Chapter I. The classical grain boundary diffusion models

Introduction

As soon as diffusion along GBs is concerned, idealized GB models need to be introduced. This is done necessarily, because the real GB structure cannot be taken into account on a continuum level. Contrary to the atomistic description, the continuum approach deals with the averaged situation in which D_{gb} becomes the most important characteristic bearing information on the structure and interaction of atoms, including the interaction of diffusing atoms with the host atoms. In some cases, one may consider the diffusivity along a particular GB from the measurements on bicrystals, for example $\Sigma 11$, when the GB structure is determined by one of the high resolution imaging techniques like HRTEM [Höc94], [Leo99] and apply the conventional models to find D_{gb} in this boundary [Lib94]. However, a polycrystalline material consists of GBs characterized by different misorientations between the grains and, as a consequence, different D_{gb}'s. Clearly, the measured D_{gb} in these materials represents some averaged value. There are also evidences that the structure of GBs in nanocrystalline materials is similar to that of coarse-grained materials [Gle89], [Wür03],

[Bar05]. Consequently, the conventional models used to find D_{gb} in coarse-grained materials may be applied to nanomaterials as well.

1.1   Grain boundary model. Guggenheim or Fisher?

There are different interface models in the literature used to analyze and describe various processes related to the interfaces, like diffusion or segregation. One of them was suggested by Gibbs [Def66]. It excludes the real GB thickness, and the concentration change at the interface in this model is step-like. Another model was proposed by Guggenheim [Gug40]. This model is more realistic in comparison with the Gibbs model, because the thickness of GB is taken into account. Fisher [Fis51] was the first who successfully used a similar model to describe diffusion along GBs by means of diffusion equations.
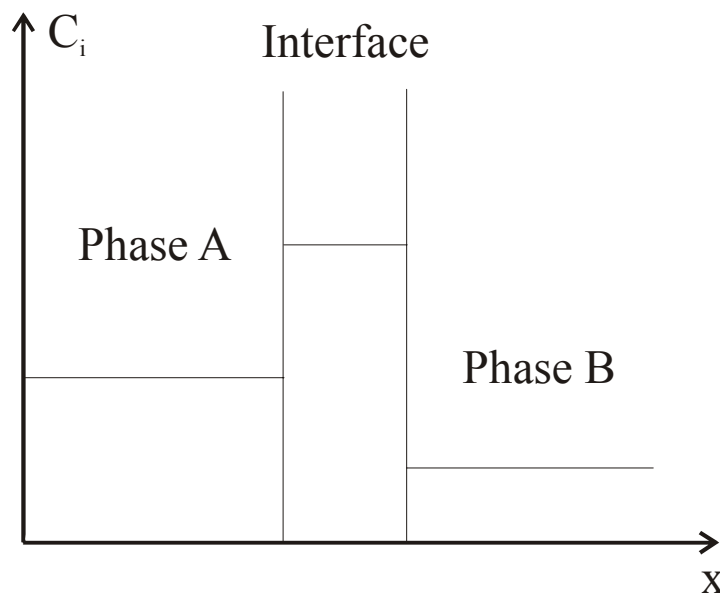

Fig. 1.1 Interfacial model according to Guggenheim [Gug40]. Adapted from [Cab91].

In fig. 1.1 the concentration C_i corresponds to a particular component (i) of a solid solution. The interface is thought to be embedded between two phases A and B. If phase A and phase B are chemically identical materials, the interface is termed a GB. Equilibrium concentration changes are supposed to occur only at the boundaries (interfaces) separating the interface and the adjacent phases, or in the case of a polycrystalline material, the GB and the grain. By supposing that the lateral change of the concentration within the GB (i.e. in the x-direction) is negligible, Fisher could describe diffusion within the GB by one dimensional

Fick's second law [Fis51]. He also supposed that concentrations at the boundaries separating the GB and grains are equal. In this way the segregation effects were excluded. All the approximations introduced by Fisher's model are discussed in the next section on a mathematical level. One should pay attention to the fact that Fisher's model refers to a quasi two dimensional (2D) representation of the GB.

1.1.1 Isolated grain boundary model

The model used by Fisher to describe diffusion along the GBs comprises the free surface carrying the diffusion source and the GB being perpendicular to that surface. The GB has a constant thickness δ (fig. 1.2), i.e. represents a slab, with the diffusion coefficient (D_{gb}) remaining constant along the GB. Therefore, the diffusion coefficients D_{gb} within the GB and D_g within the grain are not functions of concentration, time or positional coordinate. Fisher's model, known also as the isolated boundary model, represents a typical 2D semi-infinite problem. The concentrations and fluxes coincide at the boundaries separating the GB and the grain, i.e. at $x = \pm\delta/2$, allowing the leakage of atoms that exists from the GB into the grain to be taken into account. Consequently, Fisher's model is based on the assumption that $D_{gb} \gg D_g$. One can see from fig. 1.2 that the concentration distribution in this model is symmetrical with respect to the point $x = 0$. The following assumptions are assumed by Fisher's model:

1) Fick's laws are obeyed in both the crystal (grain) and the GB slab.
2) The diffusion coefficients D_g and D_{gb} are isotropic and independent of concentration, position and time.
3) The diffusant flow is continuous at the GB/grain interface (boundary).
4) The width of the GB is so small that the concentration variation across it (i.e. in the x-direction) is negligible.
5) The condition $D_{gb} \gg D_g$ is fulfilled with the consequence that the mass transport in the bulk is essentially preceded by GB transport (red arrows in fig. 1.2).

All results discussed in the present work were obtained by using these approximations except a modification related to segregation effects. The latter requires supposing that the concentrations at the boundary between the grain and the GB are not equal; however, the continuity conditions are still valid as well all the other assumptions. The segregation effects have been addressed [Bok58], analyzing derivation of D_{gb} in the case of impurity diffusion.
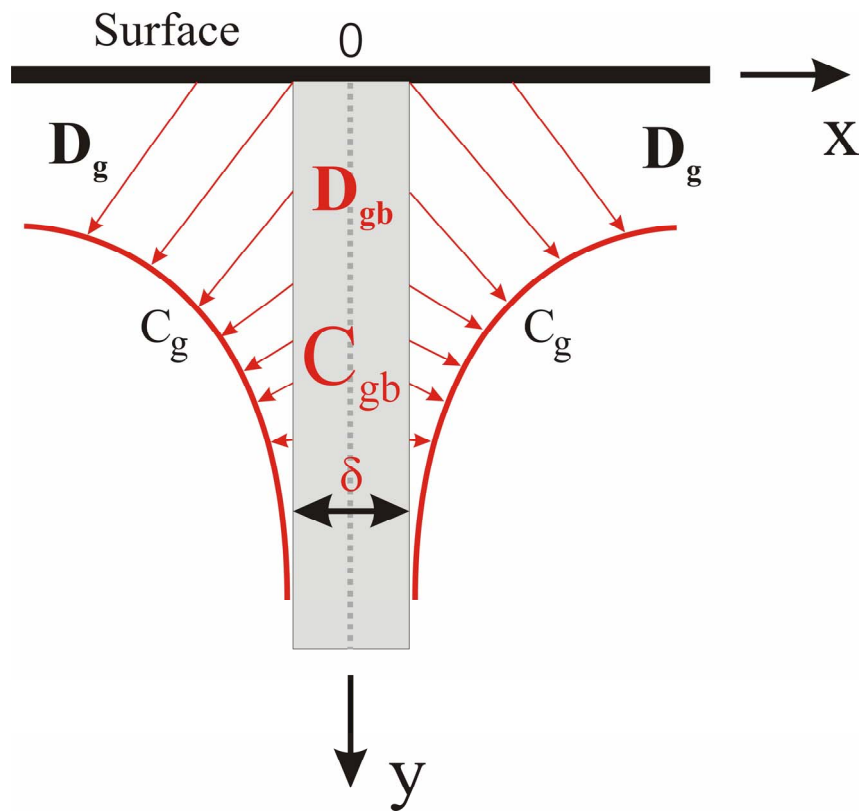
Fig. 1.2 Isolated boundary model.

1.1.2 Mathematical description of grain boundary diffusion in the isolated grain boundary model

Fisher was the first who derived the set of two diffusion equations for the GB diffusion problem and solved them approximately, whereas Whipple [Whi54] gave a rigorous mathematical analysis, including the exact analytical solution to the diffusion equations.

The first diffusion equation represents diffusion within the grain with the diffusion coefficient D_g, the second one diffusion within the GB with the diffusion coefficient D_{gb} (Eq. (1.1)):

$$\begin{cases} \dfrac{\partial C_g}{\partial t} = D_g \left(\dfrac{\partial^2 C_g}{\partial x^2} + \dfrac{\partial^2 C_g}{\partial y^2} \right), & \textbf{if } |\mathbf{x}| \geq \delta/2 \\[2em] \dfrac{\partial C_{gb}}{\partial t} = D_{gb} \left(\dfrac{\partial^2 C_{gb}}{\partial x^2} + \dfrac{\partial^2 C_{gb}}{\partial y^2} \right), & \textbf{if } |\mathbf{x}| \leq \delta/2 \end{cases} \qquad (1.1)$$

where t is the diffusion time. Both Fick's second laws [Fic55] are coupled by applying the boundary conditions of equal concentrations and fluxes at the grain/GB interface (Eq. (1.2)):

$$\begin{cases} C_g(x, y, t) = C_{gb}(x, y, t) \\ J_g(x, y, t) = J_{gb}(x, y, t) \end{cases} , \quad \textbf{if } |\mathbf{x}| = \delta/2. \tag{1.2}$$

These two continuity conditions (Eq. (1.2)) correspond to the conservative property of diffusion [Ghe88] and presuppose the steady state and diffusional equilibrium between the GB and the grain. Obviously, additional boundary and initial conditions are related to the surface. There are two important boundary conditions referring to y = 0: constant source and instantaneous source. While Whipple solved the relevant mathematical problem for the case of constant source, Suzuoka [Suz61] found the corresponding solution for the instantaneous source. For both cases the initial and boundary conditions are presented in Eqs. (1.3a) and (1.3b).

Constant source: Instantaneous source:

$$\begin{cases} C(x, y, t) = C_0 & \text{at } y = 0 \\ C(x, y, t) = 0 & \text{at } t = 0 \\ C(x, y, t) = 0 & \text{at } y \to \infty \end{cases} \tag{1.3a}$$

$$\begin{cases} C(x, y, t) = C(x, t) & \text{at } y = 0 \\ C(x, y, t) = M\delta(y) & \text{at } t = 0 \\ C(x, y, t) = 0 & \text{at } y \to \infty \\ \left. \dfrac{\partial C(x, y, t)}{\partial y} \right|_{y=0} = 0 \end{cases} \tag{1.3b}$$

In Eq. (1.3b) $\delta(y)$ is the delta function and M is the amount of diffusant deposited per unit area of the surface, whereas in Eq. (1.3a) C_0 is the constant concentration of diffusant at the surface. Correspondingly, the mathematical problem of diffusion when both bulk (grain) and GB contribute is to solve the system of differential equations (Eq. (1.2)) subject to the boundary and initial conditions given by Eqs. (1.2) and (1.3).

1.1.3 Transformations made to obtain Fisher's system

In Fisher's model the concentration can be easily expanded into a Taylor series with respect to x = 0 [Kau95], [Whi54]. Particularly, the GB concentration can be expanded, since the GB can be considered as a very thin slab, and the concentration within it is

homogeneously distributed [Sut95]. However, this is not the case for the grain concentration. Consequently,

$$C_{gb}(x,y,t) = C_{gb}(x,y,t)\big|_{x=0} + x\frac{\partial C_{gb}(x,y,t)}{\partial x}\Big|_{x=0} + \frac{x^2}{2}\frac{\partial^2 C_{gb}(x,y,t)}{\partial x^2}\Big|_{x=0} +$$
$$+\frac{x^3}{3!}\frac{\partial^3 C_{gb}(x,y,t)}{\partial x^3}\Big|_{x=0} + \frac{x^4}{4!}\frac{\partial^4 C_{gb}(x,y,t)}{\partial x^4}\Big|_{x=0} + ... + \frac{x^n}{n!}\frac{\partial^n C_{gb}(x,y,t)}{\partial x^n}\Big|_{x=0}$$

(1.4a)

The first derivative of an even function gives an odd function which is zero at the point of symmetry x = 0. Hence, one can neglect all the "odd" derivatives:

$$C_{gb}(x,y,t) = C_{gb}(x,y,t)\big|_{x=0} + \frac{x^2}{2}\frac{\partial^2 C_{gb}(x,y,t)}{\partial x^2}\Big|_{x=0} + \frac{x^4}{4!}\frac{\partial^4 C_{gb}(x,y,t)}{\partial x^4}\Big|_{x=0} + ...$$
$$+\frac{x^n}{n!}\frac{\partial^n C_{gb}(x,y,t)}{\partial x^n}\Big|_{x=0}, \textbf{ where n = 2m with m = 1,2,...}$$

(1.4b)

Substituting Eq. (1.4b) into the diffusion equation for the GB (Eq. (1.1)), one obtains the following expression

$$\frac{\partial}{\partial t}\left(C_{gb}(x,y,t)\big|_{x=0} + \sum_{n=2m}^{\infty}\frac{x^n}{n!}\frac{\partial^n C_{gb}(x,y,t)}{\partial x^n}\Big|_{x=0}\right) =$$
$$D_{gb}\left[\frac{\partial^2}{\partial x^2}\left(\sum_{n=2m}^{\infty}\frac{x^n}{n!}\frac{\partial^n C_{gb}(x,y,t)}{\partial x^n}\Big|_{x=0}\right) +\right.$$
$$\left.+\frac{\partial^2}{\partial y^2}\left(C_{gb}(x,y,t)\big|_{x=0} + \sum_{n=2m}^{\infty}\frac{x^n}{n!}\frac{\partial^n C_{gb}(x,y,t)}{\partial x^n}\Big|_{x=0}\right)\right], \textbf{ where m = 1,2,...}$$

(1.4c)

The GB concentrations are equal at x = 0 and x = ±δ/2. This property allows one to transform the last expression into a much simpler form, considering the equation at x = ±δ/2 and, neglecting the higher order terms (i.e. of order δ² and higher). Such a simplification is related to the fourth assumption supposed by Fisher's model. This yields

$$\frac{\partial}{\partial t}C_{gb}(0,y,t) = D_{gb}\left[\frac{\partial^2}{\partial x^2}C_{gb}(x,y,t)\big|_{x=0} + \frac{\partial^2}{\partial y^2}C_{gb}(0,y,t)\right].$$

(1.4d)

The latter equation can be further simplified by substituting Eq. (1.4b) into the boundary conditions (Eq. (1.2)) and keeping in mind that

$$J_{gb}\Big|_{|x|=\frac{\delta}{2}} = -D_{gb} \frac{\partial C_{gb}(x,y,t)}{\partial x}\Big|_{|x|=\frac{\delta}{2}} .$$ (1.4e)

In this way, the continuity conditions are rewritten neglecting the higher order terms as:

$$\begin{cases} C_{gb}(x,y,t)\Big|_{x=0} = C_g(x,y,t)\Big|_{|x|=\frac{\delta}{2}} \\ \pm D_{gb} \frac{\delta}{2} \frac{\partial^2 C_{gb}(x,y,t)}{\partial x^2}\Big|_{x=0} = D_g \frac{\partial C_g(x,y,t)}{\partial x}\Big|_{|x|=\frac{\delta}{2}} \end{cases} .$$ (1.5)

Finally, Eq. (1.5) allows one to write down the following equations for the GB diffusion

$$\begin{cases} \dfrac{\partial C_g(x,y,t)}{\partial t} = D_g \left(\dfrac{\partial^2 C_g(x,y,t)}{\partial x^2} + \dfrac{\partial^2 C_g(x,y,t)}{\partial y^2} \right), & \textbf{if } |\mathbf{x}| \geq \delta/2 \\ \dfrac{\partial C_g(y,t)}{\partial t} = D_{gb} \dfrac{\partial^2 C_{gb}(y,t)}{\partial y^2} + \dfrac{D_g}{\delta/2} \dfrac{\partial C_g(y,t)}{\partial x}, & \textbf{if } |\mathbf{x}| = \delta/2 \end{cases} .$$ (1.6a)

All terms in the second equation are taken at x = ±δ/2, so it exactly represents the boundary condition. Eq. (1.6a) is known as the Fisher system. It is important to note, that the solution which can be obtained by solving Eq. (1.6a) reveals the concentration within the grain and neglects the concentration within the GB. If one believes that the assumptions introduced by Fisher's model (see page 3) are reasonable and really reflect the adequate physical situation, the only approximation is related to neglecting higher orders terms in the expansion of C_{gb}.

If there is segregation, the first equation in Eq. (1.5) is replaced by [Her05]:

$$C_{gb}(x,\ y,\ t) = sC_g(x,\ y,\ t), \quad \textbf{if } |\mathbf{x}| = \delta/2$$ (1.6b)

where s is the equilibrium segregation coefficient or segregation factor. Eq. (1.6b) is known as Henry's isotherm [Cab91], which is valid for dilute conditions. By using this boundary condition Eq. (1.6a) can be rewritten in the following form [Gib66]

$$\begin{cases} \dfrac{\partial C_g\left(x,y,t\right)}{\partial t} = D_g\left(\dfrac{\partial^2 C_g\left(x,y,t\right)}{\partial x^2} + \dfrac{\partial^2 C_g\left(x,y,t\right)}{\partial y^2}\right), & \textbf{if } |\mathbf{x}| \geq \delta/2 \\[4mm] \dfrac{\partial C_g\left(y,t\right)}{\partial t} = D_{gb}\dfrac{\partial^2 C_{gb}\left(y,t\right)}{\partial y^2} + \dfrac{D_g}{s\delta/2}\dfrac{\partial C_g\left(y,t\right)}{\partial x}. & \textbf{if } |\mathbf{x}| = \delta/2 \end{cases}$$

(1.6c)

1.1.4 An alternative derivation of Fisher's system

Shewmon [She63] published a more didactic approach to arrive at Fisher's system. Interestingly, his derivation is more elegant in the sense that it allows the straightforward finding of the corresponding equations without rigorous mathematical transformations. Let us consider a 2D slab of the length dy and thickness δ (fig. 1.3). The slab is embedded into the system of two crystals (grains) from both sides, having a different diffusivity. If that slab is an element of a GB, two fluxes are possible from its GB/grain interfaces, i.e. from the GB into the grains, namely the fluxes J_x in fig. 1.3. There is also the flux coming from the top of the slab J_y and leaving some amount of material inside the slab. The amount of material is changed within the slab due to the non-zero difference of fluxes and is given by $(\partial J_y/\partial y)dy$, if dy is very small. The fluxes J_x and J_y are different, because these are determined by the diffusion coefficients D_g and D_{gb}, respectively. The volume of the element is 1dyδ, where the unity corresponds to the length along a z-direction. So the concentration changes with time. Accordingly,

$$dy\delta\frac{\partial C_g}{\partial t} = -\delta\frac{\partial J_y}{\partial y}dy - 2dyJ_x,$$

(1.7)

where the negative signs obviously correspond to out-diffusion. Introducing Fick's first law, the following final equation for diffusion along the GB results:

$$\frac{\partial C_g}{\partial t} = D_{gb}\frac{\partial^2 C_g}{\partial y^2} + \frac{2D_g}{\delta}\frac{\partial C_g}{\partial x}\bigg|_{x=\frac{\delta}{2}}.$$
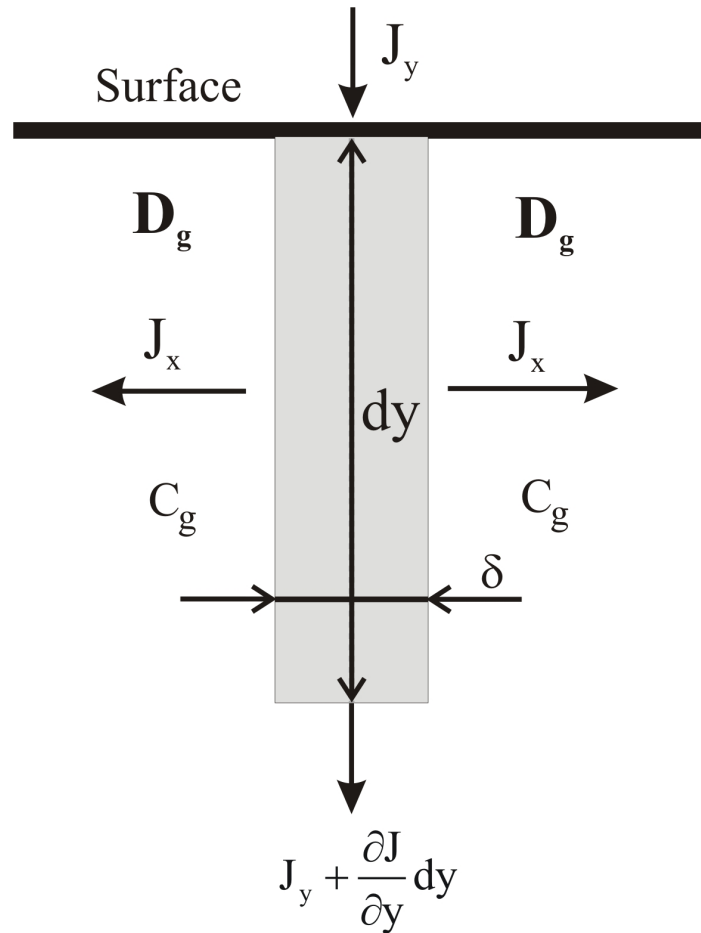
(1.8)

Fig. 1.3 Schematic representation of the GB model for deducing Eq. (1.8). Adapted from [She63].

1.1.5 Whipple's solution

Whipple [Whi54] solved Fisher's system (Eq. (1.6)) by means of the Fourier-Laplace transform [Bee03]. Properties of this solution will be discussed in chapter III. Here only the solution is presented, which reads

$$C_g(\eta,\xi,\beta) = C_0 \text{erfc}\left(\frac{\eta}{2}\right) + \frac{C_0\eta}{2\pi^{1/2}} \int_1^\Delta \frac{d\sigma}{\sigma^{3/2}} \exp\left(-\frac{\eta^2}{4\sigma}\right) \text{erfc}\left[\frac{1}{2}\left(\frac{\Delta-1}{\Delta-\sigma}\right)\left(\frac{\sigma-1}{\beta} + |\xi|\right)\right]. \qquad (1.9a)$$

The solution is of integral form with the integral being responsible for GB diffusion. The first term of the solution, obviously, represents diffusion within the grain. Different dimensionless quantities are used in the Whipple solution. The dimensionless quantities η and ξ are, in fact, dimensionless coordinates and given by

$$\eta = \frac{y}{\sqrt{D_g t}},$$

(1.9b)

$$\xi = \frac{x \pm \delta/2}{\sqrt{D_g t}}, \quad \text{if } |x| \geq \delta/2.$$

(1.9c)

Eq. (1.9a) differs from original expression by the modulus $|\xi|$. The latter is needed, if the solution is considered at $x \leq -\delta/2$ (see also Eq. (1.9c)). The meaning of the dimensionless parameter β is more complex. According to Kaur *et al.* [Kau95] it characterizes the diffusion process in the sense that a large β-value means that the diffusion along the GBs is greatly pronounced in comparison with bulk diffusion, i.e. the penetration depth along the GB is much larger. It is also related to the inclination angle between an isoconcentration line and the GB. Finally, it is not only high when Δ is large, but also when t is short. The analytical form of β is

$$\beta = \frac{(\Delta - 1)\delta}{2\sqrt{D_g t}} = (\Delta - 1)\alpha.$$

(1.9d)

Here the quantity α shows how the diffusion length in the grain ($L_g = \sqrt{D_g t}$) exceeds the GB thickness (δ).

1.2 Diffusion kinetic regimes

Diffusion in an isolated GB (fig. 1.2) can be analyzed or simulated on the basis of Eqs. (1.6c) and (1.9a). In particular, Le Claire [Cla63] could suggest a simple procedure for determining D_{gb} based on integration of Whipple's solution. However, the procedure cannot be used for any experimental condition. It is a purpose of the present study to analyze such conditions when Le Claire's procedure is not valid. GB diffusion goes through different physical situations as the temperature and/or diffusion time increase. Accordingly, Harrison [Harr61] introduced three diffusion regimes and only in one of them the Whipple solution to Fisher's system is valid. The application of Harrison's classification is also discussed in excellent reviews on GB diffusion, for example [Mis97], [Mis99]. Additionally, a new classification introduced by Mishin [Mis95] is used and discussed here in more detail as being

applicable to a variety of materials ranging from coarse grained to nanocrystalline. It should be mentioned that there are also classifications that take into account GB motion [Güt93] or GB diffusion accompanied by diffusion along dislocations [Klin99]. These are not a subject of the present study.

In the aforementioned classification it is supposed that penetration along GBs is deeper than in the remaining grains. As a consequence of the transport coefficient being larger along the GBs, diffusing atoms first move along these paths. For analyzing diffusion regimes surface diffusion is not considered as a rate-limiting process (recently, Preis and Sitte [Prei05], derived analytical solutions for the thin-film problem taking account of rate limiting surface exchange reactions).

In the very beginning of the diffusion process the atoms (traces) move through the GB without a significant contribution to the bulk. It is expected that the overall process is determined by D_{gb} only; it can be described by a complementary error-function solution to the diffusion equation in the case of a constant source. Such a situation was called by Harrison the C-kinetics and later extended by Mishin to an additional C´-regime to take into account the situations when the grain size can be very small. So the conditions of the C and C´ – regime (in terms of Mishin's classification) can be written as follows:

$$L_g \ll s\delta/2 \ll L_{gb} \ll d \quad \text{(C-regime)} \tag{1.10a}$$

and

$$L_g \ll s\delta/2 \ll d \ll L_{gb} \quad \text{(C´-regime)}. \tag{1.10b}$$

Here L_g, L_{gb} are the grain and GB diffusion lengths, respectively, d is the average grain size and s the segregation factor. The segregation factor (s) is introduced for generality and is set to 1 for self-diffusion. In fig. 4a an example of the C´-regime is given obtained by simulating diffusion using the finite element method (FEM) (the numerically obtained figures serve here as explanation figures. The quantitative analysis will be given in chapter IV). In this figure bright colors represent the enhanced concentration around the interfaces (see also color pattern in fig. 4a). However, the diffusion process is supposed to be confined within the GBs in the C (C´)-regime. The existence of the C (C´)-regime itself is still questionable, what was already mentioned in [Kau95] and is shortly discussed here. However, this is the only regime, in which D_{gb} (as it is believed) is directly obtained. This fact is used in many experiments to

find s [Her03]. It proceeds typically for a very short time which can be much shorter than in the case of type-B kinetics (fig. 5a, see also discussion below). That is why the C (C′)-regime is difficult to verify experimentally, because of short t and/or low temperatures, in which case very small GB concentrations result. Consequently, the usually studied regime is the B-regime. Its evaluation is more reliable, especially for coarse-grained materials.

The exact solution found by Whipple (Eq. (1.9a)) corresponds to the B-regime. The range of validity of this regime is defined as follows:

$s\delta/2 \ll L_g \ll L_{gb} \ll d$ (B-regime according to Harrison [Harr61] or B_2-regime according to Mishin [Mis95]) (1.11a)

and

$s\delta/2 \ll L_g \ll d \ll L_{gb}$ ($B_2′$-regime according to Mishin [Mis95]). (1.11b)

For the main results in the present study the common term B - regime is used, because the Whipple solution is valid in both the B_2- and $B_2′$-regime. It seems to be that differentiation of the B-regime into the B_2- and $B_2′$-regime is interesting only from the point of view of understanding how the diffusion process proceeds. This is also interesting in order to distinguish different types of materials as was proposed by Mishin [Mis95].

The diffusion lengths plotted on the logarithmic scale for different types of materials indicate that the B-regime is suppressed in materials with smaller grain sizes (fig. 5), while the A-regime becomes more prolonged. The plots shown in fig. 5 are very useful from the point of view of understanding diffusion in a polycrystal. These also allow to properly tune numerical experiment, because knowing penetrations is extremely important in order to avoid possible errors. Importantly, bold lines in fig. 5 correspond to the diffusion lengths responsible for the process in a particular regime. For instance, both L_g and L_{gb} can be obtained in the B-regime. All the plots were plotted for $D_g = 2.95 \cdot 10^{-4}$ nm^2/s ($2.95 \cdot 10^{-16}$ mm^2/s) and d = 25 nm. Different ratios $\Delta = D_{gb}/D_g$ were used in order to realize the different types of materials.

Two diffusion lengths (blue and red lines) shown in fig. 5 have the same slope on the logarithmic scale, as in such cases the same power law $\sim t^{1/2}$ is obeyed which is a typical diffusion dependence. In the B-regime, however, the diffusion length in the GB (green line) follows another law, *viz.* [Kau95]

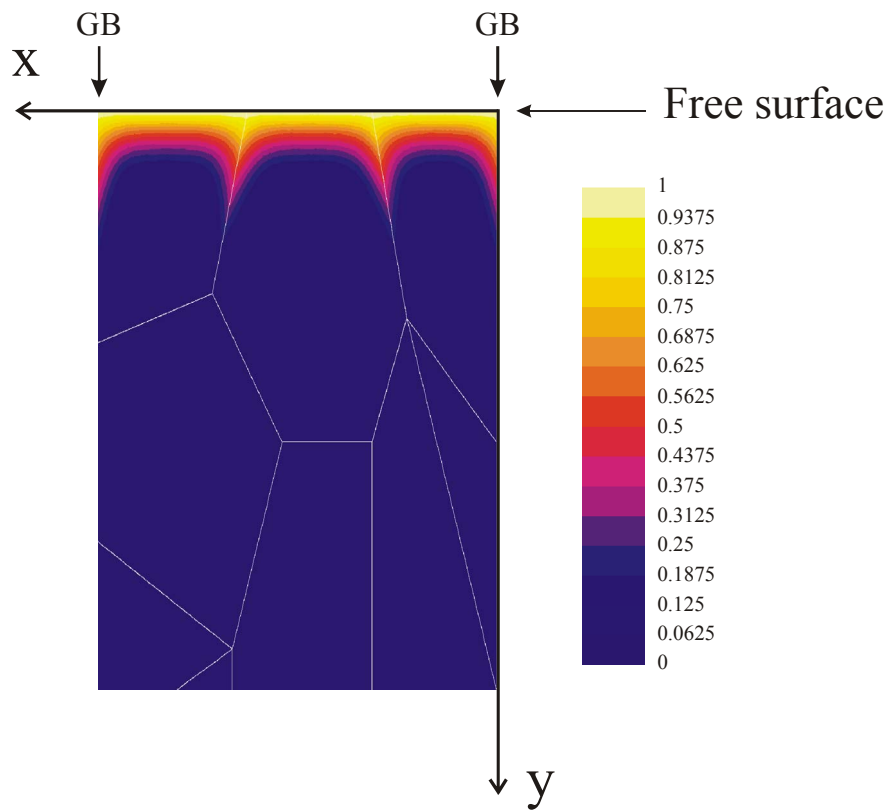$$L_{gb} = \frac{\sqrt{s\delta D_{gb}}}{(4D_g / t)^{1/4}} \, , \qquad\qquad (1.12a)$$

where s is again the segregation factor, t the diffusion anneal time and δ the GB thickness. The effects of segregation are excluded in fig. 1.5, i.e. those are plotted for s = 1 only. Moreover, not only L_{gb}, but also the parameter β depends on s as

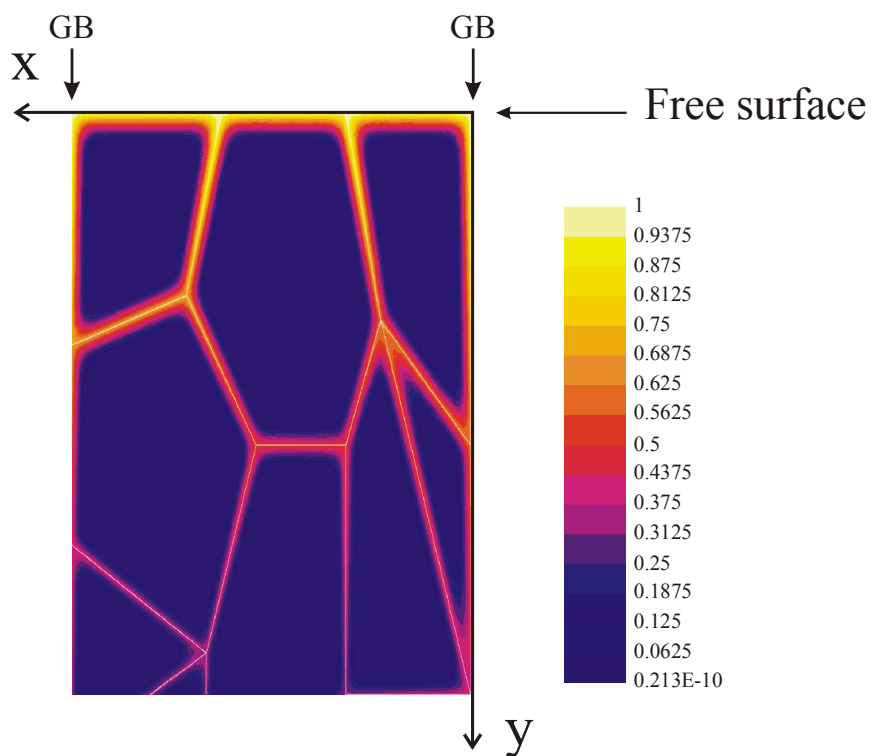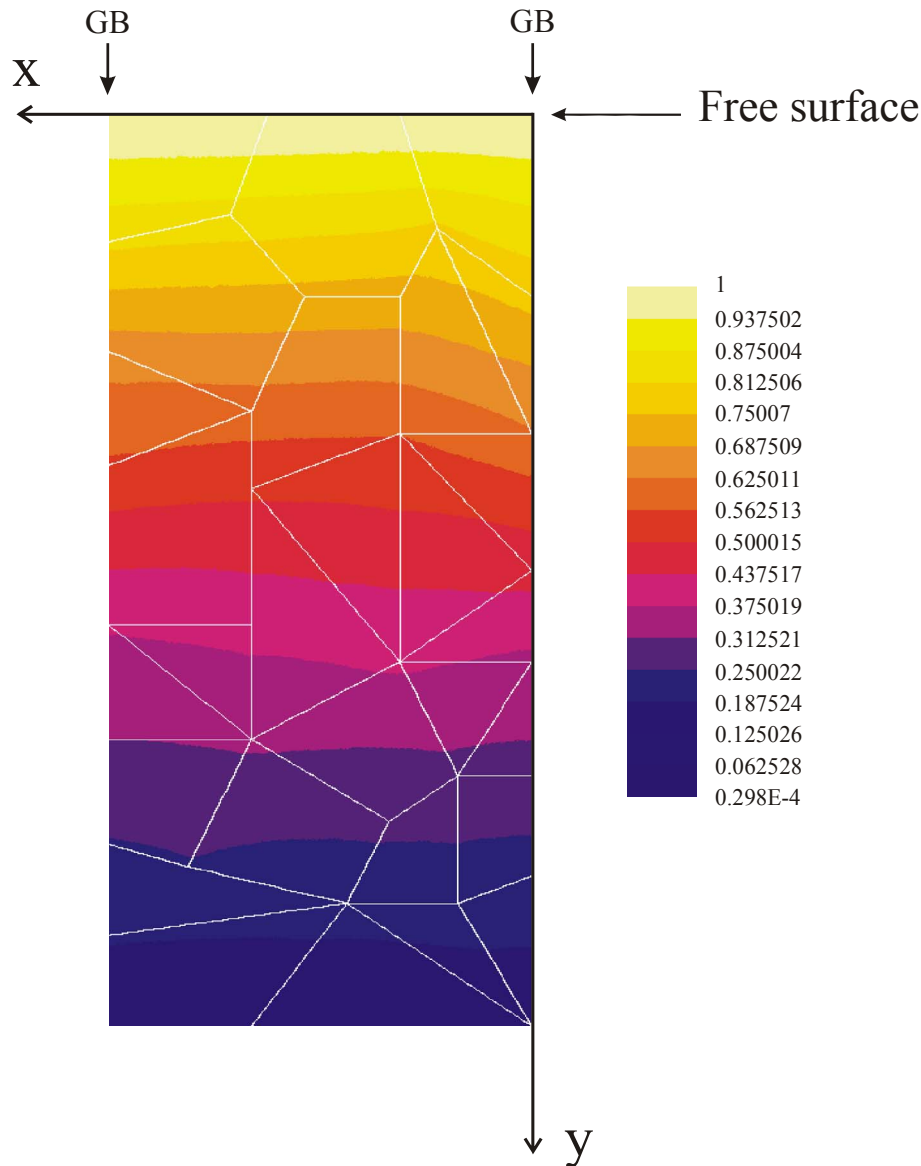$$\beta = (s\Delta - 1)\alpha \, . \qquad\qquad (1.12b)$$

a)
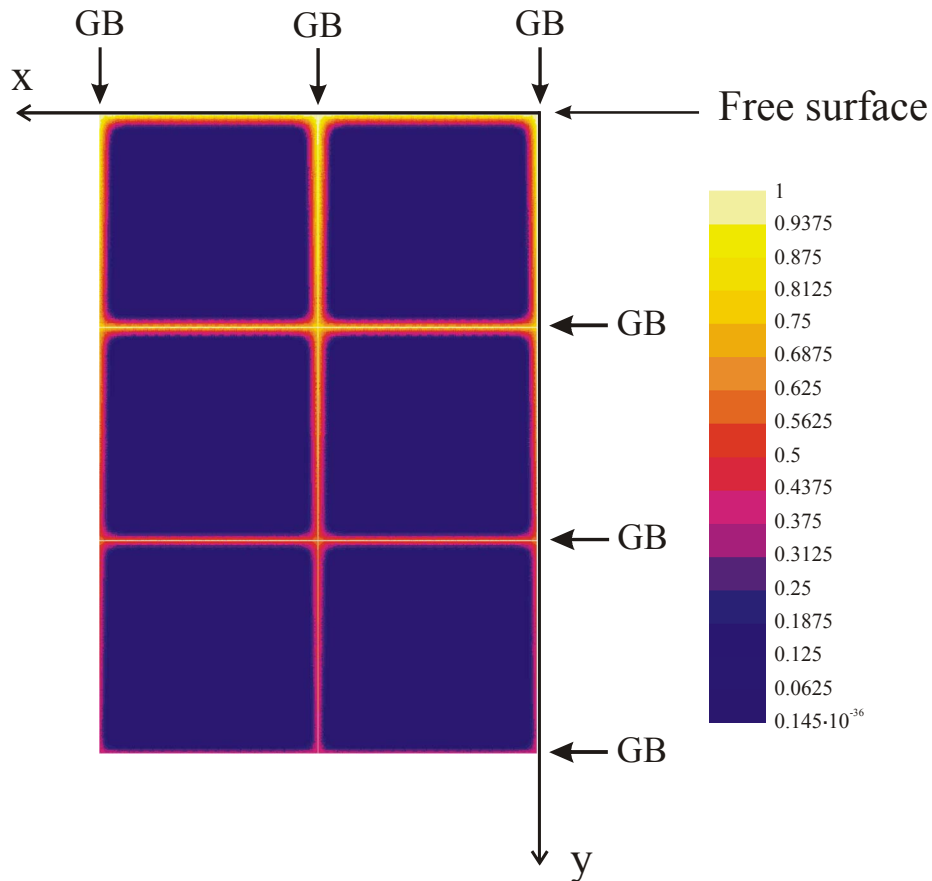
b)

b')

c)

Fig. 1.4 a) Concentration distribution in a square grain pattern under conditions of the C′ kinetics regime (d = 5 nm). b) A concentration distribution in a general polycrystal under conditions of type-B kinetics for $\Delta = 10^2$ (d = 25 nm) b') the same for $\Delta = 2.2 \cdot 10^4$ (d = 25 nm) c) A concentration distribution in a general polycrystal for the type-A kinetics for $\Delta = 10^2$ (d = 25 nm). All white lines correspond to the GBs. Also shown are relevant color patterns, in which different colors correspond to certain isoconcentration line. Distributions in b) and c) were obtained by using general model 3 used in the present study, for details see chapter IV.

The main difference between the results in figs. 1.4b and 1.4b' does not only lie in the different ratios Δ, but also in the behavior of concentration around the GBs. The inclination angle between a particular isoconcentration line (defined by a line of a particular color) and a GB is larger for smaller ratio Δ. Qualitatively speaking; the result in fig. 1.4b represents a

classical solution (distribution) in the type-B kinetics, corresponding to the B_2 – regime according to the classification of Mishin [Mis95]. Contrary to this, the inclination angle in the distribution in fig. 1.4b' is much smaller, indicating a typical situation for ultrafine-grained (nanocrystalline) materials. Because of this, the diffusion length in the GB (L_{gb}, green line in fig. 1.5) never reaches d for $\Delta = 10^2$, and the A-regime always starts before the diffusion length in the grain (L_g, red line in fig. 1.5) reaches that in the GB for $\Delta = 2.2 \cdot 10^4$, if d is 25 nm (fig. 1.5c).

The A-regime starts when the red and green lines in fig. 1.5 are crossed, or when L_g equals d. In fact, the diffusion length in the A-regime represents some effective diffusion length (not shown in fig. 1.5), which is a combination of D_g and D_{gb}. In this regime the distribution is homogeneous, what allows different theories valid for homogeneous systems to be applicable in the A-regime. High temperatures and/or long diffusion times are needed to observe the A-regime in coarse-grained materials. Contrary, it is suggested that the A-regime is important for ultrafine-grained materials (nanomaterials) due the suppression of B-regime [Bek04] (the condition discussed in reference is too rigorous and the existence of the B-regime is not questionable even for nanomaterials, what is proved in the present study). The effect is just related to the small grain sizes. The conditions for the A-regime are the following:

$$d \ll L_g \approx L_{gb}. \tag{1.13}$$

That is, the main condition for the A-regime is $L_g \gg d$. This starts at the point of equal L_g and L_{gb} (fig. 1.5). However, there is a situation when L_g reaching d is still smaller than L_{gb}. In this case the A$'$ - regime arises. One additional regime is the so called B_4-regime, in which $L_g \approx L_{gb} \ll d$. This corresponds to the situation that the diffusion fronts from the GB into the grain are not distinguishable anymore and are not overlapping. The inclination angle between the isoconcentration line and the GB is simply 90º in this case. Another possibility is shown in fig. 1.5a, in which L_g reaches d at the same point, where this equals L_{gb}. That is why it can be attributed to both A and B_4 regimes. In the distribution in fig. 1.4c the classical situation is shown, the homogeneous distribution is seen up to a very low level of the concentration. As far as the diffusion process in all of the type A regimes (B_4, A, A$'$) is obviously described by the solution to diffusion equation in homogeneous media without any exceptions. Accordingly, only one definition is used in the present work, namely the A-regime.

1.3   Deducing the grain boundary diffusivity from the diffusion profile

It is to be mentioned, that the diffusion profile is understood as the dependence $C_{av} =$ f(y) or $\ln C_{av} = f(y^{6/5})$ (see discussion below), where C_{av} is an average concentration being a function of time t and penetration depth y. Such a concentration can be found by integrating $C_g(x, y, t)$ along x for the whole range of y, what, in a sense, is a theoretical definition. Experimentally the same quantity can be found, when the sample is cut in slices, and the concentration in each slice is determined, what exactly is the case of tracer measurements [Ask70], [Meh05]. As sectioning methods, including SIMS technique in a depth profiling mode, obtain the average concentration (C_{av}) as a function of y and t, there should be a procedure which allows the grain boundary diffusivity (D_{gb}) to be found. Moreover, since diffusion in a polycrystalline sample passes different kinetic regimes, depending on t or temperature, at least three equations are needed to perform the diffusion profile measurements safely. In fact, such equations exist and intensive literature can be found on applying all the three equations. Nevertheless, these equations are still debated owing due to 1) simplifications made in the models [Chu96a], [Bel01], [Bel03] to find this or that equation and 2) special conditions [Bek04] for studying the GB diffusion and new types of materials [Mis95]. Here we essentially discuss application of two equations due to 1) obvious solution given by the complementary error-function in the type-C kinetics, which need not be explained in detail, and 2) importance of the B-regime and especially A-regime for nanocrystalline materials.

The B-regime has been remaining the most reliable regime for many years, since the grain size of tens of micrometers in the coarse grained materials determines the overall behavior. A procedure to extract D_{gb} from the measured diffusion profile was proposed by Le Claire [Cla63]. The advantage of the diffusion profile measured in the B-regime is in fact, that the bulk and GB diffusion are separable. Following mathematical intuition and knowing that the diffusion profiles are linear functions of $y^{6/5}$ [Lev60], Le Claire came up with the following expression
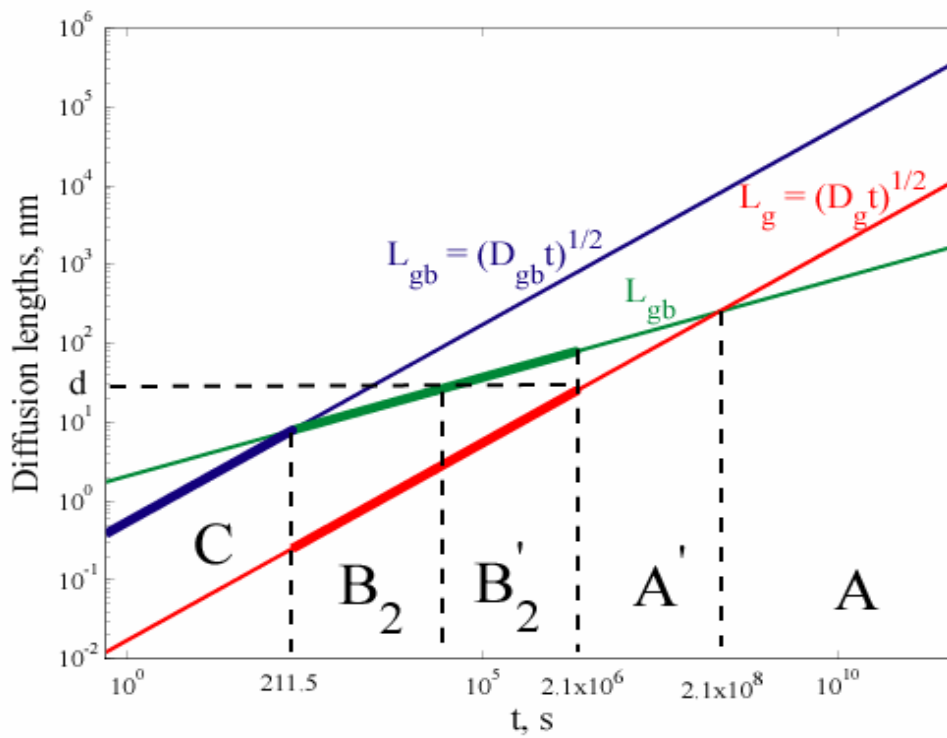
$$\delta D_{gb} = 2\sqrt{\frac{D_g}{t}} \left(-\frac{\partial \ln C_{av}}{\partial w^{6/5}}\right)^{5/3} \left(-\frac{\partial \ln C_{av}}{\partial y^{6/5}}\right)^{-5/3}, \qquad (1.14)$$

where w is the dimensionless coordinate, having a very important property of making the diffusion profile plotted as a function of w independent of Δ. This is based on the following
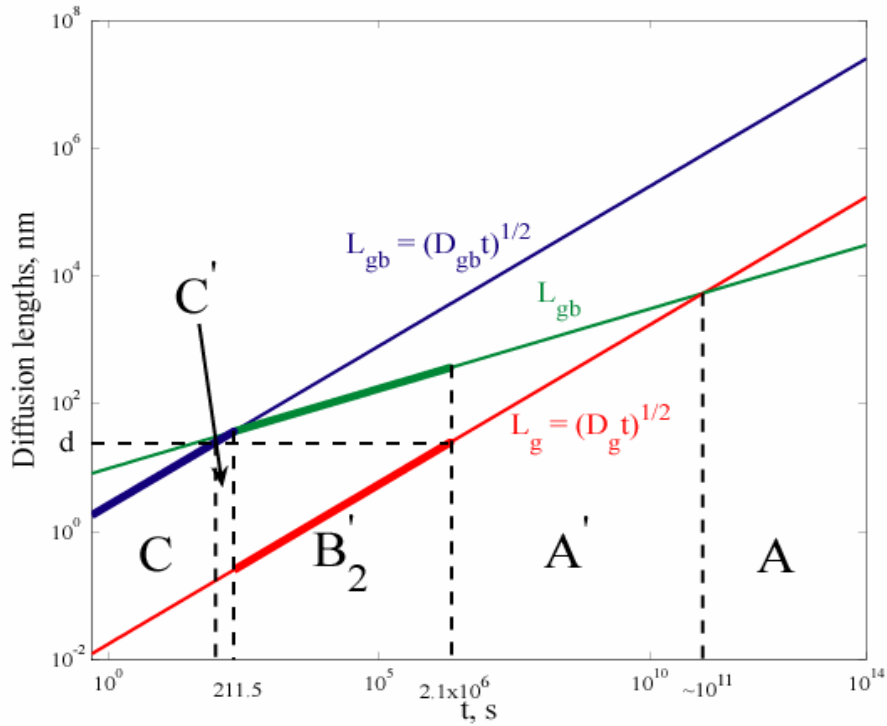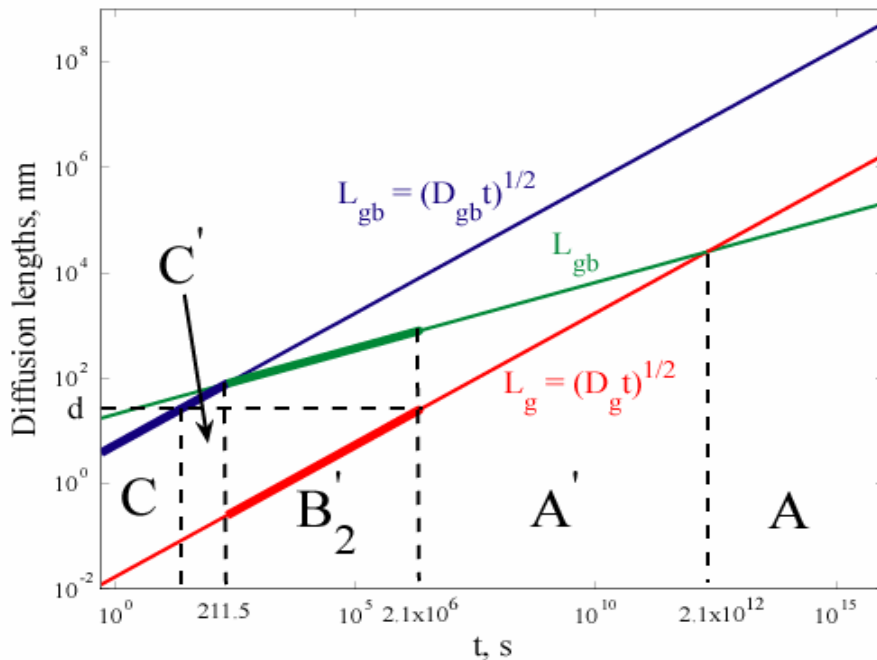
a)
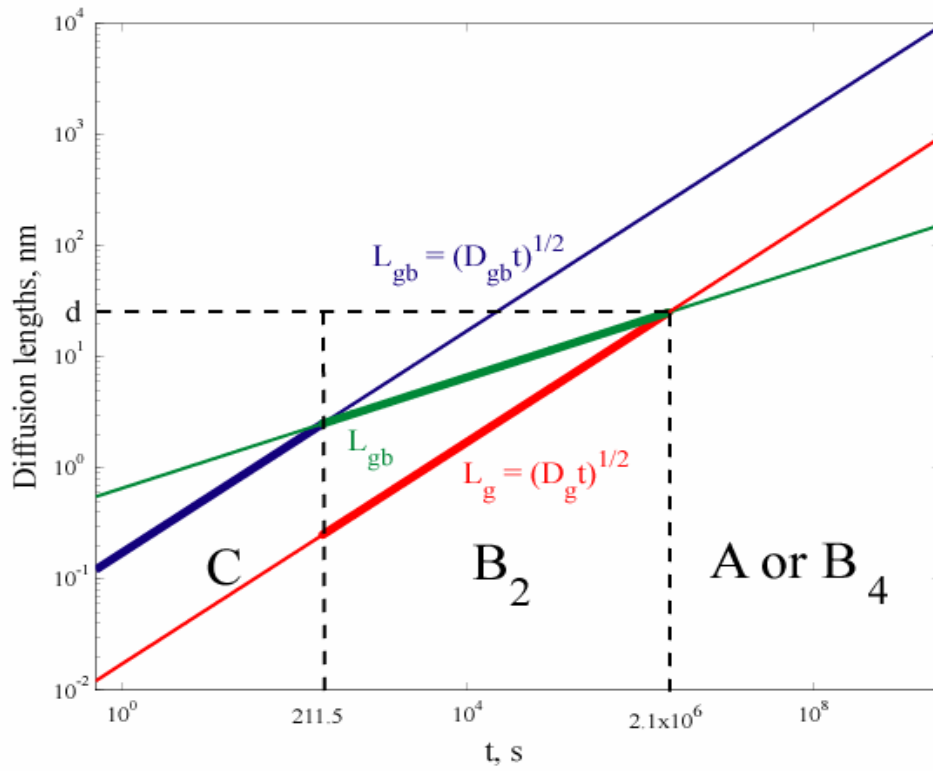
b)

c)

d)

Fig. 1.5 How diffusion lengths along the GBs (L_{gb}) and grains (L_g) vary with the diffusion time (t) for a) $\Delta = 10^2$ (coarse-grained material), b) $\Delta = 10^3$ (fine-grained material), c) $\Delta = 2.2 \cdot 10^4$ (ultrafine-grained material), d) $\Delta = 10^5$ (ultrafine-grained material). The dependences are plotted on the logarithmic scale. In the case of green line L_{gb} is given by Eq. (1.12a).

expression for w:

$$w = \frac{\eta}{\sqrt{\beta}} = \frac{y}{\sqrt{D_g t \beta}} = \frac{y}{\sqrt{\delta D_{gb}}} \left(\frac{4D_g}{t} \right)^{1/4},$$ (1.15)

where η is the dimensionless coordinate weighted to the diffusion length in grain (bulk) and used in the original Whipple solution [Whi54]. While the second derivative in Eq. (1.14) represents an experimentally measurable gradient, the derivative with respect to w can not be obtained without knowing D_{gb}. Le Claire suggested that it can be replaced by a constant value, if $\beta \gg 10$ (Eq. (1.9d)) and $w \gg 2$. Both the quantities are Δ-dependent; therefore these are also unknown for the once measured diffusion profile. However, it is believed that in most cases the conditions are satisfied. If it is really the case, the derivative is replaced by a constant value of -0.78 according to Le Claire [Cla63], giving rise to

$$\delta D_{gb} = 1.322 \sqrt{\frac{D_g}{t}} \left(-\frac{\partial \ln C_{av}}{\partial y^{6/5}} \right)^{-5/3}.$$ (1.16)

The latter expression is known as Le Claire's relation, which is the only expression used, when the gradient is measured under conditions of type-B kinetics. Eq. (1.16) is modified, if the segregation of impurities is concerned. The triple product $s\delta D_{gb}$ [Bok58] comes into play in this case. The role of segregation effects in the type-B kinetics is not discussed in the present study. Recently, Chung and Wuensch [Chu96a] observed that the conditions of validity of Eq. (1.16) were not fulfilled in the case of very shallow diffusion gradients. Such situations are discussed in the present study.

Hart's equation is widely used [Hart57], if the diffusion profile was measured at very long t and/or high temperatures. The equation represents a linear combination of diffusivities D_g and D_{gb} weighted to the volume fraction of GBs (g):

$$D_{eff} = gD_{gb} + (1-g)D_g.$$ (1.17a)

His equation was modified to take into account segregation by Mortlock [Mor60] and reads:

$$D_{eff} = sgD_{gb} + (1-sg)D_g.$$ (1.17b)

The latter expression is known as the Hart-Mortlock equation in which includes the equilibrium segregation factor s is given by Eq. (1.6b). Since this equation is valid only for the model of parallel boundaries, another expression was also suggested to deduce D_{gb} [Kal01]:

$$D_{eff} = \frac{sD_{gb}\left[(2-g)D_g + sgD_{gb}\right]}{(1-g+sg)\left[sD_{gb}(2-g)+gD_g\right]}.$$
(1.18)

This is a modified Maxwell-Garnett, or Maxwell equation [MaxG04], [Max54] which is believed to be valid for realistic polycrystalline microstructures.

All these equations are currently used to deduce D_{gb} from the measured diffusion profiles except Eq. (1.18). Up to now there are no publications demonstrating the use of Eq. (1.18) in diffusion experiments. As these equations do not take into account the conditions of small grain sizes, it is the aim here to check the validity of those theories under conditions of short t. In the next chapters the discussion of such specific conditions will be continued on the basis of numerical evaluations of Whipple's solution as well as numerical integrations of the Fisher system.