

An improved procedure for determining grain boundary diffusion coefficients from averaged concentration profiles

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Whipple’s solution of the problem of grain boundary diffusion and Le Claire’s relation, which is often used to determine grain boundary diffusion coefficients, are examined for a broad range of ratios of grain boundary to bulk diffusivities Δ and diffusion times t . Different reasons leading to errors in determining the grain boundary diffusivity (D_{GB}) when using Le Claire’s relation are discussed. It is shown that nonlinearities of the diffusion profiles in $\ln C_{av} - y^{6/5}$ plots and deviations from “Le Claire’s constant” (-0.78) are the major error sources (C_{av} =averaged concentration, y =coordinate in diffusion direction). An improved relation (replacing Le Claire’s constant) is suggested for analyzing diffusion profiles particularly suited for small diffusion lengths (short times) as often required in diffusion experiments on nanocrystalline materials. © 2008 American Institute of Physics. [DOI: 10.1063/1.2887993]

I. INTRODUCTION

Grain boundary (GB) diffusion plays a crucial role in many technological processes and can, thus, determine the kinetics of processes such as corrosion or stoichiometry variations in oxides. The number of experimental and theoretical works devoted to determining and understanding D_{GB} is enormous, and the field still benefits from recent improvements in experimental tools used for profile measurements such as secondary ion mass spectroscopy¹ or auger electron spectroscopy.² These techniques are also particularly interesting for analyzing GB diffusion in nanocrystalline materials since they allow measuring very shallow diffusion profiles and low concentrations.³ At a first glance, the procedures to find D_{GB} from measured diffusion profiles seem to have been settled since many years. In particular, Le Claire’s relation (see discussion below) is commonly used for analyzing experimental data in cases in which the diffusion profiles were measured under conditions of the so-called type-B kinetics⁴ which simply means that the diffusion length in the bulk (grain) L_G is larger than the GB thickness but much smaller than the average grain size. Limits and underlying assumptions of this model are partly discussed in the literature and can become particularly critical when dealing with nanomaterials which are in the focus of research due to size effects that can drastically change materials properties.^{5,6}

Since most of the significant contributions related to the D_{GB} determination has already been described in excellent reviews,⁷ we restrict ourselves here to a brief discussion of the basics together with some recent progress (see also Sec. II). Fisher⁸ suggested a mathematical model describing fast GB diffusion on the basis of Fick’s second law, and later Whipple⁹ obtained an analytical solution to Fisher’s system

of diffusion equations. Le Claire suggested a relation for determining D_{GB} from one-dimensional diffusion profiles based on a numerical integration of a simplified Whipple’s solution under certain assumptions.^{7,15} Later Fisher’s model and Whipple’s solution were modified to take account of various effects neglected in the model. For example, Szabo *et al.*¹⁰ described a procedure to include a segregation factor, whereas Mishin¹¹ used Whipple’s solution to analyze the effects of GB orientation to the surface. Recently, we published a paper on numerical solutions of a modified model that includes space charge layers being important in ionic materials.¹² Chung and Wuensch¹³ have reported on related problems and suggested a new analysis procedure for the determination of D_{GB} . Shaw and Shaw¹⁴ also avoided Le Claire’s relation and wrote a program for fitting the measured diffusion profile to Whipple’s solution. They applied their fitting program to several experimentally determined diffusion profiles taken from the literature but also reported cases for which the fitting program gave unreasonable results.

In the present work Le Claire’s relation is re-examined by numerical calculations, particularly for diffusion in materials with nanosized grains thus requiring small diffusion

TABLE I. A comparison of the derivatives at the maximum found by using calculated dependences (true) and Eq. (9) for $\Delta=2.2 \times 10^4$.

t (s)	$\partial \ln C_{av} / \partial w^{6/5} = f(w^{6/5})_{true}$	$\partial \ln C_{av} / \partial w^{6/5} = f(w^{6/5})_{Eq. (9)}$
2×10^3	-0.99	-1.00
3.6×10^3	-0.94	-0.94
4.7×10^3	-0.92	-0.92
8.2×10^3	-0.89	-0.88
10.7×10^3	-0.87	-0.87
13.2×10^3	-0.86	-0.86
1×10^5	-0.80	-0.80
5×10^5	-0.78	-0.78

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lengths as to stay within conditions of type-B diffusion regime.⁴ Section II deals with the basics of Fisher's system and Whipple's solution used to calculate diffusion profiles, and in Sec. III our main results are presented, revealing the problems related to the determination of D_{GB} from Le Claire's relation. In the same section an improved relation is suggested for deducing D_{GB} from measured diffusion profiles.

II. FISHER'S SYSTEM, WHIPPLE'S SOLUTION, AND LE CLAIRE'S RELATION

Fisher's system of differential equations

$$\frac{\partial C_G(x,y,t)}{\partial t} = D_G \left[\frac{\partial^2 C_G(x,y,t)}{\partial x^2} + \frac{\partial^2 C_G(x,y,t)}{\partial y^2} \right],$$

if $|x| \geq \delta/2$,

$$\frac{\partial C_G(y,t)}{\partial t} = D_{GB} \frac{\partial^2 C_{GB}(y,t)}{\partial y^2} + \frac{D_G}{\delta/2} \frac{\partial C_G(y,t)}{\partial x}, \quad \text{if } |x| = \delta/2,$$

(1)

is based on Fick's second law for both bulk and GB and deals with the situation of a single GB perpendicular to the surface of a semi-infinite material (isolated boundary model⁷). Only this situation is considered in the present paper. The isolated boundary model is symmetrical with respect to $x=0$ and two dimensional (2D). In Eq. (1) δ is the GB thickness, C_G and C_{GB} are the concentrations in grain and GB, respectively, while D_G denotes the bulk diffusion coefficient; t is the diffusion time. Lateral concentration variations in the GB are neglected.

The exact analytical solution of Fisher's system [Eq. (1)],

$$C_G(x,y,t) = C_0 \operatorname{erfc}\left(\frac{y}{2\sqrt{D_G t}}\right) + \frac{C_0 y}{2\sqrt{D_G t} \pi} \int_1^\Delta \frac{d\sigma}{\sigma^{3/2}} \operatorname{erfc}\left[\frac{1}{2} \left(\frac{\Delta-1}{\Delta-\sigma}\right) \left(\frac{\sigma-1}{\beta} + \frac{x+\delta/2}{\sqrt{D_G t}}\right)\right],$$

(2)

was obtained by Whipple⁹ for the case of a constant source at the free surface and consists of a sum of bulk and GB contributions. C_0 is the concentration at the free surface and σ the integration variable. The solution comprises the dimensionless quantities Δ and β defined by

$$\Delta \equiv D_{GB}/D_G \quad (3)$$

and

$$\beta \equiv \frac{(\Delta-1)\delta}{2\sqrt{D_G t}}. \quad (4)$$

The latter quantity includes the ratio α of the thickness δ and the diffusion length $L_G = \sqrt{D_G t}$,

$$\alpha \equiv \frac{\delta}{2\sqrt{D_G t}}. \quad (5)$$

The integration of Whipple's solution provides a 2D distribution of concentrations within the bulk. However, experimentally determined diffusion profiles usually consist of concentrations averaged in planes parallel to the surface, i.e., perpendicular to the GB. Le Claire suggested a way how D_{GB} can be obtained from such diffusion profiles by integrating Whipple's solution under certain assumptions (see below). He found¹⁵

$$\delta D_{GB} = 1.322 \sqrt{\frac{D_G}{t}} \left(-\frac{\partial \ln C_{av}}{\partial y^{6/5}} \right)^{-5/3}, \quad (6)$$

with C_{av} denoting the averaged concentration in the bulk similar to the quantity measured in experiments (Ref. 7) which is normalized to C_0 for all the results discussed in the present work. This relation is frequently used to determine D_{GB} of many different types of materials (coarse grained, nanocrystalline, ionic materials, metals, etc.), if the conditions of type-B kinetics are satisfied and δ and D_G are known or can be estimated.

III. RESULTS AND DISCUSSION

A. Accuracy of Le Claire's relation in determining D_{GB}

Whipple's solution was integrated by using the mathematical program MATLAB (Ref. 16) (function "quadl" based on adaptive Lobatto quadrature¹⁷). If not stated otherwise the integration was done over the following sizes of a sample: a length of 500 nm and a width of 25 nm. Diffusion lengths in the bulk were varied from 0.77 to 12.15 nm and δ was fixed to 0.5 nm throughout all calculations. Without loss of generality a D_G value of 2.95×10^{-4} nm²/s is taken which corresponds to the value obtained in an experimental study of diffusion of ¹⁸O in nominally pure nanocrystalline ZrO₂ at 500 °C.¹⁸ One-dimensional diffusion profiles with averaged concentrations $C_{av}(y,t)$ were calculated for ratios Δ from 10² to 10⁵ and a broad range of times (2×10^3 to 5×10^5 s). Numerical difficulties arising when integrating Whipple's solution under different conditions were mentioned by Evans¹⁹ and are mostly reflected in numerical instabilities²⁰ which are visible in the behavior of the derivative $\partial \ln C_{av} / \partial y^{6/5}$ discussed below. The instabilities increase with the ratio Δ and for small concentrations due to short t . The integration step along the penetration depth (y) has therefore to be tuned properly to minimize such problems.

After calculating the diffusion profiles, Le Claire's relation [Eq. (6)] was applied in order to determine an apparent value of GB diffusivity $D_{GB,app}$ and to compare it with the true value D_{GB} used in the integration. In other words, the diffusion profiles were fitted to straight lines in $\ln C_{av} - y^{6/5}$ plots and the slope was exploited in Eq. (6). On the basis of these values errors in determining D_{GB} were estimated for different t . In Fig. 1 the errors are shown for all ratios Δ used (solid lines). It can be seen that the errors increase with decreasing time, and the largest value observed in the calculation amounts to about 45% for $t=2 \times 10^3$ s and $\Delta=10^2$, whereas the smallest error is 1% after 5×10^5 s for $\Delta=10^3$. Interestingly, the corresponding errors also increase at long t for $\Delta=2.2 \times 10^4$ and 10^5 . This effect is discussed below.

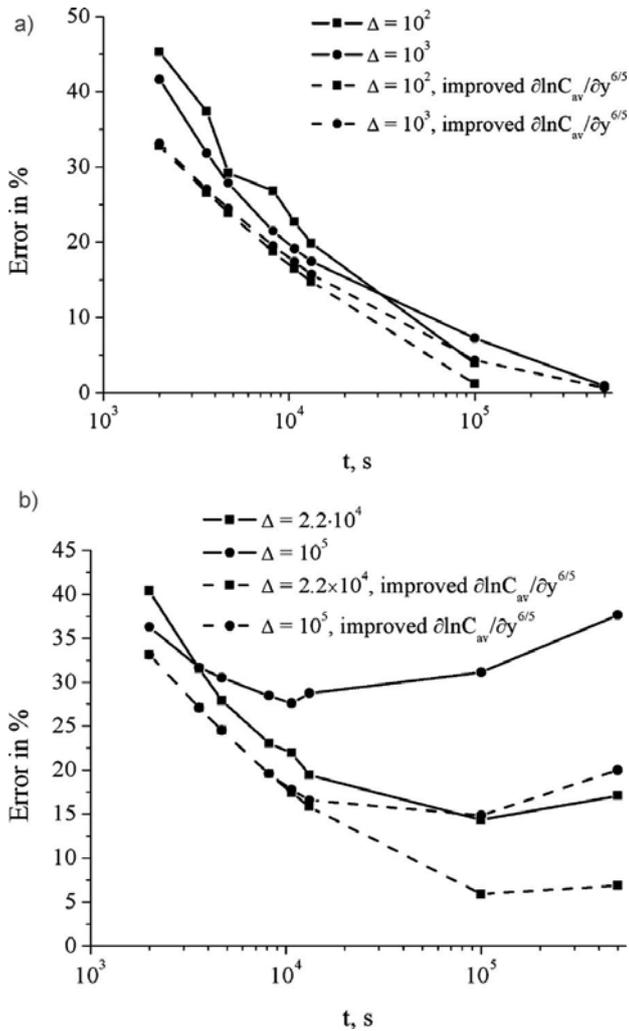


FIG. 1. Variation of the errors in determining D_{GB} with time ($D_{GB,app}$ was obtained by using Le Claire's relation): (a) $\Delta=10^2$, $\Delta=10^3$, (b) $\Delta=2.2 \times 10^4$, $\Delta=10^5$. Errors were estimated according to $(|D_{GB,app} - D_{GB,true}|/D_{GB,true}) \times 100\%$.

In order to interpret the errors one has to consider two aspects, first the assumption of a constant slope in the $\ln(C_{av}) - y^{6/5}$ plot and second the prefactor of 1.322 in Le Claire's relation [Eq. (6)]. We first discuss the alleged constancy of the slope: In Fig. 2 derivatives of the calculated diffusion profiles were plotted against $y^{6/5}$. The variation for small y -values [part left of the maxima in Fig. 2(a)] can be related to the prevalence of bulk diffusion (compared to GB diffusion). However, it can be seen that the profiles can also be rather nonlinear in the so-called GB part for larger y , especially for short t and moderate Δ . This raises the question what slope should one use in Le Claire's relation. It turns out that the errors in determining D_{GB} from Eq. (6) can be reduced when the maximum values of the derivative are used (Fig. 1, dashed lines). To give an example, the error is reduced from 45% to around 33% for $\Delta=10^2$ at $t=2 \times 10^3$ s. For large Δ -values (2.2×10^4 and 10^5) and longer t a maximum is not reached and the value used in Le Claire's relation to determine an improved D_{GB} was taken at $y=500$ nm (end of the sample).

In the remaining part of the section a second reason for the errors will be discussed. It can be understood from the expression

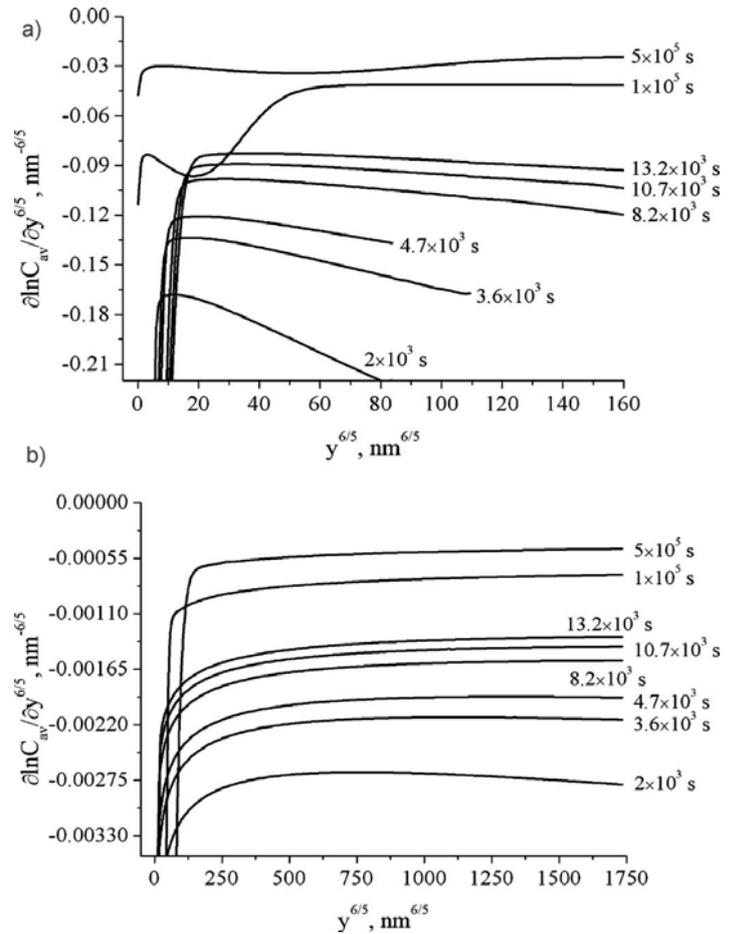


FIG. 2. Variation of the derivative $\partial \ln C_{av} / \partial y^{6/5}$ with $y^{6/5}$ obtained for (a) $\Delta=10^2$ and (b) $\Delta=10^5$.

$$\delta D_{GB} = 2 \sqrt{\frac{D_G}{t}} \left(-\frac{\partial \ln C_{av}}{\partial w^{6/5}} \right)^{5/3} \left(-\frac{\partial \ln C_{av}}{\partial y^{6/5}} \right)^{-5/3} \quad (7)$$

used by Le Claire¹⁵ to deduce Eq. (6). The symbol w denotes the dimensionless depth coordinate according to

$$w = \frac{y}{\sqrt{D_G t \beta}}. \quad (8)$$

(Diffusion profiles plotted as a function of w are independent of Δ .) From an integration of Whipple's solution, Le Claire suggested that $(-\partial \ln C_{av} / \partial w^{6/5}) = 0.78$ (Le Claire's constant) and thus $2(-\partial \ln C_{av} / \partial w^{6/5})^{-5/3} = 1.322$. The integration made by Le Claire uses the approximation that the upper limit of the integral in Whipple's solution may be replaced by infinity (i.e., $\Delta \rightarrow \infty$).¹⁵ Also, the integrand in Whipple's solution was simplified. A detailed discussion of this replacement is given by Kaur *et al.*⁷ In order to re-examine this approximation, we calculated the derivatives $\partial \ln C_{av} / \partial w^{6/5}$ for a broad range of t and Δ by using a modified Whipple solution, i.e., introducing a new integration parameter $\tau = \{[(\Delta - \sigma) / (\Delta - 1)] \times (\beta / \sigma)\}^{1/2}$. According to Kaur⁷ this replacement improves the integration for large values of β especially relevant here and/or allows the integration to be done under conditions of $\Delta \rightarrow \infty$. It has been explained in Ref. 7 that the approximation $\Delta \rightarrow \infty$ may be used when $\beta \ll \Delta$ with β remaining finite. In the present study β was varied from 2 ($\Delta=10^2, t=10^5$ s) to $32\,518$ ($\Delta=10^5, t=2 \times 10^3$ s) and is thus always smaller than Δ even though only by a factor of 3 for small t and very large

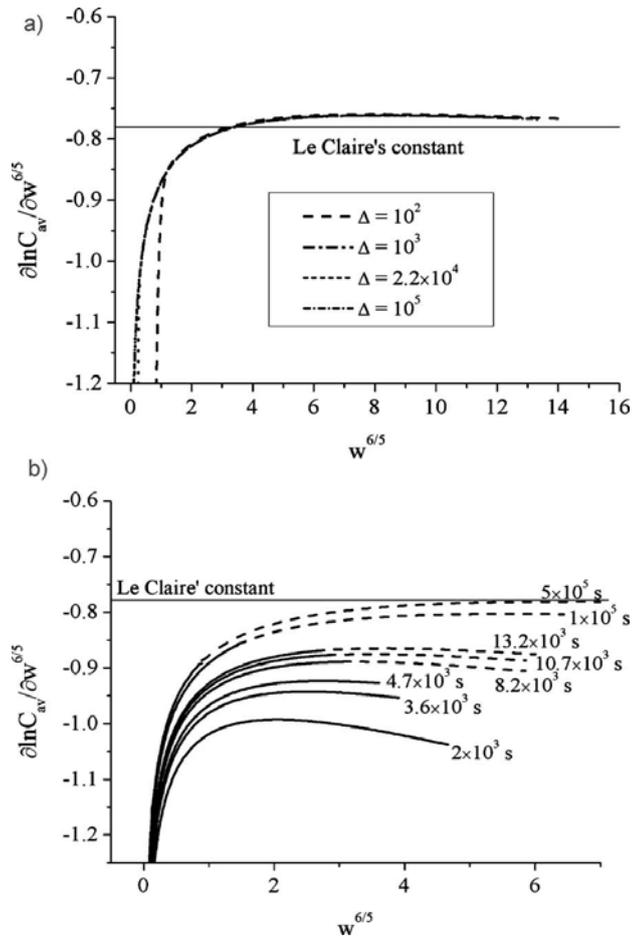


FIG. 3. (a) Variation of the derivative $\partial \ln C_{av} / \partial w^{6/5}$ as a function of $w^{6/5}$ calculated by using a modified Whipple's solution (see text) for different ratios Δ at $t = 2 \times 10^3$ s (b) Variation of the derivatives $\partial \ln C_{av} / \partial w^{6/5}$ with $w^{6/5}$ for $\Delta = 10^5$ at different diffusion times t (Whipple's original solution). Le Claire's constant is also indicated. The dashed curves were obtained for increased sample length and indicate problems related to a finite length.

Δ . According to our results the ratio $\Delta / \beta = 50$ indeed leads to Le Claire's constant and the condition $\beta \ll \Delta$ should be specified by $\Delta / \beta \geq 50$. Chung and Wuensch¹³ suggested the condition $\Delta / \beta (\approx 2L_G / \delta) \geq 10^3$ in order to justify the approximation $\Delta \rightarrow \infty$. This would mean that measurements characterized by small values of Δ could not be evaluated by Le Claire's equation.

By using MATLAB one can integrate both the modified Whipple solution to account of $\Delta \rightarrow \infty$ (also used by Le Claire) and the original one with the upper limit Δ . In Figs. 3(a) and 3(b) both integration results are compared. Note that the derivatives shown in Fig. 3(a) were obtained under the condition of $\Delta \rightarrow \infty$ at $t = 2 \times 10^3$ s, whereas the derivatives in Fig. 3(b) correspond to $\Delta = 10^5$ at different t . So only the derivative for $\Delta = 10^5$ in Fig. 3(a) can be compared with the corresponding derivative in Fig. 3(b) at $t = 2 \times 10^3$ s. An almost constant value is indeed arrived at under the approximation discussed [Fig. 3(a)] but derivatives differ significantly from 0.78 when integrating Whipple's original solution [Fig. 3(b)]. Deviations are particularly pronounced for diffusion profiles after short times, and the latter is experimentally often important when dealing with nanocrystalline materials. The results of Fig. 3(b) also explain the deviations discussed by Szabo *et al.*,¹⁰ and we have to conclude that there is a regime of short t and/or large α where Le

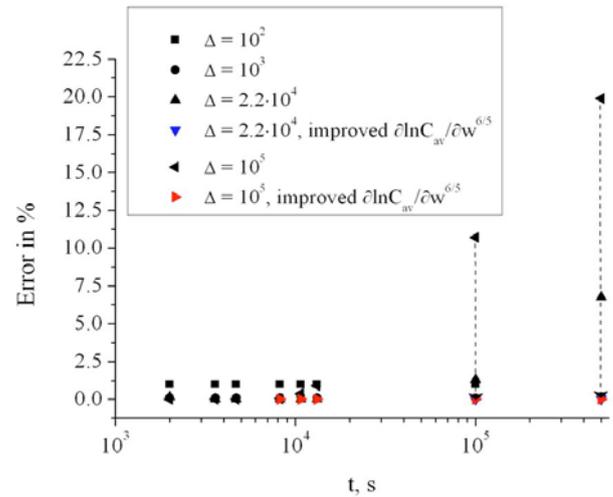


FIG. 4. (Color online) Errors in determining D_{GB} calculated by using improved derivatives ($y^{6/5}$ and $w^{6/5}$) in Le Claire's original expression [Eq. (7)].

Claire's relation indeed may not be applicable.

For a given position of the maximum derivative one could test a further criterion already discussed in the literature²¹ though often ignored in the evaluation of experiments. According to this criterion, the determination of D_{GB} should be done from those parts of a measured diffusion profile which satisfy $y \geq 5L_G$. However, in our calculations the position of the maximum for $\Delta = 10^2$ at $t = 2 \times 10^3$ s is $y_{max}^{6/5} \sim 12 \text{ nm}^{6/5}$ (the corresponding diffusion length $L_G \sim 0.77 \text{ nm}$) and thus y_{max} is ten times larger than L_G . Hence we have to conclude that the criterion is still not sufficiently strict because it would include a fit of a straight line to those parts of the diffusion profile which are still strongly influenced by bulk diffusion. It should be noted that also Chung and Wuensch¹¹ reported errors in determining D_{GB} when $y \leq 10L_G$. The diffusion profile measured or calculated for small diffusion lengths still comprises the two distinguishable parts¹⁹ and thus suggests that the second part can be fitted to a straight line according to the conventional procedure. In such cases, however, only the derivative of the profile enables us to realize to which extent the fitting corresponds to the GB diffusion part.

We showed above that the accuracy of a D_{GB} analysis can be improved when using the maximum value of $\partial \ln C_{av} / \partial y^{6/5}$. The same is true if the derivative maximum with respect to the dimensionless coordinate w is considered in Le Claire's original relation [Eq. (7)]. The corresponding reduction of the error is shown in Fig. 4 and errors result which do not exceed 1% for all the ratios Δ at short t . The error still increases for $t > 10^4$ if $\Delta = 2.2 \times 10^4$ and 10^5 . This, however, is due to the fact that the standard length of the sample used in the numerical study (500 nm) is still too short to reach the maximum of the derivative for such parameters. This is particularly well seen in the behavior of $\partial \ln C_{av} / \partial w^{6/5} = f(w^{6/5})$. The solid lines in Fig. 3(b) indicate the derivative's values for 500 nm, whereas the dashed lines were obtained by increasing the sample length. The errors in Fig. 4 were determined by using the value of $\partial \ln C_{av} / \partial w^{6/5}$ taken at the maximum; $\partial \ln C_{av} / \partial y^{6/5}$ was either taken at the maximum (if available) or at the end of the sample for

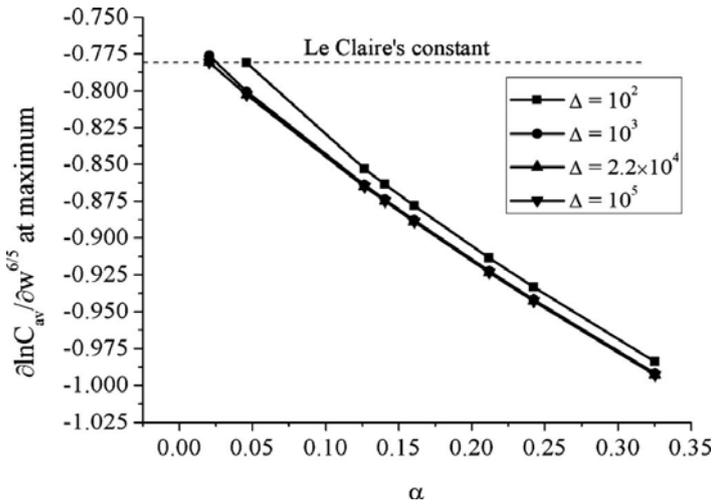


FIG. 5. The maxima of the dependences $\partial \ln C_{av} / \partial w^{6/5} = f(w^{6/5})$ plotted against the dimensionless parameter α for different ratios Δ .

$\Delta = 2.2 \times 10^4$ and 10^5 at $t > 10^4$ s. The arrows in Fig. 4 also show the effect of taking the derivative $\partial \ln C_{av} / \partial w^{6/5}$ at the end of the sample (improved derivative). If the derivatives are obtained at the same point, then D_{GB} can be determined very accurately. However, in true experiments an analysis of $\partial \ln C_{av} / \partial w^{6/5}$ is not possible since w includes the unknown parameter D_{GB} , and we suggest that both derivatives should be taken at the corresponding maxima. Hence in the following section we suggest a relation which is particularly useful for small diffusion lengths in order to properly include a meaningful value of $\partial \ln C_{av} / \partial w^{6/5}$ in the analysis.

B. An improved procedure for calculating D_{GB}

According to our calculations the validity range of Le Claire's relation is rather limited; errors may easily occur for short diffusion lengths in the bulk (short times). Hence a modified expression is desirable which avoids or minimizes errors. In the following we show how to replace Le Claire's constant [or 1.322 in Eq. (6)] by a modified expression. In Fig. 5 the maximum values of the derivatives with respect to w are plotted versus the dimensionless parameter α which is connected to \sqrt{t} . These values almost lie on a straight line and correspond to

$$\frac{\partial \ln C_{av}}{\partial w^{6/5}} = -0.77 - 0.71\alpha. \quad (9)$$

For α close to zero Le Claire's constant (-0.78) results almost exactly. Only for $\Delta = 10^2$ slightly enhanced values of $\partial \ln C_{av} / \partial w^{6/5}$ can be found and Eq. (9) becomes somewhat inaccurate. Table I provides a comparison of the derivative's values obtained by using Eq. (9) with those directly taken from the integrations discussed above. Equation (9) can thus be used to calculate the maximum value of $\partial \ln C_{av} / \partial w^{6/5}$, if α is larger than 0.02. We thus suggest replacing the value of Le Claire's constant by Eq. (9) when determining D_{GB} at short t . Please note that the value of α can be calculated only for known D_G . From the results discussed so far, it follows that at least for short diffusion lengths (i.e., nanocrystalline materials) the following steps are important to properly determine D_{GB} : (i) Plot the derivative of the measured diffusion

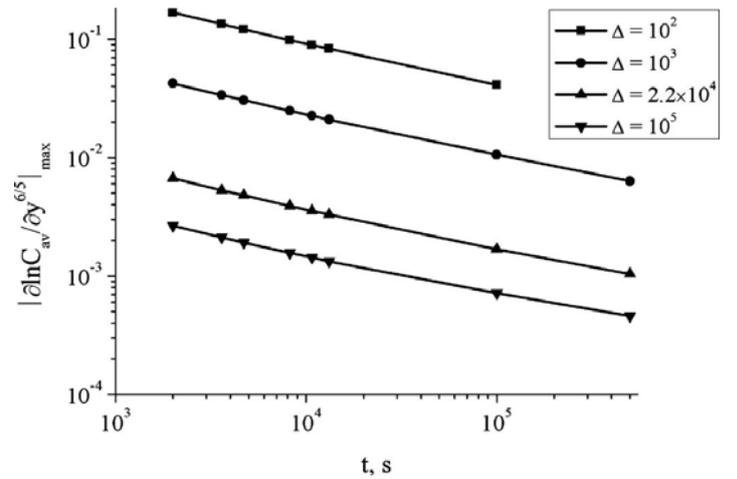


FIG. 6. Variation of the modulus of the maximum of $\partial \ln C_{av} / \partial y^{6/5}$ (in $\text{nm}^{-6/5}$) with t for different Δ . The result is shown on a logarithmic scale.

profile and identify its maximum, i.e., $(\partial \ln C_{av} / \partial y^{6/5})_{max}$. (ii) Calculate parameter α . (iii) If $\alpha > 0.02$, use Eq. (9) to find the derivative $(\partial \ln C_{av} / \partial w^{6/5})_{max}$ and put the derivatives into Eq. (7). Hence

$$\delta D_{GB} = 2 \sqrt{\frac{D_G}{t}} \left(0.77 + \frac{\delta}{\sqrt{8D_G t}} \right)^{5/3} \left(-\frac{\partial \ln C_{av}}{\partial y^{6/5}} \right)_{max}^{-5/3} \quad (10)$$

rather than Eq. (6) is suggested for determining GB diffusion coefficients in nanocrystalline materials, where the two expressions in brackets correspond to the maxima of the corresponding derivatives.

In the last part of this section we reconsider the situation by discussing how the maximum of the derivative of the diffusion profile depends on t or Δ . The values of the maximum of $\partial \ln C_{av} / \partial y^{6/5}$ can be plotted as functions of t on a logarithmic scale. This leads to almost linear dependences (constant slope) for fixed D_G [Fig. 6] which can further be approximated by

$$\log \left| \frac{\partial \ln C_{av}}{\partial y^{6/5}} \right|_{max} = \log(A) + B \log(t), \quad (11)$$

where A is a function of Δ (see discussion below) whereas the slope B is independent of t and Δ (Table II). In the Appendix we present a short mathematical transformation helpful to further interpret Eq. (11). The transformation is based on Le Claire's original relation [Eq. (7)] and demonstrates how the maximum of $\partial \ln C_{av} / \partial y^{6/5}$ analytically depends on t and Δ . The final expression

$$\left| \frac{\partial \ln C_{av}}{\partial y^{6/5}} \right|_{max} = C \Delta^{-3/5} t^{-3/10}, \quad (12)$$

with $C = [2/\delta]^{3/5} (-\partial \ln C_{av} / \partial w^{6/5})_{max} D_G^{-3/10}$ may be compared to experimental results of Atkinson,²² who found from the diffusion profiles of cation diffusion in NiO that slopes of the profiles [$\ln C_{av} = f(y^{6/5})$] can linearly depend on $t^{-0.3}$. From Eq. (12) it also becomes clear that the parameter A in Eq. (11) can be expected to depend on D_G , D_{GB} , δ , and $\partial \ln C_{av} / \partial w^{6/5}$.

TABLE II. The values of the slope B for various Δ ($D_G=2.95 \times 10^{-4} \text{ nm}^2/\text{s}$).

Δ	B
10^2	-0.32
10^3	-0.33
2.2×10^4	-0.34
10^5	-0.36

IV. CONCLUSIONS

Le Claire's relation for determining the GB diffusion coefficient (D_{GB}) was tested under conditions of type-B kinetics for very short as well as long diffusion times (t). Errors of the order of 50% in the evaluation of D_{GB} can result when using the standard procedures to find D_{GB} . Errors are related to the nonlinearity of diffusion profiles in $\ln C_{av} - y^{6/5}$ plots. Consequently, the derivative of the diffusion profile $\partial \ln C_{av} / \partial y^{6/5}$ should be plotted in order to estimate the effect of profile nonlinearity. The maximum value of the derivative should be used rather than fitting the profile to a straight line. Also, the derivative $\partial \ln C_{av} / \partial w^{6/5}$ is not constant but depends on the dimensionless parameter α which is the ratio of bulk diffusion length and GB thickness. Consequently, Le Claire's constant should be replaced by an improved value calculated from Eq. (9). Only if the dimensionless parameter α is smaller than 0.02, the conventional value (≈ -0.78) may safely be used. The parameter α can easily be estimated from experimental data if D_G and δ are known. On the basis of these observations the procedure to properly deduce D_{GB} is explicitly discussed which is straightforward without introducing new parameters.

APPENDIX

The equation originally used by Le Claire is Eq. (7). It can be rephrased into

$$\left| \frac{\partial \ln C_{av}}{\partial y^{6/5}} \right| = \left[\frac{2}{\delta D_{GB}} \left(\frac{D_G}{t} \right)^{1/2} \right]^{3/5} \left(- \frac{\partial \ln C_{av}}{\partial w^{6/5}} \right), \quad (\text{A1})$$

where the first expression in bracket can be rewritten as

$$\begin{aligned} \left[\frac{2}{\delta D_{GB}} \left(\frac{D_G}{t} \right)^{1/2} \right]^{3/5} &= \left[\frac{2}{\delta \Delta \sqrt{t D_G}} \right]^{3/5} \\ &= \left[\frac{2}{\delta} \right]^{3/5} \Delta^{-3/5} D_G^{-3/10} t^{-3/10}. \end{aligned} \quad (\text{A2})$$

The derivative with respect to the real coordinate thus reads

$$\left| \frac{\partial \ln C_{av}}{\partial y^{6/5}} \right| = C \Delta^{-3/5} t^{-3/10}, \quad (\text{A3})$$

where $C = [2/\delta]^{3/5} (-\partial \ln C_{av} / \partial w^{6/5}) D_G^{-3/10}$. From Eq. (10) and the result in Fig. 6, we see that the parameter A in Eq. (11) is given by $C \Delta^{-3/5}$.

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