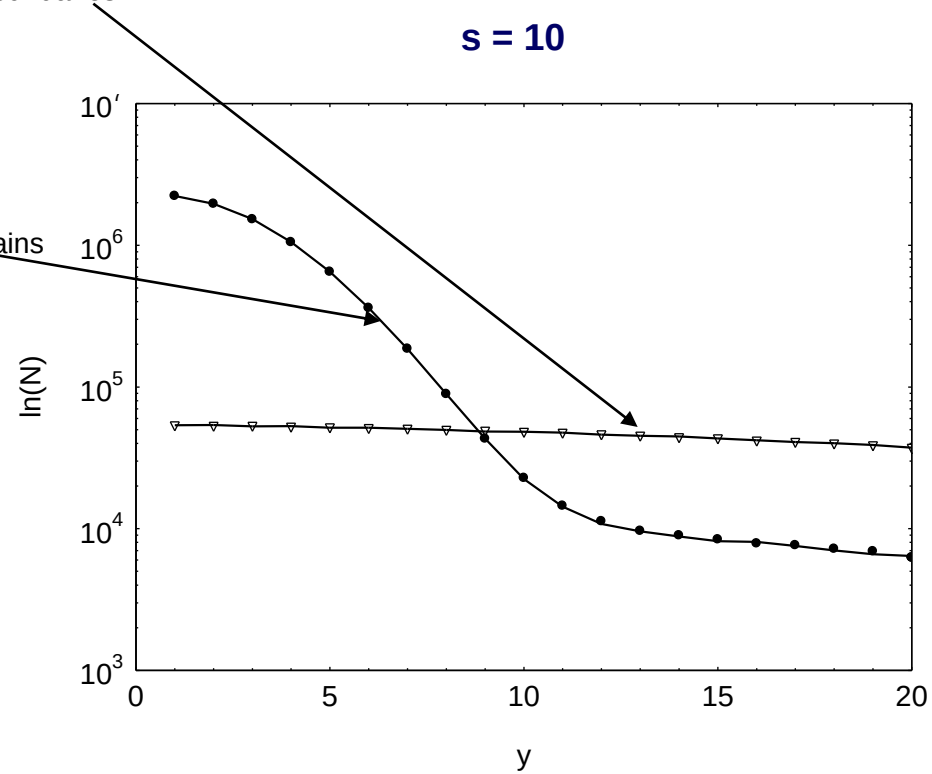
B-C, B and B-A regimes have been extensively checked as well.

LMC results

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

Symbols: Model I
Lines: Model II





LMC results, 2D model
(For the 3D model see the last page of this presentation)

Conclusions:

Models I and II have really close solutions;

Harrison's regimes classification must be the same for the two Models;

Therefore:

Regime C – $\alpha^* > 5.0$;

(Regime BC – $0.1 > \alpha^* > 5.0$;)

Regime B – $\{\Lambda^* > 3\} \cap \{\alpha^* < 0.1\}$; (may be $\varnothing$ for large *s*)

(Regime AB – $0.4 < \Lambda^* < 3$;)

Regime A – $\Lambda^* < 0.4$.

$$\alpha^* = \frac{s\delta}{2\sqrt{Dt}} \qquad \Lambda^* = \frac{L + (s-1)\delta}{\sqrt{Dt}}$$

Summary I:

- It was shown that for the parallel slabs model AND with the specific boundary condition at source plane the equilibrium segregation effect is equivalent to have an *effective* grain boundary width $\delta_{eff} = s\,\delta$.
(The specific condition is this: THE SAME equilibrium segregation effect must be 'somehow' present at the source plane, i.e. the GB structure must be "imprinted" there.)

- Then the transition points between the grain boundary kinetic regimes can be derived from the equivalent transition points obtained for self-diffusion.

Investigation of the time-dependent solute segregation in grain boundary diffusion

1. The specific boundary condition at the source plane (discussed in the first part of the talk) will never be true in a real grain boundary diffusion experiment.

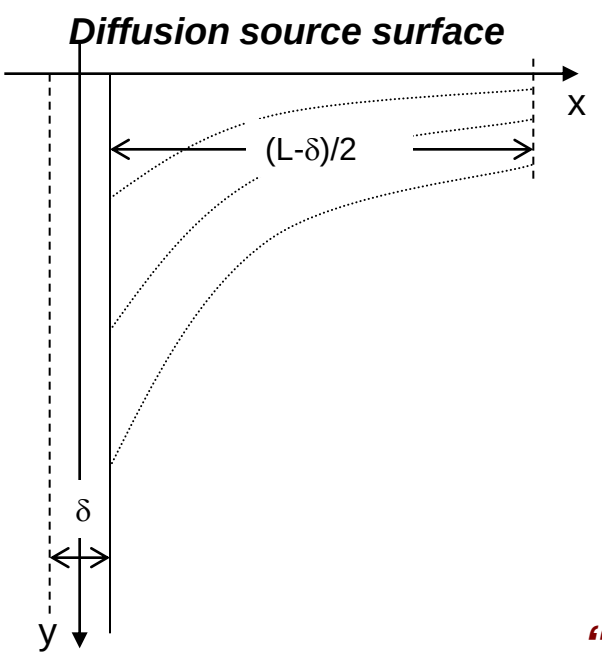
2. A simple homogeneous distribution of the solute atoms ALONG the source plane is the most probable boundary condition.

3. At this condition, the segregation effect may not follow its equilibrium form.

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

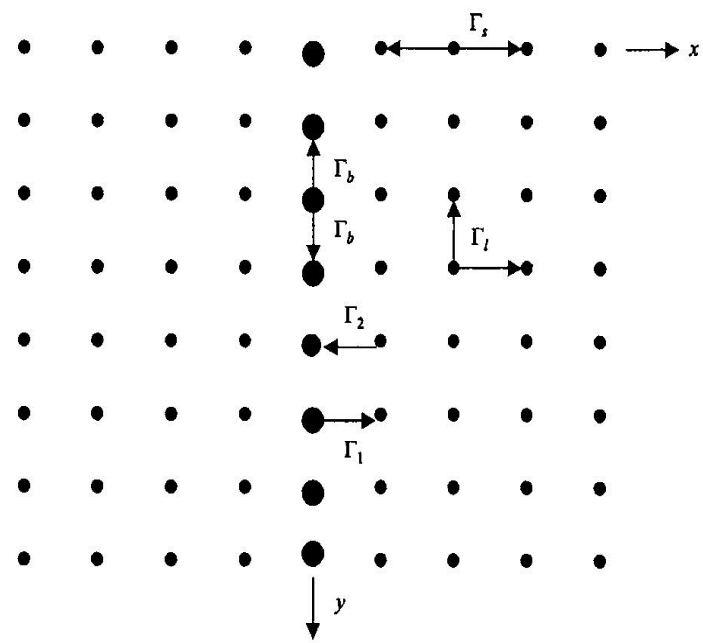
The usual definition of the segregation factor for the dilute regime of solute solution (Henry's isotherm/law) as was used in the boundary conditions:

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



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

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

At the equilibrium (not quasi-equilibrium) the following must be true:

$$s = \frac{c_b}{c_g} = \exp(-Q_{bind} / kT)$$

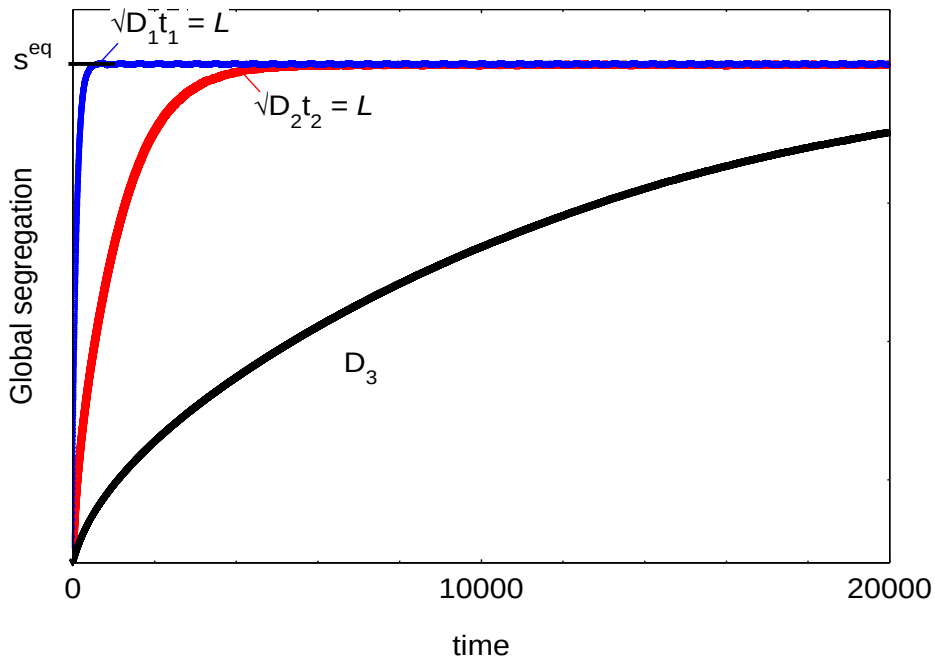
where c_b and c_g are <u>average</u> concentrations of solute atoms in the grain boundaries and in the grains respectively

This is a "Global" definition

Results of grain boundary time-dependent “global” segregation by means of LMC.

Obviously, by implementing our simulation scheme as was just defined, the ‘local’ segregation effect will be kept at equilibrium correctly.

What about the “global” segregation effect?
This depends on time and grain size:



Time-dependence of the global segregation during grain boundary solute diffusion computer experiment.

Different lattice diffusivities were used:

$D_1 > D_2 > D_3$

Results of grain boundary time-dependent ‘global’ segregation by means of LMC.

The main conclusion of the simulation is that:

Global segregation approaches the equilibrium value (from below) at times when:

$$\sqrt{Dt} \approx L$$

or, in terms of the parameter Λ

$$\Lambda \approx 1.0$$

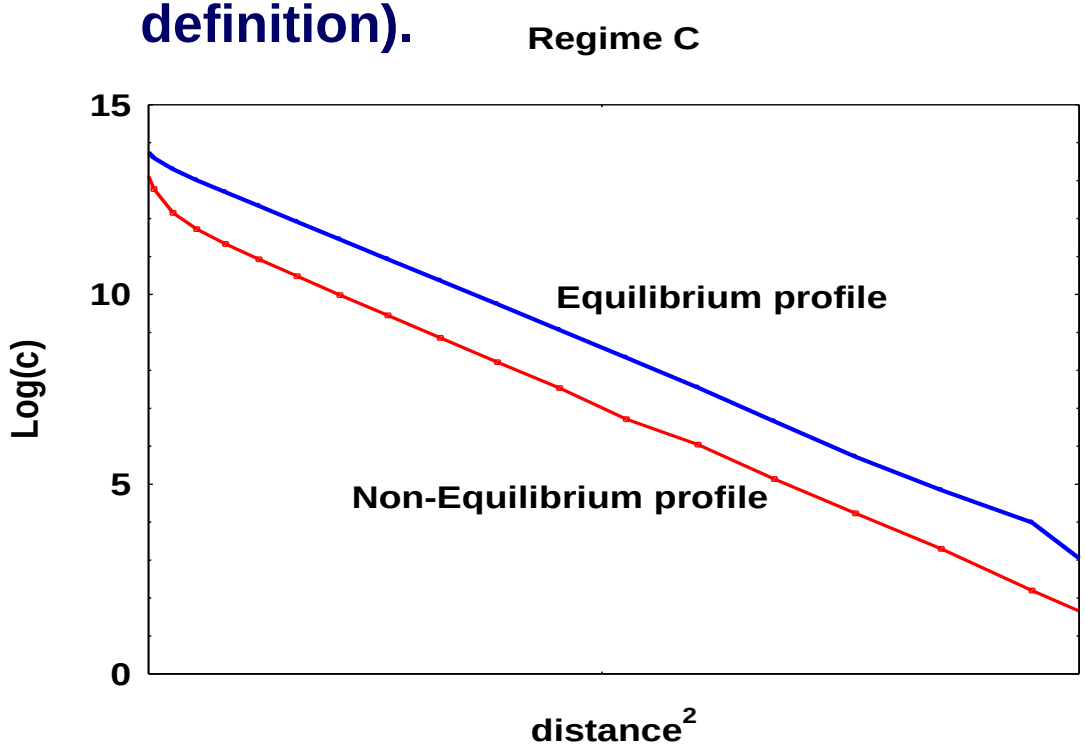
This is a long time tendency, which is actually outside the Type-B regime and well into the A-B regime

Harrison Type-C kinetics regimes.

Are there any adjustments for the non-equilibrium segregation effect?

No.

Because the shape of the profiles must be the same (only GB diffusion occurring and no lattice diffusion by definition).



Example of equilibrium and non-equilibrium segregation effect on the concentration profiles in the Type-C kinetic regime:

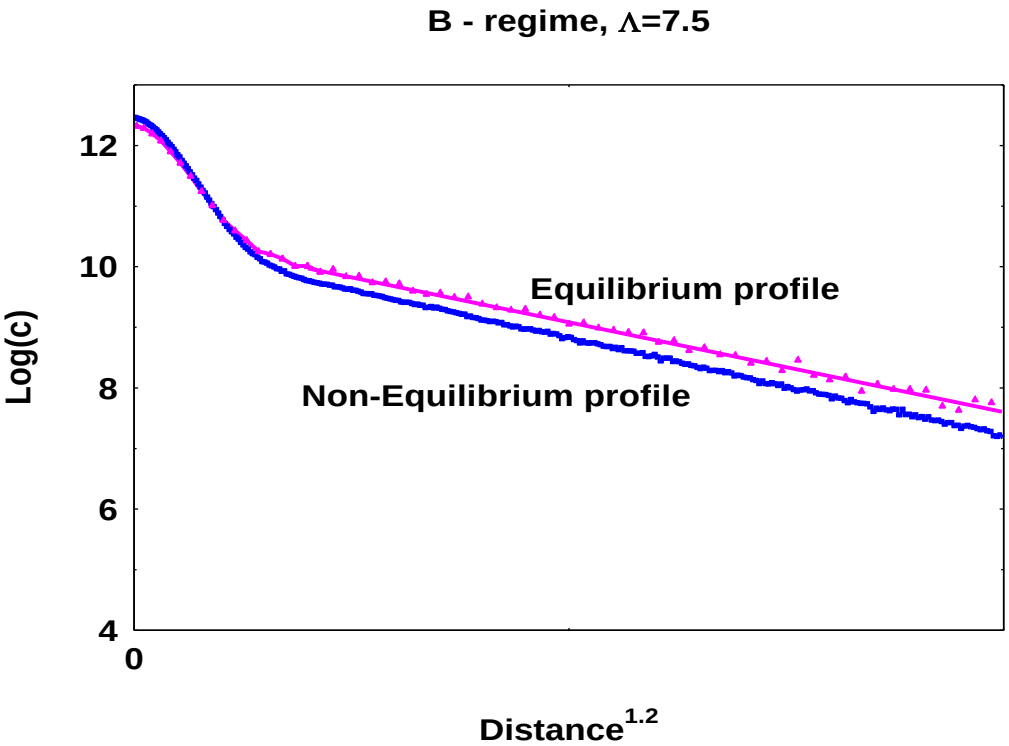
-only some shift of the (Gaussian) profile is evident
-the slope is unchanged

Harrison Type-B kinetics regimes.

Are there any adjustments for the non-equilibrium segregation effect?

YES.

Now the shapes of the profiles are affected by the non-equilibrium global segregation.



Example of equilibrium and non-equilibrium segregation effect on the concentration profiles in the Type-B kinetic regime:

-the 1.2 exponent analysis is valid;

-altogether the non-equilibrium profiles are "steeper" than the corresponding equilibrium ones.

Harrison Type-B kinetics regimes.

- **The 1.2 exponent analysis of the tail region is possible.**

- **All the non-equilibrium profiles are steeper in this regime**

and

- **Therefore the final values for the triple product $s\delta D_{gb}$ are lower than the corresponding equilibrium values.**

- **When the other diffusion parameters in $s\delta D_{gb}$ are known, then the segregation factor is always somewhat underestimated.**

- **Preliminary analysis has shown that the (under) correction is at least 15% and can be as much as 50%.**

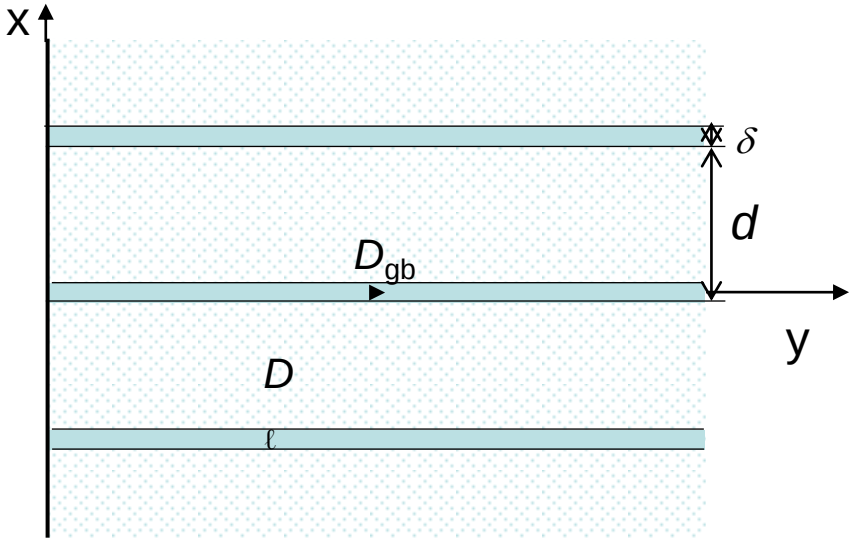
Summary II:

- The time-dependence of the segregation factor during grain boundary diffusion experiment is real and occurs primarily in the Type-B regime. This leads to at least a 15% and up to 50% underestimation of the equilibrium segregation factor.

- The Type-C regime analysis is not much affected by non-equilibrium segregation and the corresponding D_{gb} should be the real one.

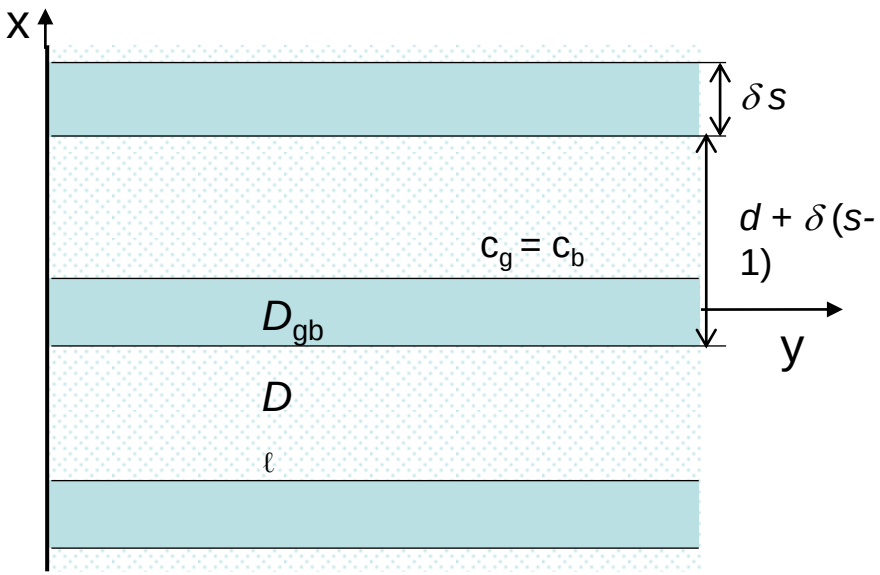
- The Type-A kinetics regime should not be affected by this, because the time for this regime is long enough to bring the segregation factor to its equilibrium value at least for the initial part of the concentration profile. (Numerical experiments have not been done.)

Thank you!



Additional information:

Geometrical model – parallel slabs, 2-dimensional



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Therefore:

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(Regime BC – $0.5 > \alpha > 5.0$;)

Regime B – $\{\Lambda > 6.0\} \cap \{\alpha < 0.5\}$;

(Regime AB – $3.5 < \Lambda < 6.0$;)

Regime A – $\Lambda < 3.5$.

$$\alpha = \frac{\delta}{2\sqrt{Dt}} \qquad \Lambda = \frac{L}{\sqrt{Dt}}$$