Numerical Integration of Grain Boundary Diffusion

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Abstract

This study presents a numerical analysis of concentration level changes in a normalized two-dimensional grain boundary-grain region using *Mathematica*, based on the expressions developed by R. T. P. Whipple in 1954. The results are consistent with those obtained in 1997 by J. W. Evans in his analysis of Whipple's exact solution and its various approximations. In this work, the grain boundary width (α), the ratio of the diffusive coefficients between the grain boundary and the grain (Δ), the transverse (ξ) and longitudinal (η) coordinates of points, and the combined effect (β) of α and Δ are taken into consideration. The main conclusions are that the factors β, ξ, and η regulate concentration levels, while Δ and α are inversely correlated. A higher β value leads to a higher concentration gradient between the grain boundary region and the grain region at the interface, leading to steeper concentration contour lines. At β=0.1, the presence of the grain boundary is negligible.

Abrégé

Cette étude présente une analyse numérique des changements de niveau de concentration dans une région bidimensionnelle normalisée de limite de grain à l'aide de *Mathematica*, basée sur les expressions développées par R. T. P. Whipple en 1954. Les résultats sont cohérents avec ceux obtenus en 1997 par J. W. Evans dans son analyse de la solution exacte de Whipple et de ses diverses approximations. Dans ce travail, la largeur de la limite du grain (α), le rapport des coefficients de diffusion entre la limite du grain et le grain (Δ), les coordonnées transversales (ξ) et longitudinales (η) des points, et l'effet combiné (β) de α et Δ sont pris en considération. Les principales conclusions sont que les facteurs β, ξ, et η régulent les niveaux de concentration, tandis que Δ et α sont inversement corrélés. Une valeurβ plus élevée entraîne un gradient de concentration plus important entre la région de la limite du grain et la région du grain à l'interface, ce qui conduit à des lignes de contour de concentration plus raides. À β=0,1, la présence du joint de grain est négligeable.

Acknowledgements

During the writing of this dissertation, I have received a great deal of support and assistance.

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Chapter 1

Introduction

1.1 Thesis Background

Engineering materials, especially metals and ceramics, commonly exhibit a polycrystalline microstructure. As the name implies, the structure is a collection of many crystals. Each crystal, also called a grain, consists of an ordered array of atoms. The surfaces that separate adjacent crystals are called grain boundaries [1]. Matter is transported in solids by the diffusion of atoms. The rate of transport is determined by the diffusion coefficient, also called diffusivity. Many studies show that the diffusive transfer along the grain boundaries occurs much faster than bulk diffusion but slower than surface diffusion. Grain-boundary diffusion is an important mechanism for many natural and engineering processes in metallurgy; therefore, this mechanism has been studied extensively by scientists and engineers. Diffusive transfer of matter is mathematically identical to heat conduction in solids. There is an equivalence

between solutions for boundary-value problems in the two domains [2].

1.2 Earlier Studies

1.2.1 Whipple's Study

In his paper *CXXXVIII. Concentration Contours in Grain Boundary Diffusion*, R. T. P Whipple worked on a simplified model for studying grain boundary diffusion [3]. Whipple has given formulae for the concentration distribution in a semi-infinite region bisected by a thin well-diffusing slab at different times after the concentration of the boundary of the semi-infinite region has been raised suddenly from zero to unity at time t=0. At times t<0, the concentration is everywhere zero. In this idealized model, as depicted schematically in Figure 1.1, the half-space y>0 is fulfilled with a type of grains of diffusivity D, and a grain boundary of diffusivity D' (D'»D) is treated as a slab with width 2a parallel to the y axis. It is convenient to place both the grain boundary and the grain region symmetric about the y axis for further analysis. The thickness of the grain boundary is considered small compared with the grains on either side, and this system is treated as two-dimensional on the x-y plane.

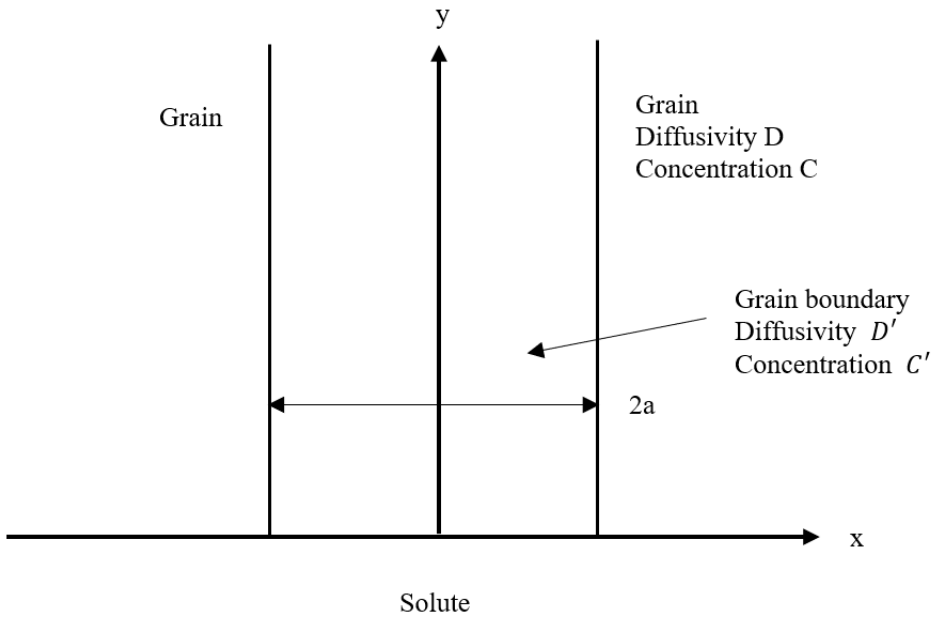

Figure 1.1: Whipple's model of diffusion in a grain boundary and adjacent grains

In this model, Fick's second law holds in both the grain regions and the grain boundary region, and there is no interface resistance at the slab edges such that the concentration is continuous at the grain-grain boundary interface. The grain boundary is assumed to have diffusivity D' with concentration C', while the grains are supposed to have diffusivity D with concentration C on either side. Within the grain boundary region, the concentration is governed by:

$$D'\nabla^2 C' = \frac{\partial C'}{\partial t} \tag{1.1}$$

Outside the slab, the concentration in the grains is governed by:

$$D\nabla^2 C = \frac{\partial C}{\partial t} \tag{1.2}$$

The concentrations at the grain boundary-grain interface satisfy the following conditions:

$$C = C' \tag{1.3}$$

$$D'\frac{\partial C'}{\partial x} = D\frac{\partial C}{\partial x} \tag{1.4}$$

In addition, at the plane y=0

$$C = C(x, 0, t) = H(t) \tag{1.5}$$

where, H(t) is the Heaviside unit function.

By normalizing the concentration on the surface, this diffusion model can be widely applied. Whipple pointed that the diffusion coefficient of the grain boundary is much larger (by at least one order of magnitude) than the diffusion coefficient of the grains, therefore he defined the ratio as

$$\Delta \equiv \frac{D'}{D} \tag{1.6}$$

At times t>0, the solute substance diffuses in the two-dimensional x-y plane, and in the dimensionless system, the diffusion in the x-direction and in the y-direction will be independent of each other. The diffusion in the x-direction in the scalable system is defined as

$$\xi \equiv \frac{x - a}{\sqrt{Dt}} \tag{1.7}$$

The y coordinate in the dimensionless system is defined as

$$\eta \equiv \frac{y}{\sqrt{Dt}} \tag{1.8}$$

The width of the slab is assumed to be 2a, and it is evident that the width of the grain

boundary region will influence the diffusion process. Therefore, this effect is also taken into consideration as

$$\alpha \equiv \frac{a}{\sqrt{Dt}} \tag{1.9}$$

Finally, Whipple introduced another parameter

$$\beta \equiv (\Delta - 1)\alpha \equiv \frac{(\Delta - 1)a}{\sqrt{Dt}} \tag{1.10}$$

Whipple has provided an exact solution for concentration by means of a Fourier-Laplace transform, henceforth referred to as *Whipple's Exact Solution*:

$$C = erfc\frac{\eta}{2} + \frac{\eta}{2\sqrt{\pi}} \int_1^{\Delta} \frac{1}{\sigma^{3/2}} \exp\left(\frac{-\eta^2}{4\sigma}\right) \times erfc\left[\frac{1}{2}\sqrt{\frac{\Delta - 1}{\Delta - \sigma}}\left(\frac{\sigma - 1}{\beta} + \xi\right)\right] d\sigma \tag{1.11}$$

Studying equation (1.11), Whipple found that at low value of the upper limit Δ, the integrand vanished quickly beyond its maximum, such that the result could be easily obtained from equation (1.11). However, at larger values of Δ, the integrand displays a long "tail" which cannot be ignored for several decades of σ [4]. Therefore, Whipple has given an alternative approximation solution, which is commonly called *Whipple's First Approximation*:

$$C = erfc\frac{\eta}{2} + \frac{\eta}{\sqrt{\pi}} \int_0^{1} \exp\left(\frac{-\eta^2\tau^2}{4}\right) \times erfc\left[\frac{1}{2}\left(\frac{1}{\tau^2\beta} - \frac{1}{\beta} + \xi\right)\right] d\tau \tag{1.12}$$

1.2.2 Evan's Study

J. W. Evans in his study *Approximations to the Whipple solution for grain boundary diffusion and an algorithm for their avoidance* worked further on Whipple's exact solution (1.11)

and Whipple's first approximation (1.12), by numerically solving these two integrals. Evans evaluated Whipple's first approximation (1.12) by Romberg integration; Whipple's exact solution (1.11) was obtained by an algorithm which was described in his paper [4].

Evans aimed to determine the concentration levels in the grain region, by working on both Whipple's exact solution and Whipple's first approximations with different Δ, ξ, η, α values. Evans stated that Whipple's exact solution (1.11) could be applied to avoid approximations, and he further developed an algorithm for fitting Whipple's equation to experimental data [4].

1.3 Motivation

Computing power has advanced tremendously during the past two decades. These advances are matched by the growing power and reliability of computational software. Hence, many problems can now be solved without the need to use approximations or develop customized algorithms and codes. In that spirit, the primary motivation for the thesis is to investigate the utility of standard commercial software (*Mathematica*) for analyzing grain boundary diffusion.

1.4 Thesis Objectives and Thesis Outlines

In this study, *Mathematica* is applied as the computing method. The first stage of this study is to evaluate the concentration values at the grain boundary-grain interface by *Mathematica* based on Whipple's exact solution (1.11) and Whipple's first approximation (1.12). The functions used in *Mathematica* will be described in Chapter 2.

Subsequently, the values obtained by *Mathematica* will be compared with the data provided by Evans. It is vital to determine how the concentration level changes inside the grain region, thus, the second stage of this study is to demonstrate the concentration level at various locations in the region $\xi>0$ and $\eta>0$. Chapter 3 mainly describes the relation between concentration level and the parameters β, ξ, and η.

Based on the data gathered in Chapter 3, Chapter 4 focuses on the analysis of concentration contour lines. In these sections, how the concentration level associated with the presence of the grain boundary will be investigated. Furthermore, Chapter 5 gives a conclusion for this research.

Chapter 2

Mathematica Computation

2.1 Whipple's First Approximation

Whipple in his paper derived an approximate solution for large Δ, and this expression is expressed in (1.12). The expression (1.12) is a summation of two parts: one is a complementary error function and another is integral. The goal of this study is to find concentration at various points, and the concentration values depend on the parameters ξ, η, α, Δ, and β. In expression (1.12), τ is a dummy variable, and the parameters η, β, and ξ can have various values. According to Evans's study, he focused on the points located at the grain boundary-grain interface such that ξ=0, after that he considered β value from very small β=0.1 to very large β=10^5 by one magnitude increment each time. In each case, he plugged a series of η values into the expression (1.12) to determine the concentration levels.

In this study, *Mathematica* is introduced as the computing technique. To obtain a numerical approximation to an integral, the function *NIntegrate[f,(x,x_{min},x_{max})]* can be applied, in which f indicates the integrand, x represents the dummy variable, and x_{min} and x_{max} are the lower and upper bounds of x. *Mathematica* allows the direct computation of a numerical integral. Besides, it is necessary to determine outputs from a complementary error function. *Mathematica* can compute a complementary error function by applying the *Erfc[z]* function, in which z indicates the input function. In this study, a four-digital precision is sufficient, therefore, a *NumberForm[expr,(n,f)]* function is involved to truncate the final result to four decimal points, in which *expr* is the value needed to be truncated, n indicates the number of significant digits, while f is the number of digits to the right of the decimal point.

Figure 2.1 shows a sample calculation for Whipple's first approximation (1.12) evaluated at β=10^4 along with the grain boundary-grain interface (ξ=0). In this case, the parameter η is evaluated at η=6, η=12, η=20, η=40, η=60, and η=100 respectively. All the η values are directly plugged into expression (1.12). Therefore, the last curly bracket from Figure 2.1 groups all the concentrations evaluated at the corresponded η values with four decimal points. The calculated concentrations will be summarized in the next chapter.

```
In[•]:= η = {6, 12, 20, 40, 60, 100}
Out[•]= {6, 12, 20, 40, 60, 100}

In[•]:= NumberForm[η/√π * NIntegrate[Exp[-1/4 η^2 τ^2] Erfc[1/2 (1/(10^4 * τ^2) - 1/10^4)], {τ, 0, 1}] + Erfc[η/2], {∞, 4}]

Out[•]//NumberForm=
{0.9521, 0.9061, 0.8478, 0.7158, 0.6022, 0.4215}
```

Figure 2.1: *Mathematica* sample calculation for β=10^4 obtained by Whipple's first approximation

2.2 Whipple's Exact Solution

The process to evaluate Whipple's exact solution (1.11) is similar to the one in Whipple's first approximation. The expression (1.11) also contains a complementary error function and an integral, in which the values of parameters Δ, η, β, and ξ are needed to be settled, while σ is the dummy variable in this case. As indicated in section 2.1, the *Erfc[z]* function is applied to evaluate the complementary error function, the *NIntegrate[f,(x,x_{min},x_{max})]* function is involved to numerically evaluate the integral, and the final result is truncated to four decimal points by the *NumberForm[expr,(n,f)]* function.

A sample example is also considered at β=10^4 at the grain boundary-grain interface (ξ=0), such that the considered η values are the same as those in section 2.1. Another parameter Δ=10^6+1 should be considered in this case. The result for each η value is shown in the last row of Figure 2.2. Furthermore, all the concentration values obtained by Whipple's exact solution will also be contained in the next chapter.

```
In[•]:= η = {6, 12, 20, 40, 60, 100}
Out[•]= {6, 12, 20, 40, 60, 100}

In[•]:= NumberForm[Erfc[η/2] + η/(2 √π) * NIntegrate[1/σ^(3/2) Exp[-η^2/(4 σ)] Erfc[1/20000 (σ - 1) √(10^6/(10^6 + 1 - σ))], {σ, 1, 10^6 + 1}],
        {∞, 4}]
Out[•]//NumberForm=
        {0.9520, 0.9059, 0.8475, 0.7153, 0.6014, 0.4204}
```

Figure 2.2: *Mathematica* sample calculation for β=10^4 obtained by Whipple's exact approximation

2.3 Concentration Contours

As will be described in Chapter 3, the concentration level is associated with the parameters β, ξ, and η, in which the variables ξ and η indicate the coordinate of a point, and β fully defines the geometric and diffusive properties of a grain boundary-grain model. To determine how the concentration level changes in a given diffusion model, it is more convenient to focus on the concentration contour lines. Whipple draws three concentration contours for β=0.1, β=1.0, and β=10.0 in his paper [3], and in this study, the concentration contours for this diffusion model will also be studied. In this section, the procedure of drawing concentration contours by *Mathematica* will be explained.

For a concentration contour, the parameter β is constant for each case, such that the product of the variables α and Δ is specified. As will be discussed in Chapter 3, once the value of β is specified, the concentration level at a specific point will no longer be influenced by α or Δ. Therefore, it is convenient to set α=0.01, and the Δ values will be determined based on different β values. A contour line is a curve connecting all the points with the same concentration value. One approach to draw the contour lines is to group all the points with concentration values in a three-dimensional space, in which the horizontal x-y plane indicates the ξ and η coordinates, while the vertical z-axis represents the concentration level. The inserted horizontal planes indicate a data set with the same concentration level regardless of the coordinates. The intersections of the calculated data space with the horizontal concentration planes are the concentration contour lines. It is convenient to visualize them in a two-dimensional plane. In this section, a sample calculation for β=1.0 case will be shown.

In Whipple's study, the range of both parameters η and ξ is taken to be from 0 to 3, and the η range can be subdivided to have 11 values, while the ξ range can be subdivided to have 4 values. The function *Subdivide*[x_{min},x_{max},n] used in *Mathematica* is indicated in Figure 2.3, in which n is the total intervals needed to be subdivided.

```
In[ ]:= η = Subdivide[0.1, 3, 10]
Out[ ]= {0.1, 0.39, 0.68, 0.97, 1.26, 1.55, 1.84, 2.13, 2.42, 2.71, 3.}

In[ ]:= ξ = {0, 1, 2, 3}
Out[ ]= {0, 1, 2, 3}
```

Figure 2.3: The values taken for η and ξ; β=1.0 case

The next step is to determine the concentration value for each point at a specific (ξ,η) coordinate. The process is already explained in section 2.2, and the results are shown in Figure 2.4. In addition, all the points with their concentration are collected in a three-dimensional space, in the form (ξ,η,concentration). The data set contains all the points' coordinates is called "Points". The results are shown in Figure 2.5.

Since the concentration values for the points with certain (ξ,η) coordinates are determined, all the points can be visualized in a three-dimensional space, in which, an axis "C" representing concentration values is perpendicular to the ξ-η plane. Then, using the three-dimensional points to interpolate a three-dimensional surface, while the interpolation order is 3, as indicated in Figure 2.6.

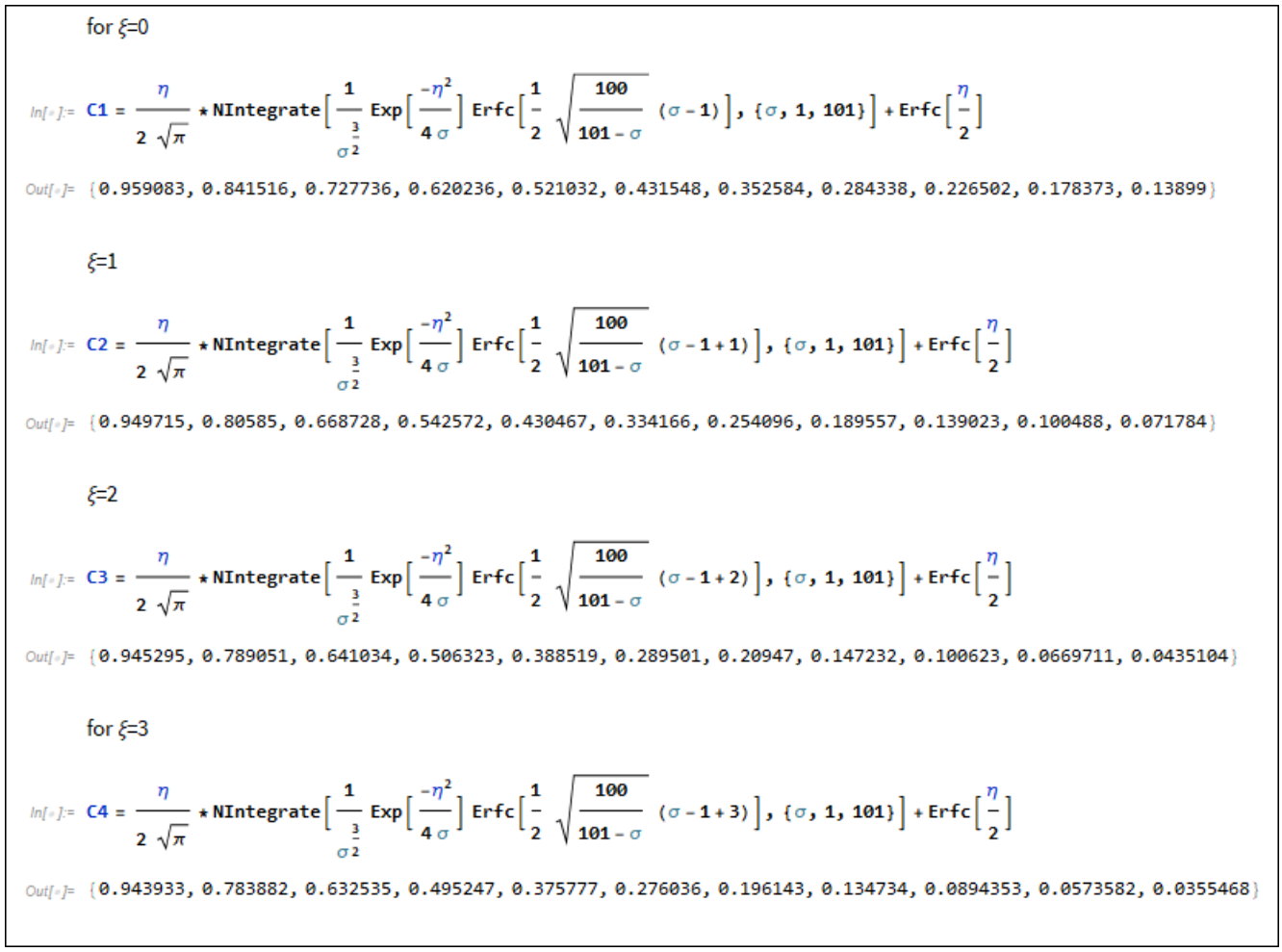

Figure 2.4: Concentrations obtained from specific ξ and η values; β=1.0 case

```
In[•]:= Points = {{Part[η, 1], 0, Part[C1, 1]}, {Part[η, 2], 0, Part[C1, 2]}, {Part[η, 3], 0, Part[C1, 3]},
    {Part[η, 4], 0, Part[C1, 4]}, {Part[η, 5], 0, Part[C1, 5]}, {Part[η, 6], 0, Part[C1, 6]},
    {Part[η, 7], 0, Part[C1, 7]}, {Part[η, 8], 0, Part[C1, 8]}, {Part[η, 9], 0, Part[C1, 9]},
    {Part[η, 10], 0, Part[C1, 10]}, {Part[η, 11], 0, Part[C1, 11]}, {Part[η, 1], 1, Part[C2, 1]},
    {Part[η, 2], 1, Part[C2, 2]}, {Part[η, 3], 1, Part[C2, 3]}, {Part[η, 4], 1, Part[C2, 4]},
    {Part[η, 5], 1, Part[C2, 5]}, {Part[η, 6], 1, Part[C2, 6]}, {Part[η, 7], 1, Part[C2, 7]},
    {Part[η, 8], 1, Part[C2, 8]}, {Part[η, 9], 1, Part[C2, 9]}, {Part[η, 10], 1, Part[C2, 10]},
    {Part[η, 11], 1, Part[C2, 11]}, {Part[η, 1], 2, Part[C3, 1]}, {Part[η, 2], 2, Part[C3, 2]},
    {Part[η, 3], 2, Part[C3, 3]}, {Part[η, 4], 2, Part[C3, 4]}, {Part[η, 5], 2, Part[C3, 5]},
    {Part[η, 6], 2, Part[C3, 6]}, {Part[η, 7], 2, Part[C3, 7]}, {Part[η, 8], 2, Part[C3, 8]},
    {Part[η, 9], 2, Part[C3, 9]}, {Part[η, 10], 2, Part[C3, 10]}, {Part[η, 11], 2, Part[C3, 11]},
    {Part[η, 1], 3, Part[C4, 1]}, {Part[η, 2], 3, Part[C4, 2]}, {Part[η, 3], 3, Part[C4, 3]},
    {Part[η, 4], 3, Part[C4, 4]}, {Part[η, 5], 3, Part[C4, 5]}, {Part[η, 6], 3, Part[C4, 6]},
    {Part[η, 7], 3, Part[C4, 7]}, {Part[η, 8], 3, Part[C4, 8]}, {Part[η, 9], 3, Part[C4, 9]},
    {Part[η, 10], 3, Part[C4, 10]}, {Part[η, 11], 3, Part[C4, 11]}}

Out[•]= {{0.1, 0, 0.959083}, {0.39, 0, 0.841516}, {0.68, 0, 0.727736}, {0.97, 0, 0.620236},
    {1.26, 0, 0.521032}, {1.55, 0, 0.431548}, {1.84, 0, 0.352584}, {2.13, 0, 0.284338}, {2.42, 0, 0.226502},
    {2.71, 0, 0.178373}, {3., 0, 0.13899}, {0.1, 1, 0.949715}, {0.39, 1, 0.80585}, {0.68, 1, 0.668728},
    {0.97, 1, 0.542572}, {1.26, 1, 0.430467}, {1.55, 1, 0.334166}, {1.84, 1, 0.254096}, {2.13, 1, 0.189557},
    {2.42, 1, 0.139023}, {2.71, 1, 0.100488}, {3., 1, 0.071784}, {0.1, 2, 0.945295}, {0.39, 2, 0.789051},
    {0.68, 2, 0.641034}, {0.97, 2, 0.506323}, {1.26, 2, 0.388519}, {1.55, 2, 0.289501}, {1.84, 2, 0.20947},
    {2.13, 2, 0.147232}, {2.42, 2, 0.100623}, {2.71, 2, 0.0669711}, {3., 2, 0.0435104}, {0.1, 3, 0.943933},
    {0.39, 3, 0.783882}, {0.68, 3, 0.632535}, {0.97, 3, 0.495247}, {1.26, 3, 0.375777}, {1.55, 3, 0.276036},
    {1.84, 3, 0.196143}, {2.13, 3, 0.134734}, {2.42, 3, 0.0894353}, {2.71, 3, 0.0573582}, {3., 3, 0.0355468}}
```

Figure 2.5: Three-Dimensional Data Space

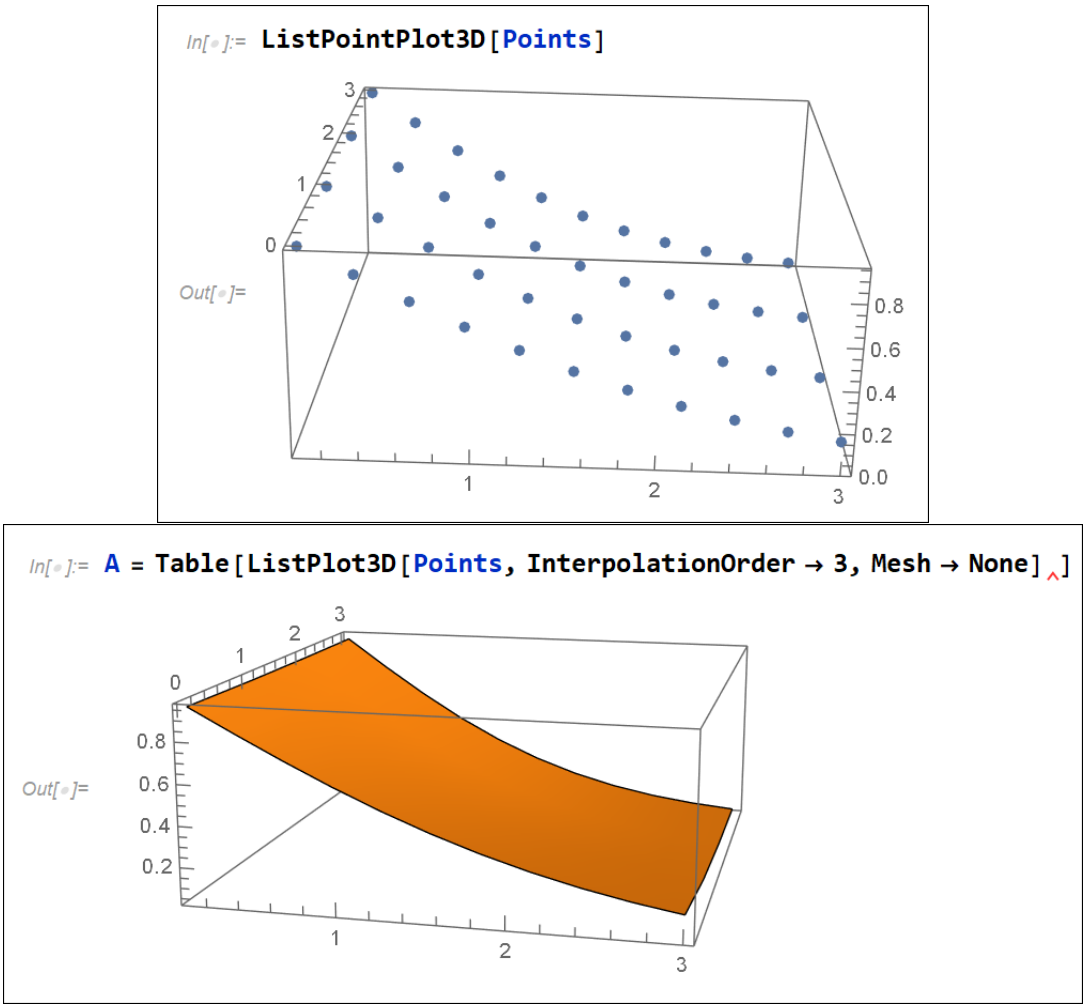

Figure 2.6: Points in three-dimensional space; β=1.0 case

Since the concentration is normalized at the surface, the maximum value is 1.0, and Whipple chose to study the concentration contour lines at 0.8, 0.6, 0.4, and 0.2. The horizontal planes with C=0.8, C=0.6, C=0.4, and C=0.2 can be created. Figure 2.7 shows an example of creating the horizontal plane with C=0.8. Also, the intersections between the horizontal planes and the three-dimensional surface are indicated in Figure 2.8. This section only shows the *Mathematica* codes and the visualizations of results. The more

detailed graphs will be represented in Chapter 4.

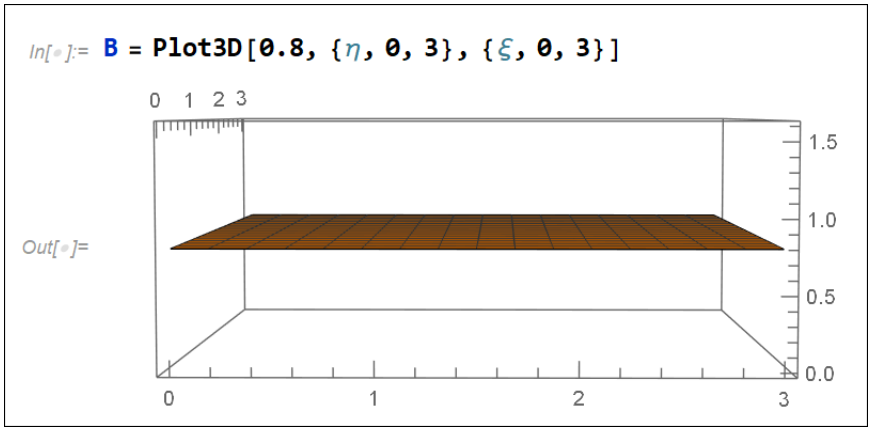

Figure 2.7: Horizontal plane with C=0.8 in three-dimensional space; β=1.0 case

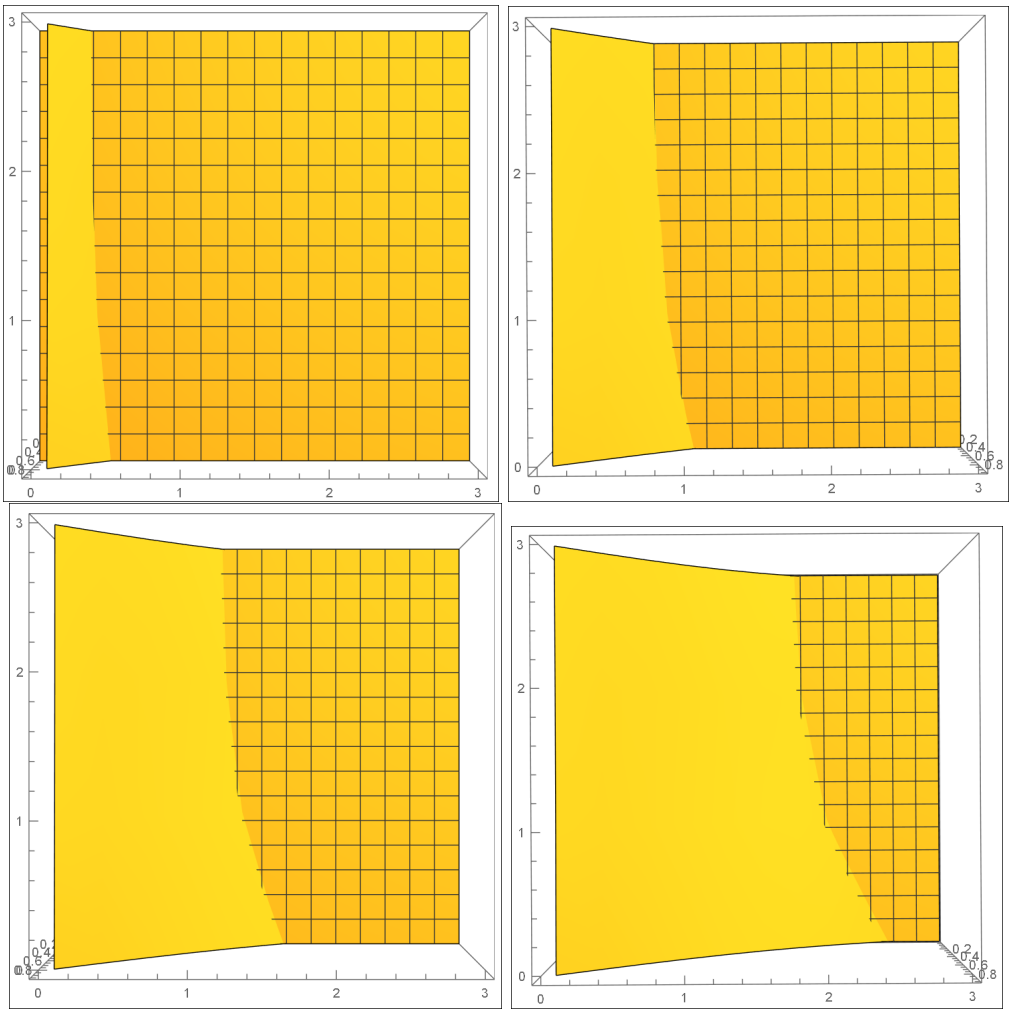

Figure 2.8: The intersections between the three-dimensional surface and C=0.8, C=0.6, C=0.4, C=0.2 planes; β=1.0 case

Chapter 3

Evans's Study for Grain Boundary Diffusion

3.1 Whipple's Exact Solution and Whipple's First Approximation

Whipple claimed that the exact solution (1.11) was exact, but there was difficulty in evaluating the integral numerically. Therefore, he considered an alternative approximation (1.12) to avoid the "long tail" displayed by the integrand at large values of Δ. Evans in his paper examined Whipple's exact solution, to determine whether it can be used alternatively to avoid approximations. Evans tested the numerical evaluation of Whipple's first approximation against the right-hand side of the equation (1.11). The values of Whipple's first approximation (1.12) were obtained by Romberg integration while the

values of Whipple's exact solution (1.11) were obtained by an algorithm, which was explained in his paper [4]. The concentration levels are evaluated at the grain boundary-grain interface (ξ=0), and the other parameters are assigned with a sequence of values. Table 3.1 summarizes the concentration levels obtained by Whipple's exact solution (1.11) and Whipple's first approximation (1.12). Evans listed these values in his paper, and all the concentration levels were evaluated again by *Mathematica*.

It would take a considerable amount of time to evaluate the integrals by hand; a computing technique can be used to simplify the calculation process. In this study, *Mathematica* is introduced as an assisting computing technique. As described in sections 2.1 and 2.2, the numerical values of both integrals can be directly obtained. As the comparisons of column 2 and column 3, and of column 4 and column 5 indicate, the consequences received by *Mathematica* match the values provided by Evans, although some instances have solely ten thousand difference. The precision in results illustrates that the values acquired through Evans and *Mathematica* are accurate. By comparing the outcomes from column 2 and column 4, Evans noted that Whipple's exact solution (1.11) ought to be used sufficiently to avoid any approximations [4]. The last column in Table 3.1 summarizes the absolute error between column 3 and column 5, such that the distinction between values bought by Whipple's exact solution (1.11) and Whipple's exact solution is strictly less than 1 %. Hence, Evans's assertion is corroborated through column 6 in Table 3.1.

α=0.01 ξ=0					
η	Exact Solutions		First Approximations		Error%
	Evans	*Mathematica*	Evans	*Mathematica*	
β=0.1 (Δ=11)					
1	0.5017	0.5017	0.5019	0.5019	0.0398
2	0.1795	0.1795	0.1796	**0.1797**	0.1113
3	0.0444	0.0444	0.0445	0.0445	0.2247
6	0.0001	0.0001	0.0001	0.0001	0
β=1 (Δ=101)					
1	0.6096	0.6096	0.6101	0.6101	0.0820
2	0.3136	0.3136	0.3144	0.3144	0.2545
3	0.1390	0.1390	0.1397	0.1397	0.5011
6	0.0067	0.0067	0.0069	0.0069	0.0290
β=10 (Δ=1001)					
1	0.8006	0.8006	0.8009	0.8009	0.0375
2	0.6214	0.6214	0.6221	0.6221	0.1125
3	0.4729	0.4729	0.4738	0.4738	0.1900
6	0.1955	0.1955	0.1966	0.1966	0.5595
β=100 (Δ=10^4+1)					
1	0.9248	0.9248	0.9250	0.9250	0.0216
3	0.7837	0.7837	0.7841	0.7841	0.0510
6	0.6054	0.6054	0.6061	**0.6062**	0.1320
10	0.4235	0.4235	0.4246	0.4246	0.2591
16	0.2413	0.2413	0.2425	0.2425	0.4948
β=10^3 (Δ=10^5+1)					
1	0.9748	0.9748	0.9749	0.9749	0.0103
3	0.9255	0.9255	0.9256	0.9256	0.0108
6	0.8553	0.8553	0.8555	0.8555	0.0234
10	0.7688	0.7688	0.7692	0.7692	0.0520
16	0.6532	0.6532	0.6538	0.6538	0.0918
β=10^4 (Δ=10^6+1)					
6	0.9520	0.9520	0.9521	0.9521	0.0105
12	0.9059	0.9059	0.9061	0.9061	0.0221
20	0.8475	0.8475	0.8478	0.8478	0.0354
40	0.7153	0.7153	0.7158	0.7158	0.0699
60	0.6014	0.6014	0.6022	0.6022	0.1328
100	0.4204	0.4204	0.4215	0.4215	0.2610
β=10^5 (Δ=10^7+1)					
6	0.9846	0.9846	0.9846	0.9846	0
12	0.9694	0.9694	0.9694	0.9694	0
20	0.9494	0.9494	0.9495	0.9495	0.0105
40	0.9010	0.9010	0.9012	0.9012	0.0222
60	0.8547	**0.8548**	0.8550	0.8550	0.0234
100	0.7683	0.7683	0.7687	0.7687	0.0520

Table 3.1: Numerical results of *Exact Solution* and *First Approximation* obtained by Evans and *Mathematica*; results for ξ=0; for α=0.01

In Table 3.1, the parameters α and ξ are given as constants, such that the concentration levels depend on the variables β (or Δ) and η. The subsequent step performed using Evans's technique is to investigate how the concentration levels are associated with the values of α. As mentioned before, the parameter α is a dimensionless quantity that represents the impact of the width of the grain boundary, while the ratio of diffusive coefficients between the grain boundary and grain is described as Δ. The variable β is defined as the product of α and Δ. In Table 3.1, the value of α is chosen at 0.01, while the values of β are raised from 0.1 to 10^5 by one order of magnitude increment each time. Hence, the corresponding Δ values are ranged from Δ=11 to Δ=$10^7 + 1$ by one order of magnitude increment each time. At this stage, Evans chose to text another two α values whilst the β values have been maintained constantly: for α=0.05, the corresponding Δ values were ranged from Δ=3 to Δ=$2 \times 10^6 + 1$; for α=10^{-4}, the corresponding Δ values were raised from 10^3+1 to 10^9+1. The concentration levels evaluated at α=0.1 and α=0.05 are accrued in Table 3.2.

As illustrated in Table 3.1, the outcomes acquired using *Mathematica* and Evans are close enough; the results in Table 3.2 attain the same conclusion. To track the concentration level changes, it is convenient to group all the data in Table 3.1 and Table 3.2 to Table 3.3. It is observed that the concentration levels on the same row in Table 3.3 with constant β, η, and ξ values are almost the same. Even though the parameters α and Δ have different values in different cases, the product of α and (Δ-1) is consistent with β value, according to the expression (1.10). It concludes that as long as the product of α and Δ is consistent with β, the concentration levels are independent of α and Δ, therefore, the concentration levels are only strongly associated with the parameters β, ξ, and η.

η	α=0.05		α=10^{-4}	
	Evans	*Mathematica*	Evans	*Mathematica*
	β=0.1 (Δ=3)		β=0.1 (Δ=10^3+1)	
1	0.5011	0.5011	0.5019	0.5019
2	0.1788	0.1788	0.1797	0.1797
3	0.0440	0.0440	0.0445	0.0445
6	0.0001	0.0001	0.0001	0.0001
	β=1 (Δ=21)		β=1 (Δ=10^4+1)	
1	0.6075	0.6075	0.6100	**0.6101**
2	0.3105	0.3105	0.3144	0.3144
3	0.1361	0.1361	0.1397	0.1397
6	0.0061	0.0061	0.0069	0.0069
	β=10 (Δ=201)		β=10 (Δ=10^5+1)	
1	0.7991	0.7991	0.8009	0.8009
2	0.6186	0.6186	0.6221	0.6221
3	0.4691	**0.4692**	0.4738	0.4738
6	0.1908	0.1908	0.1966	0.1966
	β=100 (Δ=2001)		β=100 (Δ=10^6+1)	
1	0.9243	0.9243	0.9250	0.9250
3	0.7821	0.7821	0.7841	0.7841
6	0.6025	**0.6024**	0.6061	**0.6062**
10	0.4193	**0.4192**	0.4245	0.4245
16	0.2364	**0.2363**	0.2425	0.2425
	β=10^3 (Δ=$2\times10^4+1$)		β=10^3 (Δ=10^7+1)	
1	0.9746	**0.9747**	0.9749	0.9749
3	0.9250	0.9250	0.9256	0.9256
6	0.8542	0.8542	0.8555	0.8555
10	0.7671	0.7671	0.7692	0.7692
16	0.6506	0.6506	0.6538	0.6538
	β=10^4 (Δ=$2\times10^5+1$)		β=10^4 (Δ=10^8+1)	
6	0.9517	0.9517	0.9521	0.9521
12	0.9053	0.9053	0.9061	0.9061
20	0.8464	0.8464	0.8487	0.8487
40	0.7132	0.7132	0.7158	0.7158
60	0.5984	0.5984	0.6021	0.6021
100	0.4161	0.4161	0.4214	0.4214
	β=10^5 (Δ=$2\times10^6+1$)		β=10^5 (Δ=10^9+1)	
6	0.9845	0.9845	0.9846	0.9846
12	0.9692	0.9692	0.9694	0.9694
20	0.9491	0.9491	0.9495	0.9495
40	0.9003	0.9003	0.9012	0.9012
60	0.8537	0.8537	0.8550	0.8550
100	0.7666	0.7666	0.7687	0.7687

Table 3.2: Whipple's approximations for the concentration at a point; results for ξ=0; for α=0.05 and α=10^{-4}

η	α=0.01	α=0.05	α=10^{-4}
(β=0.1)	Δ=11	Δ=3	Δ=10^3+1
1	0.5017	0.5011	0.5019
2	0.1795	0.1788	0.1797
3	0.0444	0.0440	0.0445
6	0.0001	0.0001	0.0001
(β=1)	Δ=101	Δ=21	Δ=10^4+1
1	0.6096	0.6075	0.6101
2	0.3136	0.3105	0.3144
3	0.1390	0.1361	0.1397
6	0.0067	0.0061	0.0069
(β=10)	Δ=1001	Δ=201	Δ=10^5+1
1	0.8006	0.7991	0.8009
2	0.6214	0.6186	0.6221
3	0.4729	0.4692	0.4738
6	0.1955	0.1908	0.1966
(β=100)	Δ=10001	Δ=2001	Δ=10^6+1
1	0.9248	0.9243	0.9250
3	0.7837	0.7821	0.7841
6	0.6054	0.6024	0.6062
10	0.4235	0.4192	0.4245
16	0.2413	0.2363	0.2425
(β=10^3)	Δ=10001	Δ=$2\times10^4+1$	Δ=10^7+1
1	0.9748	0.9747	0.9747
3	0.9255	0.9250	0.9256
6	0.8553	0.8542	0.8555
10	0.7688	0.7671	0.7692
16	0.6532	0.6506	0.6538
(β=10^4)	Δ=10^6+1	Δ=$2\times10^5+1$	Δ=10^8+1
6	0.9520	0.9517	0.9521
12	0.9059	0.9053	0.9061
20	0.8475	0.8464	0.8487
40	0.7153	0.7132	0.7158
60	0.6014	0.5984	0.6021
100	0.4204	0.4161	0.4214
(β=10^5)	Δ=10^7+1	Δ=$2\times10^6+1$	Δ=10^9+1
6	0.9846	0.9845	0.9846
12	0.9694	0.9692	0.9694
20	0.9494	0.9491	0.9495
40	0.9010	0.9003	0.9012
60	0.8548	0.8537	0.8550
100	0.7683	0.7666	0.7687

Table 3.3: Whipple's approximations for the concentrations at a point; results for ξ=0; obtained from *Mathematica* approach

3.2 Whipple's Approximations for the Concentration at A Point

In the previous section, all the concentration values are evaluated at the grain boundary-grain interface (ξ=0), in this section, the concentration levels will be regarded in the grain region. According to expression (1.7), ξ=0 is equitable with x=a, therefore, in the grain region (x>0), the parameter ξ will be assigned with positive values. Following Evans's procedure, the concentration levels are evaluated at ξ=1, ξ=2, and ξ=3. The outcomes corresponding to each ξ value are gathered in Table 3.4, Table 3.5, and Table 3.6 respectively.

The data in Table 3.4, Table 3.5, and Table 3.6 meet the conclusion that the concentration levels are independent of α and Δ for a given β value since the values on the same row are close to each other. In each table, the parameter ξ is given as a constant, therefore, the substance propagation in the longitudinal (η) direction is shown. On the other hand, from Table 3.3 to Table 3.6, the ranges of η are identical, thus, the concentration propagation in the transverse (ξ) direction can be observed. Based on the data provided by Table 3.3 to Table 3.6, the relation between concentration levels and the parameters β, ξ, and η will be investigated.

η	α=0.01	α=0.05	α=10^{-4}
(β=0.1)	Δ=11	Δ=3	Δ=10^3+1
1	0.4875	0.4872	0.4876
2	0.1652	0.1649	0.1653
3	0.0376	0.0374	0.0376
6	0	0	0
(β=1)	Δ=101	Δ=21	Δ=10^4+1
1	0.5303	0.5290	0.5306
2	0.2167	0.2148	0.2171
3	0.0718	0.0702	0.0722
6	0.0018	0.0016	0.0018
(β=10)	Δ=1001	Δ=201	Δ=10^5+1
1	0.6196	0.6183	0.6199
2	0.3559	0.3536	0.3565
3	0.2156	0.2127	0.2163
6	0.0699	0.0670	0.0706
(β=100)	Δ=10001	Δ=2001	Δ=10^6+1
1	0.6859	0.6853	0.6861
3	0.3745	0.3728	0.3749
6	0.2612	0.2585	0.2619
10	0.1703	0.1670	0.1712
16	0.0877	0.0845	0.0885
(β=10^3)	Δ=10001	Δ=$2\times10^4+1$	Δ=10^7+1
1	0.7144	0.7142	0.7144
3	0.4538	0.4532	0.4540
6	0.3961	0.3949	0.3964
10	0.3479	0.3461	0.3483
16	0.2856	0.2831	0.2863
(β=10^4)	Δ=10^6+1	Δ=$2\times10^5+1$	Δ=10^8+1
6	0.4514	0.4510	0.4515
12	0.4248	0.4241	0.4250
20	0.3916	0.3904	0.3919
40	0.3187	0.3166	0.3193
60	0.2585	0.2558	0.2592
100	0.1685	0.1651	0.1693
(β=10^5)	Δ=10^7+1	Δ=$2\times10^6+1$	Δ=10^9+1
6	0.4705	0.4703	0.4705
12	0.4615	0.4613	0.4616
20	0.4499	0.4495	0.4500
40	0.4220	0.4212	0.4222
60	0.3957	0.3945	0.3960
100	0.3475	0.3457	0.3480

Table 3.4: Whipple's approximations for the concentration at a point; results for ξ=1

η	α=0.01	α=0.05	α=10^{-4}
(β=0.1)	Δ=11	Δ=3	Δ=10^3+1
1	0.4815	0.4814	0.4816
2	0.1593	0.1592	0.1593
3	0.0348	0.0348	0.0348
6	0	0	0
(β=1)	Δ=101	Δ=21	Δ=10^4+1
1	0.4933	0.4928	0.4934
2	0.1731	0.1724	0.1732
3	0.0435	0.0430	0.0436
6	0.0004	0.0003	0.0004
(β=10)	Δ=1001	Δ=201	Δ=10^5+1
1	0.5215	0.5209	0.5217
2	0.2158	0.2147	0.2161
3	0.0858	0.0844	0.0861
6	0.0173	0.0163	0.0176
(β=100)	Δ=10001	Δ=2001	Δ=10^6+1
1	0.5450	0.5447	0.5451
3	0.1399	0.1390	0.1402
6	0.0774	0.0760	0.0777
10	0.0471	0.0456	0.0475
16	0.0220	0.0207	0.0223
(β=10^3)	Δ=10001	Δ=$2\times10^4+1$	Δ=10^7+1
1	0.5557	0.5556	0.5558
3	0.1693	0.1689	0.1694
6	0.1256	0.1250	0.1258
10	0.1079	0.1069	0.1081
16	0.0857	0.0844	0.0860
(β=10^4)	Δ=10^6+1	Δ=$2\times10^5+1$	Δ=10^8+1
6	0.1465	0.1463	0.1466
12	0.1364	0.1359	0.1365
20	0.1239	0.1232	0.1241
40	0.0974	0.0962	0.0976
60	0.0763	0.0748	0.0766
100	0.0464	0.0449	0.0468
(β=10^5)	Δ=10^7+1	Δ=$2\times10^6+1$	Δ=10^9+1
6	0.1538	0.1537	0.1538
12	0.1504	0.1502	0.1504
20	0.1459	0.1457	0.1460
40	0.1353	0.1348	0.1354
60	0.1255	0.1248	0.1256
100	0.1077	0.1067	0.1080

Table 3.5: Whipple's approximations for the concentration at a point; results for ξ=2

η	α=0.01	α=0.05	α=10^{-4}
(β=0.1)	Δ=11	Δ=3	Δ=10^3+1
1	0.4799	0.4798	0.4799
2	0.1576	0.1576	0.1576
3	0.0341	0.0340	0.0341
6	0	0	0
(β=1)	Δ=101	Δ=21	Δ=10^4+1
1	0.4820	0.4819	0.4820
2	0.1601	0.1600	0.1602
3	0.0355	0.0354	0.0356
6	0.0001	0.0001	0.0001
(β=10)	Δ=1001	Δ=201	Δ=10^5+1
1	0.4878	0.4876	0.4879
2	0.1687	0.1684	0.1688
3	0.0437	0.0434	0.0438
6	0.0029	0.0026	0.0029
(β=100)	Δ=10001	Δ=2001	Δ=10^6+1
1	0.4932	0.4931	0.4932
3	0.0557	0.0554	0.0557
6	0.0152	0.0148	0.0153
10	0.0086	0.0082	0.0087
16	0.0037	0.0034	0.0037
(β=10^3)	Δ=10001	Δ=$2\times10^4+1$	Δ=10^7+1
1	0.4958	0.4957	0.4958
3	0.0626	0.0625	0.0626
6	0.0262	0.0260	0.0263
10	0.0220	0.0217	0.0221
16	0.0170	0.0166	0.0171
(β=10^4)	Δ=10^6+1	Δ=$2\times10^5+1$	Δ=10^8+1
6	0.0313	0.0312	0.0313
12	0.0288	0.0286	0.0288
20	0.0258	0.0256	0.0259
40	0.0196	0.0192	0.0197
60	0.0149	0.0144	0.0150
100	0.0085	0.0081	0.0086
(β=10^5)	Δ=10^7+1	Δ=$2\times10^6+1$	Δ=10^9+1
6	0.0331	0.0330	0.0331
12	0.0322	0.0321	0.0322
20	0.0311	0.0310	0.0311
40	0.0285	0.0284	0.0286
60	0.0262	0.0260	0.0262
100	0.0220	0.0217	0.0221

Table 3.6: Whipple's approximations for the concentration at a point; results for ξ=3

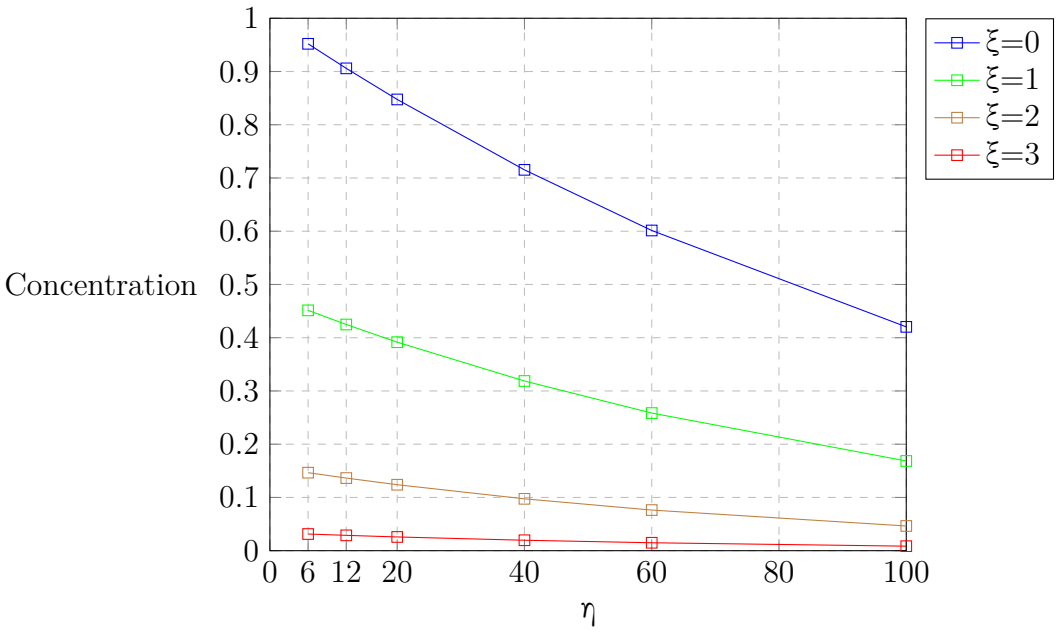

Figure 3.1: Concentration at a point for β=10^4

Recall the definition of β governed by expression (1.10), β is strongly associated with α and Δ, in which α represents the geometric property (the width of the grain boundary) of the grain boundary-grain model governed by (1.6), while Δ illustrates the diffusive property (the ratio of diffusive coefficients between the grain boundary and the grain) governed by (1.9). Figure 3.1 features the concentration propagation in both ξ and η directions for a given β value. To have consistent results, all the data are evaluated at α=0.01.

Through a single curve, all the concentration values are with identical ξ value, and the concentration level is observed to reduce as η value increases. Hence, the concentration level reduces in the longitudinal direction. Similarly, at the same η altitude, the concentration level drops as the variable ξ increases. Therefore, for a fully described grain boundary-grain model, the concentration level in the grain region reduces smoothly in both the longitudinal

and transverse directions.

An observation is that the gap between the curves ξ=0 and ξ=1 is much larger than the gap between ξ=2 and ξ=3. Since the grain boundary width α is kept constant at 0.01, a high β value leading to a high Δ value. In this case, the diffusivity of the grain boundary is one million times higher than the grains, therefore, a more aggressive diffusion process occurs inside the grain boundary region. At the grain boundary-grain interface (ξ=0), the concentration gradient between the grain boundary region and the grain region is the highest. The substance has a strong willingness to spread into the grain region, therefore, the gap between the curves ξ=0 and ξ=1 is the largest. As the substance propagates inside the grain region regardless of the η effect, the concentration gradient is weakened, thus, the gaps between the ξ curves are narrowed. On the other hand, the concentration levels at high η values are lower than the concentration levels at low η values, so do the concentration gradient. Hence, the gap between curves ξ=0 and ξ=1 is narrowed as the substance propagates in the longitudinal direction. It is apparent to conclude that the concentration level is higher and the substance has a stronger willingness to propagate in both transverse and longitudinal directions if the point is located close to (ξ=0,η=0).

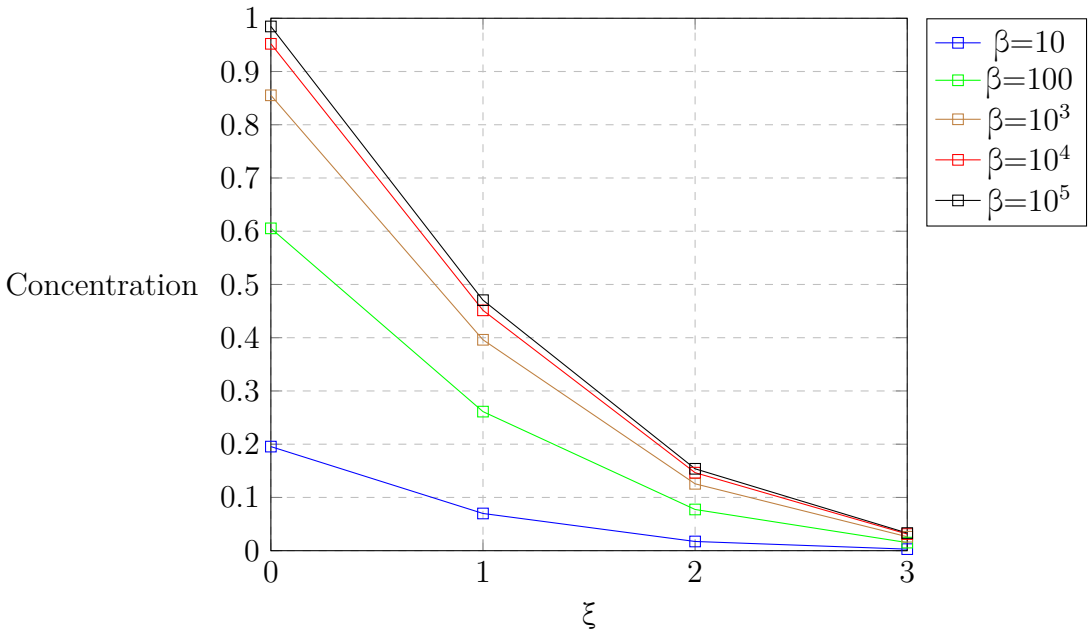

Figure 3.2: Concentrations at points for constant η=6

The previous Figure 3.1 investigates how the parameters ξ and η influence the concentration levels, and Figure 3.2 studies how the concentration values associate with β and ξ. In Figure 3.2, η=6 is chosen as a constant, whilst β ranges from β=10 to β=10^5, and ξ ranges from ξ=0 to ξ=3.

Along the same curve, the β value is given, such that the geometric and diffusive properties of a grain boundary-grain model are specified. As the substance propagates transversely away from ξ=0, the concentration level reduces continuously. This observation is consistent with the result obtained from Figure 3.1. For the comparison between curves at a constant ξ value, the curve with a higher β value reaches a higher concentration level with a steeper slope. For a specified α value, a higher β suggests a higher Δ value results in a more comprehensive diffusion process inside the grain boundary region. The

concentration gradient at the interface is the greatest, therefore, the slope of β=10^5 is the steepest amongst the curves. As the substance propagates transversely, the concentration gradient inside the grain region is reduced, such that the curves grow to be flat. This result is consistent with Figure 3.1. Furthermore, for η=6, the concentration levels nearly vanish at ξ=3 regardless of the β values. A prediction can be easily yielded that in the region ξ>3, the concentration level vanishes.

On the other hand, between β=10 and β=100, the concentration level is tremendously increased, and the curves of β=10^4 and β=10^5 are almost overlapped with each other. At a given grain boundary width, β=10^3 can generate a sufficiently high concentration level, and a ratio larger than 10^4 is not imperative for practical applications.

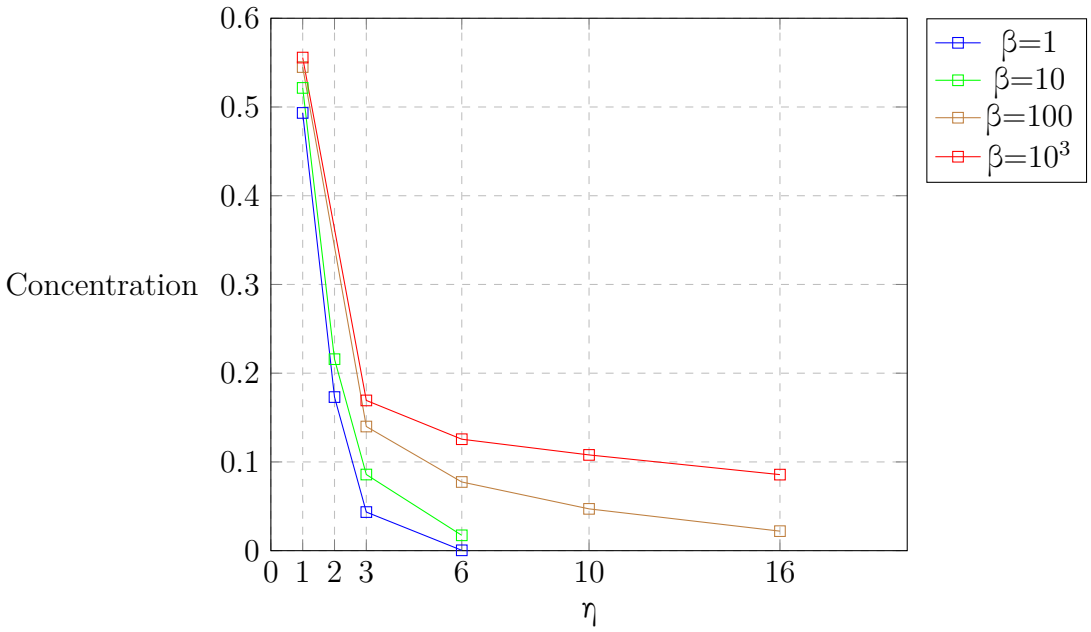

Figure 3.3: Concentration change for constant ξ=2

After testing the relation between concentration level and variables β and ξ, it is also critical to determine how the concentration level changes regarding parameters β and η. As shown in Figure 3.3, ξ=2 is given as a constant, while η is ranged from η=1 to η=16. As the variable η increases, the concentration level decreases. The behavior is consistent with the conclusion obtained from Figure 3.1.

At a constant η value, the curve with β=10^3 is positioned above the other curves. For β of lower values at β=1 and β=10, the concentration almost vanishes at η=6, and for β=10^3, the concentration can remain 0.1 at η=10. As indicated in Table 3.5: the concentration level holds at 0.1 at η=40 for β=10^4, and the concentration level holds at 0.1 for η=100 at β=10^5. Hence, a higher β value helps to preserve concentration level in the longitudinal direction. In mathematical analysis, 10 % of substance can diffuse 100 units away from η=0,

it can be difficult to achieve $\beta=10^5$ in practice, therefore, $\beta=10^3$ is reasonable to maintain concentration level at a considerable distance range.

Besides the fact that there is a huge drop in concentration level between $\eta=1$ and $\eta=3$, regardless of the β value, at $\eta>3$, the curves grow to be flat. This grain boundary-grain diffusion model is semi-infinite in $\eta>0$ by design, and the space with $\eta<0$ is fulfilled with solute with a concentration value of 1. Therefore, in the longitudinal direction, the concentration gradient is the largest at $\eta=0$, the solute-grain interface. For instance, for $\beta=10^3$ at $\xi=2$: the concentration is 1 at $\eta=0$, the concentration level drops to 0.56 at $\eta=1$, while only 17 % of substance reaches $\eta=3$. It is obvious that as substance propagates in the longitudinal direction, both the concentration level and concentration gradient reduce. Moreover, the longitudinal direction has a better potential to hold concentration levels than the transverse direction.

Chapter 4

Concentration Contours

4.1 Whipple's Concentration Contours

Three concentration contours for β=10.0, β=1.0, and β=0.1, as depicted schematically in Figure 4.1, Figure 4.2, and Figure 4.3, are explored adequately by Whipple. The process to obtain these figures by *Mathematica* is illustrated in section 3.2. For each case, the parameter β maintains constantly, such that the only factors to influence the concentration level are the coordinates of the points (ξ,η). Figure 3.1 evidences that the concentration level reduces smoothly in both ξ-direction and η-direction whilst β remains constant. Since the value β=10^4 is relatively high in Figure 3.1, the reduction in concentration level in both directions near (ξ=0,η=0) is high. On the contrary, β with relatively low values are evaluated in this section. From Figure 4.1 to Figure 4.3, the concentration change is consistent with the conclusion obtained by Figure 3.1.

Along the η-direction, it is obvious that for a larger β value, the concentration level is easier to be maintained in the η-direction. At the grain boundary-grain interface, the concentration C=0.8 around η=1 for β=10; for β=1.0, C=0.8 is achieved at η=0.5, while for β=0.1, concentration drops to 0.8 at η=0.4. Although β corresponds to both α and Δ, in this case, this phenomenon is highly related to the Δ effect. A higher β value indicating a higher Δ value, such that the diffusivity of the grain boundary can be significantly higher than the diffusivity of the grain. Once this diffusion model is exposed to the solute at t>0, the molecular motion is more aggressive inside the grain boundary region. Hence, for β=10.0, 20 % of the substance reaches (ξ=0,η=6), while the concentration is probably vanished at (ξ=0,η=3) for β=0.1. Furthermore, a higher concentration level at the grain boundary-grain interface derives a higher concentration gradient between the grain boundary region and the grain region, results in a steeper slope of the concentration contour line. By visualization, the concentration contour lines are much steeper at β=10.0, than the ones at β=0.1.

Although the slopes of the concentration contour lines are regulated by the variable β, the slopes vanish around ξ=2, as illustrated in Figure 4.1 and Figure 4.2. At ξ>2, the solvent does not show a preferred net movement, such that the substance is observed with a negligible concentration gradient. The findings extrapolate that at three units transversely away from the grain boundary-grain interface, the concentration level of the grain region is maintained constantly. An opposite case with a relatively small β value is illustrated in Figure 4.3. The curves are displayed horizontally, such that the concentration levels are kept constantly from ξ=0. The concentration gradient vanished at the grain boundary-grain interface, such that the presence of the grain boundary region is negligible. Whipple in his paper defined an expression for C_1, representing the concentration that would be obtained in the absence of

the grain boundary slab [3].

$$C_1 = erfc\frac{\eta}{2} \tag{4.1}$$

The expression C_1 is independent of ξ. From Figure 4.3, the horizontal lines are located at η=0.4, η=0.76, η=1.2, and η=1.8 respectively. Based on expression (4.1), the concentration values at the corresponding locations are supposed to be C=0.78, C=0.59, C=0.4, and C=0.2. Therefore, the fact that the presence of the grain boundary slab is negligible at β=0.1 is corroborated by both Figure 4.3 and expression (4.1). On the other hand, for a given value β=0.1, the concentration level at any η altitude can be obtained through the error function table.

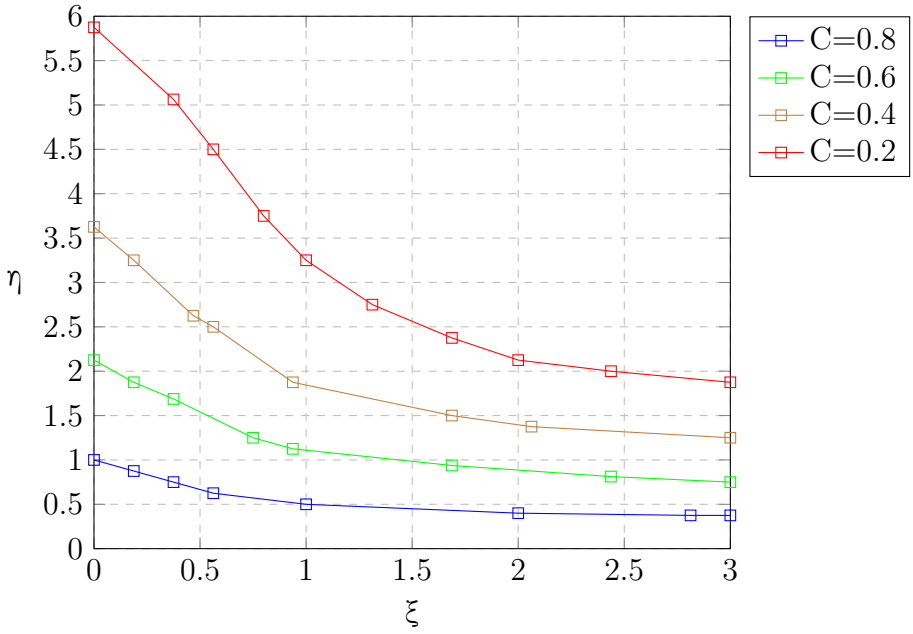

Figure 4.1: Concentration Contours for β=10.0

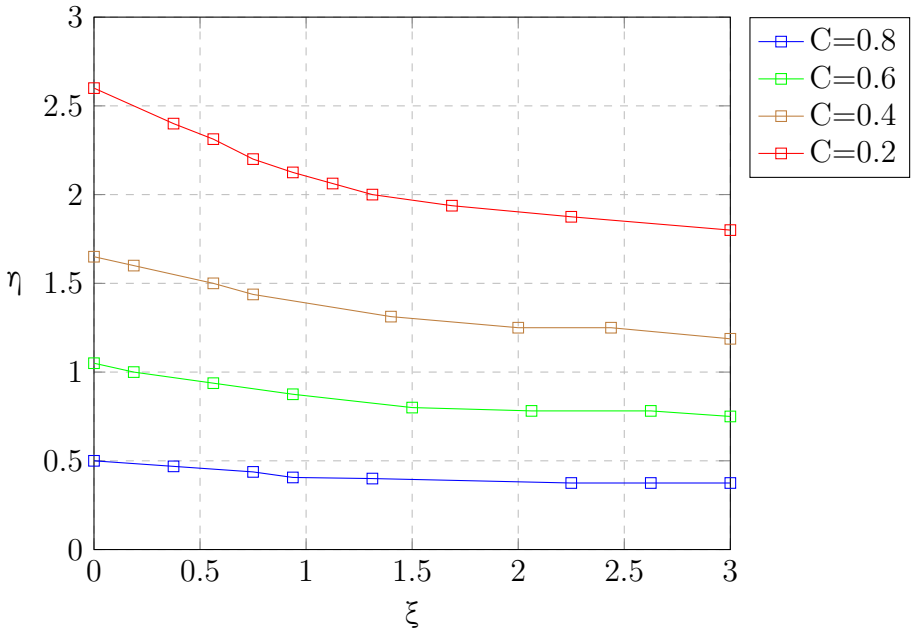

Figure 4.2: Concentration Contours for β=1.0

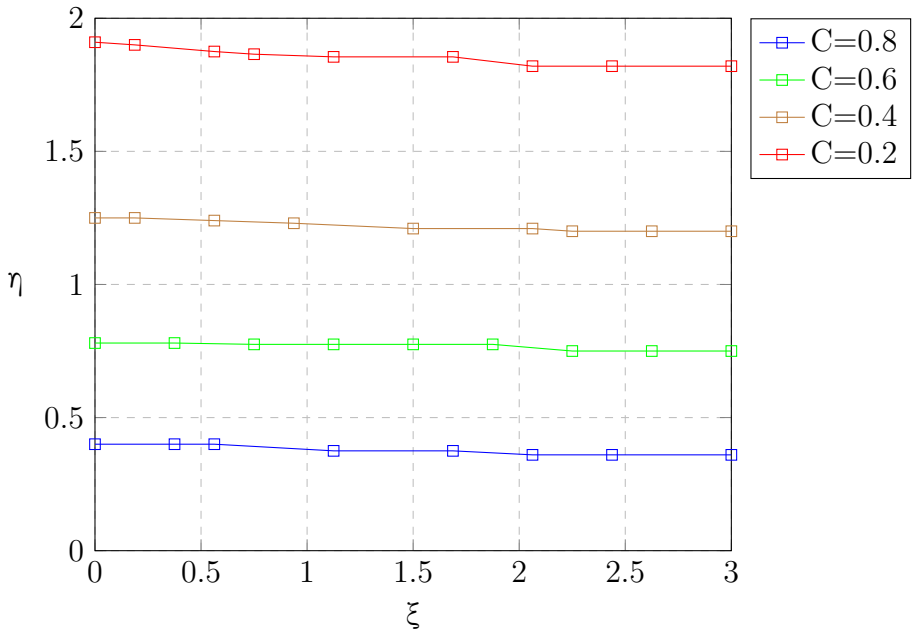

Figure 4.3: Concentration Contours for β=0.1

4.2 Concentration Contour Study Extension

In this section, a concentration contour with β=100, as indicated in Figure 4.4, will be discussed. The previous studies have proven that the parameter β plays a vital role in the concentration gradient at the grain boundary-grain interface. A larger β value indicates a larger Δ value, which results in a more aggressive diffusion process inside the grain boundary region. Therefore, the concentration gradient for β=100 at the grain boundary-grain interface is supposed to be the largest. In Figure 4.4, at ξ=0, the concentration level maintains constantly at 0.8 at η=3, and the concentration may vanish around η=30. Therefore, among these figures, the curves obtained from β=100 have the steepest slopes. The result is consistent with the findings from section 4.1, such that at ξ>2.5, the concentration contour lines are horizontally displayed. The observation in the ξ-direction obtained by Figure 4.4 supports the prediction, such that at three units transversely away from the grain boundary-grain interface, the concentration level remains constant.

Moreover, at ξ=3, the concentration level vanishes at η>5. Prior findings from Figure 3.2 suggests that at ξ=3, the concentration level vanishes at η=6, regardless of the parameter β. Based on these observations, it is apparent to predict that, at three units transversely and six units longitudinally away from (ξ=0,η=0), the concentration level vanished. Besides this fact, inside the grain region with ξ>3 and η<6, the concentration gradient is negligible, such that the concentration contour lines are displayed horizontally. Therefore, the concentration level only reduces smoothly in the longitudinal direction.

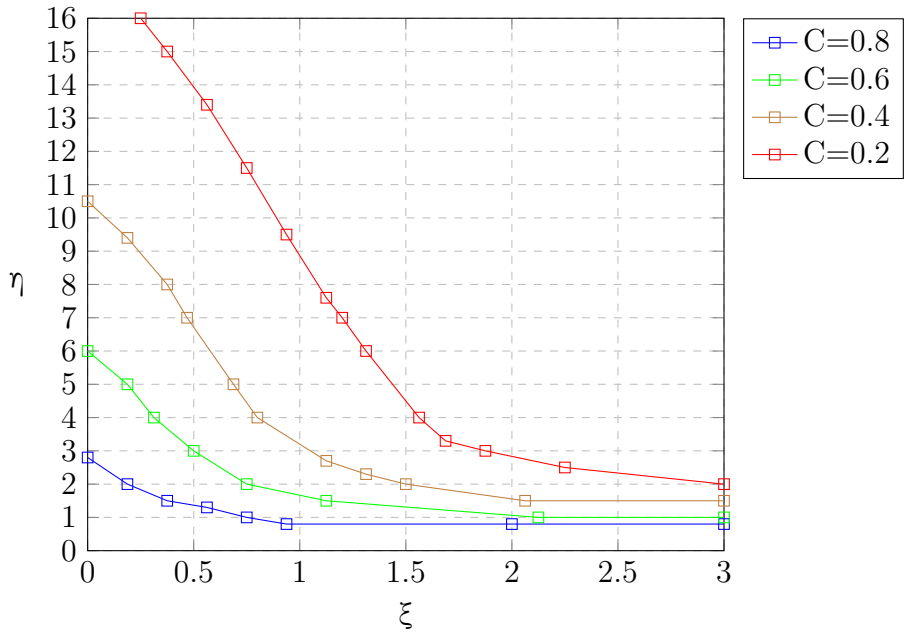

Figure 4.4: Concentration Contours for β=100

Chapter 5

Conclusions

R. T. P Whipple obtained the "exact" solution and the "first approximation" solution to determine the concentration levels of a two-dimensional grain boundary-grain diffusion model [3], and J. W. Evans developed an algorithm to obtain the numerical values [4]. This study aims to implement a numerical method to evaluate Whipple's integrals, and to compare the results with Evans's study. In this study, all the data are evaluated by *Mathematica*.

By evaluating the concentration values of various cases applying both Whipple's first approximation and Whipple's exact solution, the difference between the obtained values is strictly less than 1 %. As Evans claimed in his paper, Whipple's exact solution can be applied directly to avoid approximations [4]. Besides, it can be concluded that, as long as the value of β remains constant, the concentration values only depend on the coordinates of the points. Evans mainly focused on the concentration change at the grain boundary-grain interface (ξ=0); the concentrations evaluated at ξ=1, ξ=2, and ξ=3 are summarized in section 3.2. It is apparent to conclude that at t>0, the concentration is unity at ξ=0 and η=0, and

the concentration level decreases in both the ξ-direction and the η-direction. As β increases whilst α remains constant, the parameter Δ also increases. Hence, the grain boundary has a significantly larger diffusivity than the grain region, and the longitudinal η direction has a better ability to maintain the concentration level. On the other hand, the concentration value begins to vanish at $\xi>3$ and $\eta>3$ regardless of the β value. In other words, the grain region takes three transverse and longitudinal units to eliminate the grain boundary effect.

Following Whipple's process, the concentration contours for β=0.1, β=1.0, β=10.0, and β=100 have been studied. At a constant α value, a larger β value results in a larger Δ value. A higher diffusivity ratio leads to a higher concentration gradient between the grain boundary region and the grain region at the grain boundary-grain interface, such that the curves are steeper at a larger β value. On the other hand, at β=0.1, the presence of the grain boundary region is negligible, and the concentration values are only related to parameter η.

In conclusion, Whipple's exact solution is sufficient to determine the concentration values, and the concentration level has almost completely vanished at three units away from (ξ=0,η=0) transversely and longitudinally. The parameter β defines the diffusive properties of the diffusion model, a higher β value indicating a larger diffusivity ratio between the grain boundary region and the grain region. The diffusion process is more aggressive inside the grain boundary region, and this concentration gradient results in steeper slopes of the concentration contour lines. Furthermore, the parameters ξ and η follow an inverse correlation, if the β value maintains constantly.

This study provides theoretical support for evaluating the concentration levels of a grain boundary-grain diffusion model. From a practical aspect, the results can be used as a reference to predict concentration levels for grain boundary-grain diffusion problems.

Furthermore, the concentration contours can contribute to grain boundary designs, either for specified materials or for constant grain boundary width.

This framework, however, solely pertains to a mathematical model with assumptions. These results require experimental support. The environmental factors and tested material properties may cause variances between the theoretical results and experimental data. The fluctuations in diffusivity should be eliminated as much as possible, such that the ratio between diffusive coefficients is a constant. Besides, the period of experiments should be considered, since the time effect is not included in this theoretically based work.

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