



WPI

Diffusion Coefficient Matrix in Ternary Diffusion Systems

A Major Qualifying Project Report

Submitted to the Faculty of the

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirements for the

Degree of Bachelor of Science

in Physics and Mathematics

By

Rui Yu

April 27, 2017

Major Project Advisor:

Professor L. Ramdas Ram-Mohan

Professor Marcus Sarkis

Abstract

The diffusion coefficient matrix provides a direct relation between flux and concentration gradient for almost all of the diffusion process. It is the essential quantity of predicting the behaviors of the diffusion process. This report focuses on the ternary diffusion, which is one of the most common diffusion processes in industry. The major approaches in this report for solving the diffusion coefficients are based on the finite different method, Hermite least square fitting, and the transfer matrix method. The data is provided in terms of concentration values at a time when the diffusion couples close to their equilibrium state. First, functions are generated for flux, concentration, and the derivative of concentration with respect to position. From there, the assumption that the diffusion coefficient is a constant in the small region was made. Based on this assumption, a system of equations was derived to calculate the diagonalized diffusion coefficient matrix. As for the element that contains an interface, special methods were introduced to overcome the discontinuity from the jump condition.

Acknowledgments

The completion of this project could not have been done without help and assistance from many people. I would like to thank Professor Ram-Mohan and Professor Marcus Sarkis, for guiding me in the right direction for this report, providing suggestions, and inspiring me. I would like also to thank all my relatives, friends, and people from Center of Computational NanoScience at WPI, for the kindest physical and mental support. Finally, I would like to thank Worcester Polytechnic Institute, for giving me such a good opportunity and environment to work at.

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1 Introduction

The analytical solutions obtained from directly analyzing Fick's equations can only be obtained by making non-general assumptions for the diffusion systems and therefore, can provide limited useful results. The alternative of a numerical approach will be considered in this report. The main goal of this report is to obtain the diffusion coefficients matrix for the entire diffusion domain. In general, the diffusion coefficients are functions of position and time. However, Diffusion coefficients are passive quantities which can be determined only when the concentration gradient and flux value have been obtained. There is no theory to tell what form these functions would be in. Therefore, it would not make any sense if we define a form of function for the diffusion coefficient at the very beginning. However, in order to make some progress, we note that the diffusion coefficients cannot remain the same all the time. A better approach is to restrict the diffusion coefficient matrix to be a constant in small regions and reassemble them later. Details of the meaning of the small region are introduced in Sec.2.

This project uses data from experimental measurements. The data provides values of the concentration at selected points. Therefore, some information is not obvious as the concentration profile is not continuous. Therefore, the first challenge of this report is to extract more information from a given data set. Sec.3 introduces a process of generate concentration functions from the the set of discrete concentration values by applying the Hermite least square fitting. A nice property is given by the hermite least square fitting: the values of the concentration profile and the concentration gradient at shared boundary points are same for both the interpolation functions in two adjacent elements. Then the continuity condition is guaranteed. Once the concentration function is approximated, the concentration gradient with respect to position is trivial to obtain. From there, the flux function can be derived from the continuity equation. All the necessary data can then be calculated from these three functions over the entire domain.

However, since the governing equation of the diffusion process, Fick's law, is a coupled

system. For a diffusion process which has more than two diffusion components, the flux and the concentration will be coupled. For ternary diffusion, the diffusion coefficients can be reduced to four components for Fick's equations. However, there are only two equations which are stated from governing equations. Therefore, the information of flux and concentration could not directly give the value for diffusion coefficients. If the Fick's equation could be decoupled, then the value of flux and concentration should be enough to solve for the diffusion coefficients. The transfer matrix method is introduced in Sec.4 to decouple the Fick's equation. The diffusion coefficient matrix is assumed to be diagonalizable. The transfer matrix method expresses the value of flux and concentration in the space formed by the eigenvector of the diffusion coefficients matrix. In this space, the components of flux are no longer coupled with the components of concentration. Therefore, the relation between the flux and concentration is now in terms of the eigenvalues and eigenvectors of the diffusion coefficient matrix. the result of the value of diffusion coefficient matrix for each element is given in Sec. 5.

Another important phenomenon in the multiphase diffusion process is the dramatic change of the concentration value at the interface. The interface is the boundary of two sides dominated by different components. The location of the interface can be detected by putting an inert marker material in and observing the position of the inert material. Due to the jump condition, the slope of the concentration profile is too steep to be described by the normal interpolation functions. Sec. 6 discusses the jump condition and provides alternative methods to obtain information of elements at an interface. The first method is to connect the two boundary points of that element by a desired function which satisfies the condition discussed in Sec.6. This method is applicable when the size of the element is small. If the element has a moderate size, then the information provided by the measured points in that element will be omitted. The other method is to use special base functions to approximate the concentration profile. Both of the method can be used to further divide the region close to the interface.

When the diffusion coefficients have been determined for all the elements, we should take a look at how this quantity changes over the diffusion domain. Sec.7 provides figures to discuss the trend of the diffusion coefficients. This is also related to the future effort which is to include the contribution from the dimension of time.

2 Dividing the Diffusion Zone

For one experiment, a large amount of observations are essential to provide information close to the continuous assumption of physical variables. Typically for numerical analysis, it is ideal to keep the number of points in a manageable range. Several well-known methods are based on this idea, such as the finite volume method and the finite element method which will be used in this report. The first step of the finite element method is to divide the domain of interest to small sub-domains. As the number of sub-domains can be chosen properly, the number of observations in one sub-domain will consequently be sufficient to do a local analysis.

This section introduces briefly two alternate methods of dividing the whole diffusion zone. Since the idea and the methodology are not hard to apply for higher dimension, the diffusion is assumed to process only in one direction to simplify the calculation.

Before dividing the whole diffusion zone to small elements, two more assumptions should be considered. First, the diffusion coefficients are constant inside each element. For elements whose concentration profile does not change dramatically, this assumption makes sense as long as the size of the element is small. For elements which contain an interface, a finer mesh should be applied to keep this assumption valid. The second assumption is that the concentration profile and the concentration gradient are continuous across an element to its adjacent element. This condition is not physically valid at interfaces as will be explained in Sec ???. However, the assumption is true for any other position. If the continuity were assumed, one can then set up a system of equations to interpolate or to approximate values

for parameters.

As the above assumptions were made, one then need to make sure that each element contains a manageable amount of points. The first consideration is to keep the number of measurements same for every element. Another consideration is to choose the number of elements beforehand and keep the size of each element the same. If the observations were made equally spaced, these two dividing methods are equivalent to each other.

The major advantage of the first method is that the nodal values match the boundary values of interpolation functions. On the other hand, the advantage of the second method is the simplicity. Since it is not essential in our analysis to match the boundary value between the interpolation function and the observed data, this report will choose to divide most of the diffusion zone by equally spacing divisions.

3 Generating Functions From Data

For computational physics problems, it is common that not all the necessary information can be directly obtained from experiments. There are two major types of missing information that appear in the process of the diffusion coefficients' calculation. First, the discrete concentration profile data cannot provide the high accuracy derivative value at any arbitrary position. The continuity condition of the gradient of concentration also cannot be satisfied. Second, the amount of particles that flow across the area at boundaries of each element are difficult to measure. Therefore, it is not easy to directly obtain the value of flux from experiments. The main goal of this section is to introduce methods of extracting the flux function and the concentration profile from given experiment data.

3.1 Non-dimensional Parameters

Equations which define the relations among physical variables should still be valid after rescaling of the units. For analytical solutions, this is not a problem since the units of all

variables are matched. However, when numerical approaches are applied for solving physics problems, the units of physical quantities are not necessarily considered in interpolation functions. Interpolation functions are usually used to give a continuous function to connect or approximate data values. This is a purely mathematical process. Since the data values may not remain the same after rescaling physical quantities, these interpolation functions could no longer be valid.

To avoid the issue and make sure every quantity can be rescaled, one should nondimensionalize each parameter before applying any numerical procedure. The idea of nondimensionalization is to divide the unit of each parameter by a characteristic parameter which has the same unit as the dividing parameter. The first step is to identify all the parameters in the calculation procedure and then choose the proper characteristic parameter from given values. Not all the parameters can find their characteristic parameter from the measured values. One should start the nondimensionalization by dividing through by coefficients of the highest order of derivatives or polynomial terms. Once all the parameters have been nondimensionalized, one can then rewrite the governing equation for physics problems in a new form of which has no SI units.

Let us proceed to the nondimensionalization process to the calculation of a diffusion problem. The following tables list all the parameters involved in the procedure of our calculation.

Table 1: Dimensional Parameters

Parameter	Description	Units
\mathbf{J}	the value of diffusion flux	[amount of substance per area per time]
\mathbf{D}	the diffusion coefficient matrix	[area per time]
\mathbf{C}	the concentration value	[amount of substance per volume]
x	the distance of reference points	[Length]

Table 2: Characteristic Scales for the variables.

Scale	Description	Units
L	the total length of diffusion zone	[Length]
t	the total experiment time	[time]
A	the area of cross section	[area]
V	the molar volume	[volume per mole]
N	the Avogadro constant	[amount of substance per mole]

The nondimensionlized zero order derivative quantities are

$$\hat{x} = \frac{x}{L}, \quad \hat{C}_i = \frac{V_i}{N} \cdot C_i;$$

$$\hat{D}_{ij} = \frac{t}{A} \cdot D_{ij}, \quad \hat{J}_i = \frac{At}{N} \cdot J_i$$

Here, the subscripts i and j denotes the corresponding component of the quantity. For the first order derivatives,

$$\frac{\partial C_i}{\partial x} = \frac{\partial C_i}{\partial \hat{C}_i} \cdot \frac{\partial \hat{C}_i}{\partial \hat{x}} \cdot \frac{\partial \hat{x}}{\partial x} = \frac{N}{V_i L} \frac{\partial \hat{C}_i}{\partial \hat{x}}$$

Therefore, Fick's equation becomes

$$\hat{J}_i = \frac{N}{At} \cdot \frac{t}{A} \cdot \frac{N}{V_i L} \cdot \sum_j \hat{D}_{ij} \frac{\partial \hat{C}_i}{\partial \hat{x}} = \frac{N^2}{A^2 V_i L} \cdot \sum_j \hat{D}_{ij} \frac{\partial \hat{C}_i}{\partial \hat{x}} \quad (1)$$

This procedure should be applied for the equations before interpolating data values.

3.2 Least Square Fitting for Concentration Profile

Least square fitting is a widely used method of finding an approximated function f based on the condition that the summation of squared error between f and the true value of all node is minimized. Since the experiments provide discrete values, the condition is to minimize

$$\chi^2 = \sum_i \left(\frac{f^{x_i} - f_e^{x_i}}{\sigma_i} \right)^2. \quad (2)$$

Here, f_e is the experimental value, the superscripts refer to the position of these value, and σ_i is the corresponding weight for each x_i .

It is clear that the value of χ^2 would be zero for a large group of function f . However, the function f has to provide information and satisfy physics conditions. Therefore, the form of the function f is normally prescribed by using shape functions. As its name describes, the shape function is chosen to have a desired shape. The major usage of the least square fitting in this report is to extract the concentration gradient from given concentration value. One can of course use the polynomial functions as the shape functions, that is, $f = \sum \alpha_i x^i$. Eq.2 then becomes the problem of solving for the parameters α_i . In the space α_i , the extreme value of χ^2 will occur at the point such that all derivatives of χ^2 with respect to each parameter equal to zero. For most of cases the extreme value is the minimum value since such functions consists of polynomial base functions that have no upper bound. The process of solving the system of equations from taking derivatives can be naturally processed by using the matrix representation. As the example of using the polynomial based functions, the parameters can be found by the following equation

$$\mathbf{A}^T \cdot \mathbf{A} \cdot \boldsymbol{\alpha} = \mathbf{A}^T \mathbf{b}. \quad (3)$$

Here, the superscript T denotes the transpose of the corresponding matrix, \mathbf{A} is the matrix containing all the values of the base function with its corresponding weight at each point:

$$A_{ij} = \frac{x_j^i}{\sigma_j}$$

\mathbf{b} is the list which contains all the experimental data value at each point with its weight:

$$b^T_i = \frac{f_e}{\sigma_i},$$

and matrix $\boldsymbol{\alpha}$ is the list of all the parameters α_i .

In order to match the shape of the distribution of a large amount of data values, the order of the polynomial can become very high and therefore cause the over fitting problem. To avoiding this issue, one can apply the method discussed in Sec.2 which is to split the whole region first. In each element, the number of nodal points is easy to handle. One can then find a proper fitting function for f_i in each region and the global fitting function can be made from the summation of all the local fitting functions. However, the function value of a shared nodal point is not necessarily the same for two adjacent elements by polynomial interpolation. It is not acceptable since it not only violates the physics requirement, but also make the calculation process not performable.

The method this report used to solve this issue is to use Hermite interpolation. Hermite interpolation functions also provide another nice property which is the continuity of the first derivative of the function. If the first derivative values were known for every nodal points, the general Hermite interpolation of the function is given as

$$f_e(x) = \sum_i f_e(x_i)N_i(x) + f_e'(x_i)\overline{N}_i(x).$$

Here, N_i and \overline{N}_i are shape functions for hermite interpolation. Similar to polynomial functions, the Hermite interpolation function can be applied locally. If the process were performed globally, the shape functions of hermite interpolation has to be found from element to element. An alternative method is to transfer the interval of each element to a consistent region. If the form of the shape function were not differ for elements, then the shape function will maintain the same in terms of the transferred variable. Suppose the position variable is transferred to the interval from -1 to 1 and denote the new variable as ξ . Then to make sure the continuity conditions at boundary nodes, for each region the following properties are desired:

- $N_i(\xi_j) = \delta_{ij}; \quad \frac{d}{d\xi}N_i(\xi_j) = 0;$
- $\overline{N}_i(\xi_j) = 0; \quad \frac{d}{d\xi}\overline{N}_i(\xi_j) = \delta_{ij}.$

Where ξ_i are the nodal points of each element. For one dimensional case, there will have two nodal points for each element. It is easy to check that the nodal values and the nodal derivative values are consistent across each region and therefore continuous. For one dimensional case, the four conditions of the shape function are sufficient to determine any kind of shape functions which contain four undetermined coefficients, such as the third order polynomials. Once the shape function is calculated, the fitting function in each element becomes

$$f_i(x) = \sum_i \left[f(x_i) N_i(\xi) + \left(\frac{df(x_i)}{dx} \right) \frac{dx}{d\xi} \bar{N}_i(\xi) \right].$$

An important fact is that the coefficients $f(x_i)$ and $\left(\frac{df(x_i)}{dx} \right)$ are not equivalent to the true value at x_i , they are determined by minimizing the error $\chi^2 = \sum_i (f_i - f_{ei})$ as the weight of all the points is assumed to be one. The positions of measured points are substituted into the shape function to form a system of equations which can be represented in the matrix form. As a concrete example, if there were five points in, say $x_i, i = 1..5$, in element j . the matrix \mathbf{A}_j is then

$$\mathbf{A}_j = \begin{bmatrix} N_1(x_1) & \bar{N}_1(x_1) & N_2(x_1) & \bar{N}_2(x_1) \\ N_1(x_2) & \bar{N}_2(x_2) & N_2(x_2) & \bar{N}_2(x_2) \\ N_1(x_3) & \bar{N}_3(x_3) & N_2(x_3) & \bar{N}_2(x_3) \\ N_1(x_4) & \bar{N}_1(x_4) & N_2(x_4) & \bar{N}_2(x_4) \\ N_1(x_5) & \bar{N}_1(x_5) & N_2(x_5) & \bar{N}_2(x_5) \end{bmatrix}.$$

The corresponding $\boldsymbol{\alpha}_j$ vector is

$$\boldsymbol{\alpha}_j^T = \left[f(x_1), \frac{df(x_1)}{dx}, f(x_5), \frac{df(x_5)}{dx} \right].$$

Where x_1 and x_5 are boundary positions of the j^{th} element. Denote \mathbf{b}_j^T as the vector which consists all the experiment data values and $\boldsymbol{\alpha}_j$ to be the parameters of each shape function.

Then in element j , the error from the least square fitting function is

$$\chi_j^2 = (\mathbf{b}_j - \mathbf{A}_j \cdot \boldsymbol{\alpha}_j)^T \cdot (\mathbf{b}_j - \mathbf{A}_j \cdot \boldsymbol{\alpha}_j) \quad (4)$$

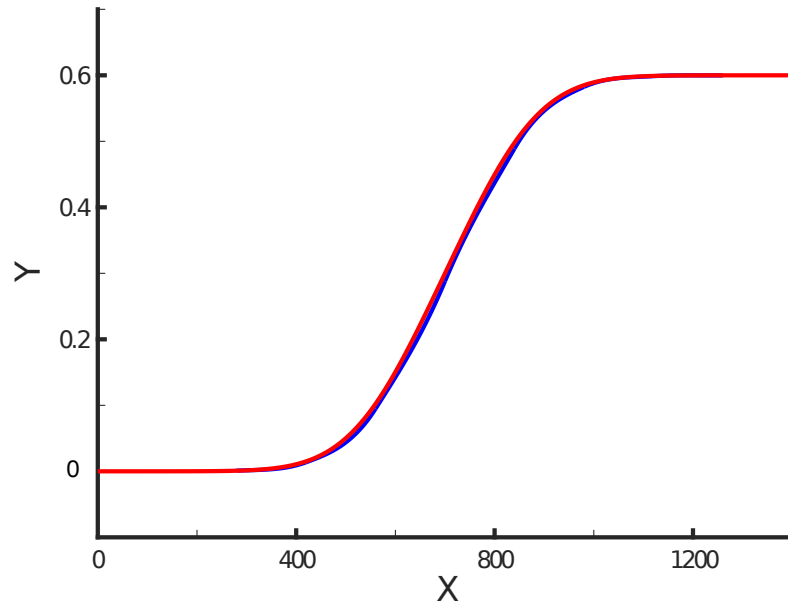
Equation 4 can be easily extended globally. Let $\boldsymbol{\alpha}$ be the vector consists all the undetermined nodal values and their derivative values, \mathbf{b} be the vector consists all the values of measured points. By carefully rewrite the system of equations in the matrix form, one can then generate a global matrix \mathbf{A} . For one dimensional, the matrix \mathbf{A} is a block-diagonal matrix. Each block is the matrix \mathbf{A}_j as defined above. Geometrically the problem is still to find the smallest χ^2 , which is same as to find the projection of $\mathbf{A} \cdot \boldsymbol{\alpha}$ on \mathbf{b} , then one can solve the parameter vector $\boldsymbol{\alpha}$ from Eq.3.

3.2.1 Concentration Profile and Flux

The first step of this project is to generate the concentration profile from the given experimental data. Typically, in the process of diffusion, concentration of components is a function of position and time. The data from experiments are usually measured when the diffusion components are very close to their equilibrium state. Therefore, the time variable in those data can be treated as a constant.

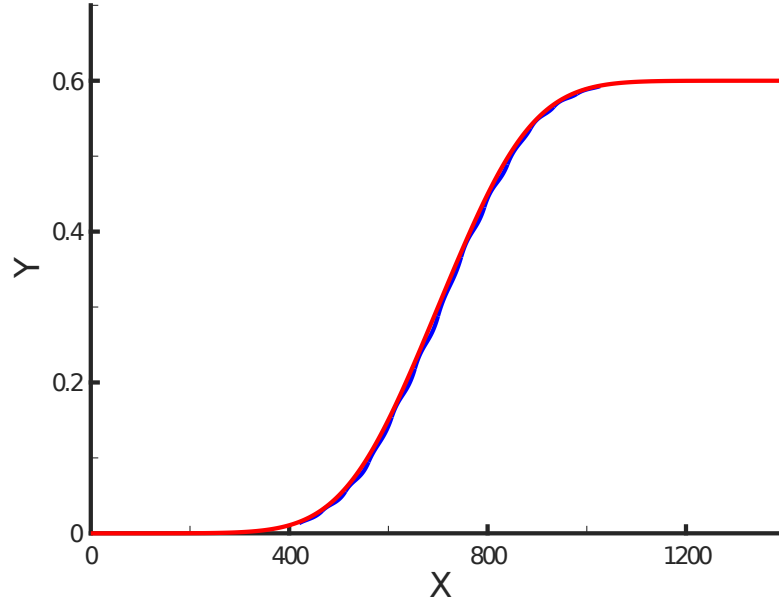
In our analysis, governing equations require to know the first derivative values. As the measured concentration values are discrete, the desired information could not be provided. Thus, the Hermite least square fitting is considered to be applied on these measured data values. The process of applying the Hermite least square fitting is given in the previous section. The obtained functions are given in Fig.1 and Fig. 2

Figure 1: Concentration profile
Number of Element = 10



This plot compares the concentration value from the Hermite least square fitting and the data. The blue line represents the approximated function based on a 10 elements partition and the red line is the experimental values.

Figure 2: Concentration profile
Number of Element = 30

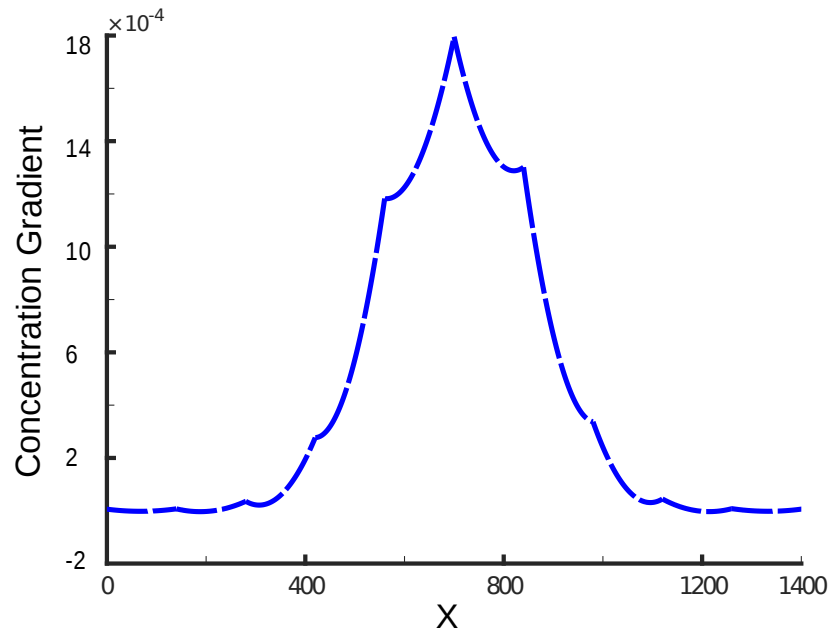


This plot compares the concentration value from the Hermite least square fitting and the data. The blue line represents the approximated function based on a 30 elements partition and the red line is the experimental values.

The total number of measured points for the above calculations is 281. Fig.1 divides the diffusion domain to 10 sub-domain and Fig.1 has 30 sub-domains. For both figures above, the red line is made from connecting data values directly and the blue line represents the function obtained concentration profile by applying Hermite least square fitting.

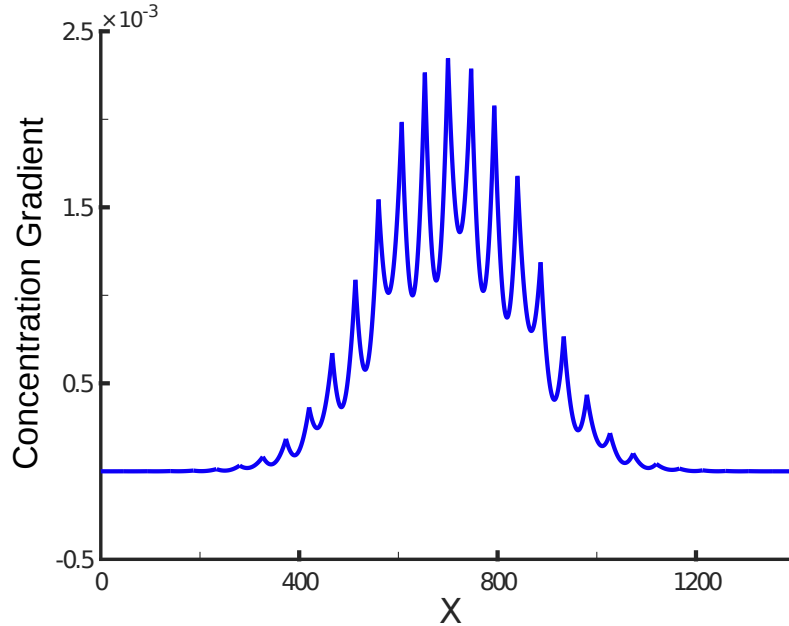
Once the concentration profile is connected as a smooth function, the concentration value and its derivative can be directly calculated from the fitting function and will be known everywhere over the whole diffusion zone. The following figures gives the function of concentration gradient

Figure 3: Concentration gradient
Number of Element = 10



This figure gives the concentration gradient function based on a 10 elements partition. Since we used the first order Hermite interpolation functions, the concentration gradient function is not a smooth function.

Figure 4: Concentration gradient
Number of Element = 30



This figure gives the concentration gradient function based on a 30 elements partition. These unnecessary oscillations implies that the second order Hermite interpolation is desired.

Figure 3 and 4 are obtained by directly taking the derivative of the approximated concentration profile. The overall tendency of both plots agree with the assumed answer which is provided in next section. Although the nodal values are close between two plots, the concentration gradient in Fig. 4 experiences unnecessary oscillation. Roughly, when the number of element is 30, the number of data points in each element is 8, which is small enough to cause over-fitting.

The value of flux is another essential quantity in the procedure of deriving the diffusion coefficients. However, it is not easy to measure the flux directly from the experiment. Fortunately, if the condition of constant interface velocity were assumed, the flux and the concentration have an inner uncoupled connection from the conservation of mass law. At a

given time t , the Matano-plane analysis gives the relation

$$\frac{\partial J}{\partial x} = -\frac{x - x_0}{2t} \frac{\partial C}{\partial x}. \quad (5)$$

Here, J is the flux, C is the concentration profile, and x_0 is the position of Matano-plan. Since the exact formula for concentration profile is approximated by the fitting function f , the right hand side of Eq.5 is known function of position. Integrating both side of the equation, the function of J is then given as

$$J = \frac{1}{2t} \int F dx + J_0. \quad (6)$$

Where $F = (x - x_0) \frac{\partial f}{\partial x}$ and J_0 is the boundary flux value which is a constant. At a given time, if the initial conditions of the diffusion process were given, then the boundary flux value can be calculated element by element. The approximated flux functions are given in following figures.

Figure 5: Flux v.s. Position
 Time = 100000
 Matano-Plane: X = 710

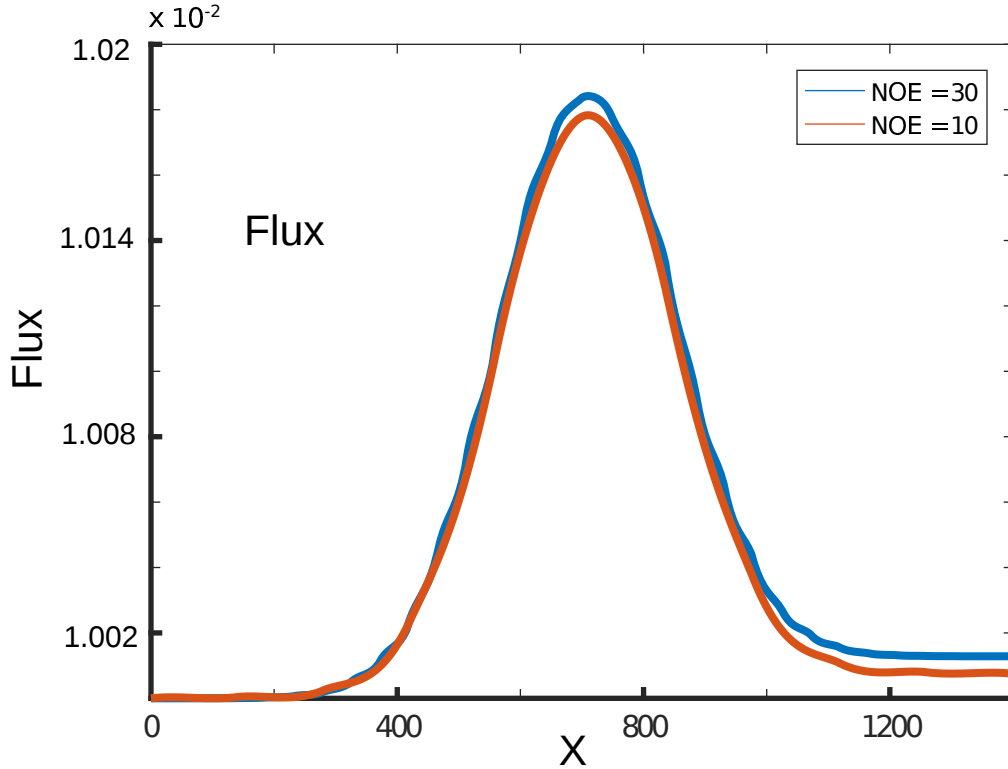
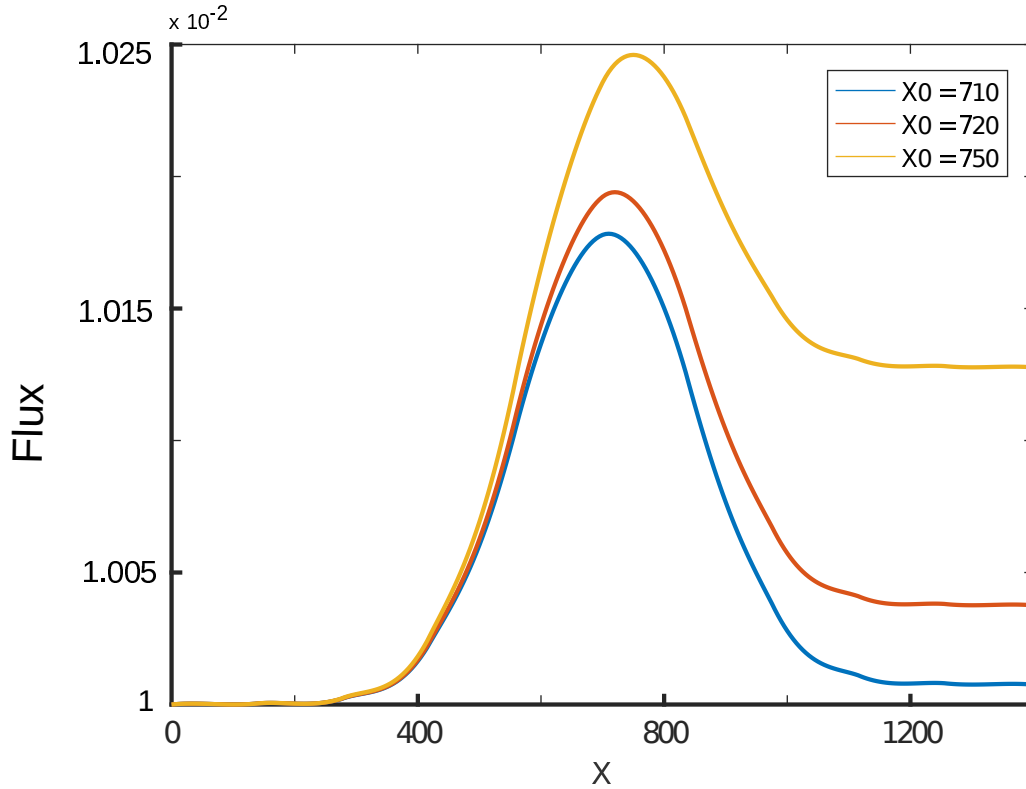


Figure 6: This plot compares two flux equations which are based on a 10 elements partition and a 30 elements partition.

Figure 5 displays the flux as a function of position. The blue line is function from the partition of 30 elements and the red line is the function from the partition of 10 elements. The initial condition for Fig. 5 is $J_i = 0.01$ for all i at $x = 0$. The initial condition usually will only shift the function upwards or downward and have no contribution to the slope.

Notice in Eq.5, the position of Matano plane plays an important role. It does not only shift the function, but also changes the shape and symmetry of the flux function as shown in Fig.7.

Figure 7: Flux function with different matano-plane position



The Figure compares the flux function based on three different X_0 value, which is the position of the Matano plane. It is clear that a small Matano plane's position can make a big change of the flux function.

From Fig.7, it is clear that the flux function is very sensitive with respect to the change of the position of Matano-plane. The Matano-plane's position is determined from the integrated concentration profile and it should be a constant. However, the concentration profile is approximated by numerical methods. Hence the accuracy of the approximated flux equation heavily depends on the accuracy of the concentration profile.

If the diffusion coefficients were constants, the concentration profile is a combination of error functions for continuous regions. The shape functions introduced before were third order polynomials which will make the fitting function be a third order polynomial as well. For most of the elements from the diffusion domain, the shape of error function is similar to the shape of the polynomial functions. Plots have also shown that the Hermite least fittings

have high accuracy of approximating the concentration profiles.

Since the flux, concentration profile, and their first derivative with respect to position are continuous functions, the velocity which is defined as the rate of flux change divided by the rate of the concentration change is also continuous except at where the concentration is at equilibrium. The continuity of velocity is important as it satisfies the physical requirement and guarantees the continuity equations to be applicable.

3.2.2 Elements Containing an Interface

Experiments show that the value of concentration profile for each component differs a lot in a tiny interval across each interface. Physically the existence of the jump is acceptable. However, for our calculation, the continuity of both the concentration profile and its derivative is required. Thus one should still find a continuous function for such elements. In the former section, the shape functions for the least square fitting were third order polynomials. The third order polynomials are not expected to have such rapid jump. Therefore, it will make no sense to use the third order polynomial shape functions here. One group of function which has similar shape is the Fermi-function. The general form of the Fermi-function is

$$F = \frac{a}{e^{\frac{x-b}{c}} + 1} + d. \quad (7)$$

There are four undetermined parameters, a , b , c , and d , for each shape function. The four conditions of the Hermite interpolation enable us to calculate these parameter. Notice that one should not transfer x to $-1 \leq \xi \leq 1$ because the value of the parameter b determines the position of the sharpest derivative of the Fermi-function. Each shape function is then in the form of a Fermi-function. The least square fitting process is same in these elements containing an interface. However, the Fermi-function is not easy to deal with as the polynomial functions. Calculating the shape functions requires too much effort. A trade off can be made by using the fact of that these regions are very small. One can choose to connect the two

nodes which are close enough. The detail of deriving the Fermi-function at interface is given in Sec.6.2 and Sec.6.3. Once the concentration profile near the interface is determined, other quantities can be obtained from the process introduced above. If a finer mesh is desired in such a region, then one can also use the information provided by the interpolated functions as boundary values.

4 Transfer Matrix Method

For a one-dimensional ternary diffusion system, Fick's equation gives $\tilde{J}_i = -\sum_j^2 \tilde{D}_{ij} \frac{\partial C_j}{\partial x}$. Here, \tilde{J}_i is the inter-diffusion flux for component i , $\tilde{\mathbf{D}}$ is the inter-diffusion coefficient matrix, and $\frac{\partial C_j}{\partial x}$ is the partial derivative of the j^{th} component's concentration with respect to position. The Fick's equation illustrates that the flux of each diffusion component is related to the concentration gradient from all components. The coupled system makes the analysis of the diffusion process much harder than a two component system. However, this problem can be solved by the transfer matrix method. Generally, the diffusion coefficients are functions of the position, however, as the entire region of the diffusion zone is divided to small enough elements, the diffusion coefficients can be assumed as constants for each element.

4.1 Background of Linear Algebra

Let \mathbf{A} be a $n \times n$ square matrix over the real number field, the sufficient and necessary condition for \mathbf{A} to be diagonalizable is that the dimension of eigen-space of \mathbf{A} is equal to n . If this matrix has n distinct eigenvalues, one can then write the matrix as

$$\mathbf{A} = \mathbf{P}\mathbf{H}\mathbf{P}^{-1}.$$

Here, \mathbf{P} is the matrix composed of eigenvectors of \mathbf{A} , \mathbf{P}^{-1} is the inverse matrix of \mathbf{P} , and \mathbf{H} is the diagonalized matrix which contains eigenvalues as its trace.

The diffusion coefficient matrix, $\tilde{\mathbf{D}}$, is a two-by-two matrix. Let the assumption that

the matrix has two distinct eigenvalues be made, then the diffusion coefficient matrix can be decomposed in the above form. In order to obtain the explicit diagonalized matrix, one need to know the eigenvalues and eigenvector of $\tilde{\mathbf{D}}$. It is equivalent to solving the following equation

$$\tilde{\mathbf{D}} * \Psi = d \mathbf{I} \Psi. \quad (8)$$

Here, \mathbf{I} is the identity matrix, d is the vector contains the two possible eigenvalues, and Ψ is the corresponding eigenvector. The eigenvalues can be determined by the solving the characteristic polynomial and the result is

$$d_1 = \frac{1}{2} \left[\left(\tilde{\mathbf{D}}_{11} + \tilde{\mathbf{D}}_{22} \right) + \sqrt{\left(\tilde{\mathbf{D}}_{11} - \tilde{\mathbf{D}}_{22} \right)^2 + 4\tilde{\mathbf{D}}_{12}\tilde{\mathbf{D}}_{21}} \right]$$

$$d_2 = \frac{1}{2} \left[\left(\tilde{\mathbf{D}}_{11} + \tilde{\mathbf{D}}_{22} \right) - \sqrt{\left(\tilde{\mathbf{D}}_{11} - \tilde{\mathbf{D}}_{22} \right)^2 + 4\tilde{\mathbf{D}}_{12}\tilde{\mathbf{D}}_{21}} \right]$$

Let the corresponding eigenvectors are $\Psi_i = \begin{bmatrix} \alpha_i \\ \beta_i \end{bmatrix}$ for $i = 1, 2$. Based on the assumption made before, one will be able to re-scale the eigenvectors and normalize α_1 in Ψ_1 . Then the corresponding β_1 will be

$$\beta_1 = -\frac{\tilde{\mathbf{D}}_{11} - d_1}{\tilde{\mathbf{D}}_{12}}$$

similarly, by normalizing β_2 , one can obtain

$$\alpha_2 = -\frac{\tilde{\mathbf{D}}_{22} - d_2}{\tilde{\mathbf{D}}_{21}}.$$

Let \mathbf{P} be a 2×2 matrix whose columns are consisting of two eigenvectors from above, i.e.

$$\mathbf{P} = \begin{bmatrix} 1 & \alpha_2 \\ \beta_1 & 1 \end{bmatrix}$$

The inverse matrix of \mathbf{P} is then obtained as

$$\mathbf{P}^{-1} = \frac{\mathbf{1}}{\mathbf{1} - \alpha_2\beta_1} \begin{bmatrix} 1 & -\alpha_2 \\ 2 & -\beta_1 \end{bmatrix}.$$

Then every term of the diagonalized diffusion coefficient matrix is explicitly expressed by the components of the matrix and it is denoted as

$$\tilde{\mathbf{D}} = \mathbf{P}\mathbf{\Delta}\mathbf{P}^{-1} \quad (9)$$

Here $\mathbf{\Delta}$ is the diagonalized matrix:

$$\mathbf{\Delta} = \begin{bmatrix} d_1 & 0 \\ 0 & d_2 \end{bmatrix}.$$

4.2 Transfer Matrix for the Flux

Substituting the decomposed diffusion coefficient matrix into Fick's equation, one can directly obtain

$$\tilde{\mathbf{J}} = \mathbf{P}\mathbf{\Delta}\mathbf{P}^{-1} \cdot \frac{\partial \mathbf{C}}{\partial \mathbf{x}}. \quad (10)$$

Multiplying by \mathbf{P}^{-1} on both sides of Eq.10, one has

$$\mathbf{P}^{-1}\tilde{\mathbf{J}} = -\mathbf{\Delta}\mathbf{P}^{-1} \cdot \frac{\partial \mathbf{C}}{\partial \mathbf{x}}. \quad (11)$$

Let $\hat{\mathbf{J}}$ denote $\mathbf{P}^{-1}\tilde{\mathbf{J}}$ and $\hat{\mathbf{C}}$ denote $\mathbf{P}^{-1} \cdot \mathbf{C}$. Eq.11 then becomes

$$\hat{\mathbf{J}} = -\mathbf{\Delta} \frac{\partial \hat{\mathbf{C}}}{\partial \mathbf{x}}, \quad (12)$$

or explicitly,

$$\hat{\mathbf{J}} = \frac{1}{1 - \alpha_2\beta_1} \begin{bmatrix} \tilde{J}_1 - \alpha_2\tilde{J}_2 \\ -\beta_1\tilde{J}_1 + \tilde{J}_2 \end{bmatrix}$$

$$\frac{\partial \hat{\mathbf{C}}}{\partial x} = \frac{1}{1 - \alpha_2\beta_1} \begin{bmatrix} \frac{\partial C_1}{\partial x} - \alpha_2 \frac{\partial C_2}{\partial x} \\ -\beta_1 \frac{\partial C_1}{\partial x} + \frac{\partial C_2}{\partial x} \end{bmatrix}$$

Substituting $\hat{\mathbf{J}}$, $\partial_x \hat{\mathbf{C}}$, and $\mathbf{\Delta}$, Eq.12 becomes

$$\begin{bmatrix} \tilde{J}_1 - \alpha_2\tilde{J}_2 \\ -\beta_1\tilde{J}_1 + \tilde{J}_2 \end{bmatrix} = - \begin{bmatrix} d_1 \left(\frac{\partial C_1}{\partial x} - \alpha_2 \frac{\partial C_2}{\partial x} \right) \\ d_2 \left(-\beta_1 \frac{\partial C_1}{\partial x} + \frac{\partial C_2}{\partial x} \right) \end{bmatrix} \quad (13)$$

Notice that the Fick's equation for ternary diffusion becomes an uncoupled function of the concentration gradient in the coordinate system which has the diffusion coefficient matrix diagonalized, i.e, the base vector rotated from $\left(\frac{\partial C_1}{\partial x}, \frac{\partial C_2}{\partial x} \right)$ to $\left(\frac{\partial \hat{C}_1}{\partial x}, \frac{\partial \hat{C}_2}{\partial x} \right)$.

Under the assumption of conservation of total mass, one can show $\frac{\partial \tilde{J}_i}{\partial x} = -\frac{\partial C_i}{\partial t}$. One can further hold the time as a constant and derive the continuity equation

$$\frac{\partial J}{\partial x} = v \cdot \frac{\partial C}{\partial x}$$

Where v is the velocity of the propagating of concentration level and

$$v = \frac{x - x_0}{2t},$$

where x_0 is the position of the Matano-plane. Notice that the continuity equation is not coupled by its definition. Substituting the relation $\tilde{J}_i = -\sum_j^2 \tilde{D}_{ij} \frac{\partial C_j}{\partial x}$ one can obtain

$$\frac{\partial \tilde{J}_i}{\partial x} = -\frac{x - x_0}{2t} [(\tilde{\mathbf{D}})^{-1}]_{ij} \tilde{J}_j \quad (14)$$

Or in a more compact expression

$$\frac{\partial \tilde{\mathbf{J}}}{\partial x} = -\frac{x - x_0}{2t} (\tilde{\mathbf{D}})^{-1} \tilde{\mathbf{J}} \quad (15)$$

Substituting the decomposed form of flux and $\mathbf{\Delta}$, one can replace Eq.15 and obtain

$$\frac{\partial \hat{\mathbf{J}}}{\partial x} = -\frac{x - x_0}{2t} (\mathbf{\Delta})^{-1} \hat{\mathbf{J}}. \quad (16)$$

Equation.16 is in the form of

$$\dot{x} = Ax + b.$$

The general solution is given in Appendix 1 For the diffusion process, the solution can be expressed in the form of an exponential matrix

$$e^{\mathbf{A}} = \sum \frac{1}{k!} \mathbf{A}^k.$$

Then, the solution of Eq.16 can be obtained as

$$\tilde{\mathbf{J}}(\mathbf{x}, t) = \exp\left(-\frac{(\mathbf{x} - \mathbf{x}_0)^2 - (\mathbf{x}_s - \mathbf{x}_0)^2}{4t} ((\tilde{\mathbf{D}})^{-1})\right) \cdot \tilde{\mathbf{J}}(\mathbf{x}_s, t). \quad (17)$$

The solution is valid in the region of $x_s \leq x \leq x_{s+1}$. $\tilde{\mathbf{J}}(x_s, t)$. is the initial flux value at position $x = x_s$. To simplify the writing, let \mathbf{T} be a function of $x, x_s, t, \tilde{\mathbf{D}}$, and set \mathbf{T} to be

$$\mathbf{T} = \exp\left(-\frac{(\mathbf{x} - \mathbf{x}_0)^2 - (\mathbf{x}_s - \mathbf{x}_0)^2}{4t} ((\tilde{\mathbf{D}})^{-1})\right). \quad (18)$$

Then the solution in that element can be expressed as

$$\tilde{\mathbf{J}}(\mathbf{x}, t) = \mathbf{T}(\mathbf{x}, \mathbf{x}_s, t, \tilde{\mathbf{D}}) \cdot \tilde{\mathbf{J}}(\mathbf{x}_s, t). \quad (19)$$

Furthermore, the solution of flux contains the inverse of diffusion coefficient matrix terms. If

one plug the diagonal transformation $(\tilde{\mathbf{D}})^{-1} = \mathbf{P} \cdot \mathbf{\Delta} \cdot \mathbf{P}^{-1}$ and expand the matrix exponential back to the Peano-Baker series, all the middle terms of $\mathbf{P} \cdot \mathbf{P}^{-1}$ in the series will be normalized.

Then one has

$$\mathbf{T} = \mathbf{P} \cdot \tau \cdot \mathbf{P}^{-1}. \quad (20)$$

Here τ is the diagonal matrix

$$\begin{bmatrix} \cdot & & & & 0 \\ & \cdot & & & \\ & & \exp\left(-\frac{(x-x_0)^2-(x_s-x_0)^2}{4t}((\tilde{\mathbf{d}}_i)^{-1})\right) & & \\ & & & \cdot & \\ 0 & & & & \cdot \end{bmatrix}$$

An al-

ternate way to write the solution of flux inside the element is to substitute Fick's equation to replace the flux value at nodal points:

$$\tilde{\mathbf{J}}(\mathbf{x}, t) = \mathbf{T}(\mathbf{x}, \mathbf{x}_s, t, \tilde{\mathbf{D}}) \cdot \frac{\partial \mathbf{C}(\mathbf{x}_s, t)}{\partial \mathbf{x}}. \quad (21)$$

This section has shown that the inter-diffusion flux can be obtained everywhere inside any given element by providing either the nodal concentration gradient value or the nodal flux value. Notice that one can also choose x_{s+1} as the nodal value and calculate backwards by choosing the corresponding value in transfer matrix.

4.3 Concentration Profiles

The Fick's equation gives a direct relation between concentration gradient and the inter-diffusion flux. In Sec.4.2, a method is generated to describe the inter-diffusion flux for each element in terms of diffusion coefficients and the boundary nodal values of either the concentration gradient or the flux. If the concentration is of interested, one can start the analysis by rearrange the Flux's first law as

$$\frac{\partial}{\partial x} \mathbf{C} = -(\tilde{\mathbf{D}})^{-1} \cdot \tilde{\mathbf{J}}.$$

By replacing the flux function in above equation by the relation obtain in Eq.21 and integrate both sides of the equation, the concentration profile can be expressed as

$$\mathbf{C}(\mathbf{x}, \mathbf{t}) = \mathbf{C}(\mathbf{x}_s, \mathbf{t}) - (\tilde{\mathbf{D}})^{-1} \cdot \int_{\mathbf{x}_s}^{\mathbf{x}} \exp\left(-\frac{(\mathbf{x} - \mathbf{x}_0)^2 - (\mathbf{x}_s - \mathbf{x}_0)^2}{4\mathbf{t}} ((\tilde{\mathbf{D}})^{-1})\right) \mathbf{d}\mathbf{x}' \cdot \mathbf{J}(\mathbf{x}_s, \mathbf{t}). \quad (22)$$

For solving the concentration profile, let us take a close look of the exponential term, which is the parameter defined in Eq.18. Rewriting \mathbf{T} in the form of

$$\mathbf{T} = \frac{\exp\left(-\frac{(\mathbf{x} - \mathbf{x}_0)^2}{4\mathbf{t}} ((\tilde{\mathbf{D}})^{-1})\right)}{\exp\left(-\frac{(\mathbf{x}_s - \mathbf{x}_0)^2}{4\mathbf{t}} ((\tilde{\mathbf{D}})^{-1})\right)}$$

With the assumption of that the diffusion coefficient matrix is constant in each element, the denominator of \mathbf{T} is also a constant. Then the only variable appears in the integral is the numerator term. The integrated function of such form is the error function. Following the decoupling process introduced before, the remaining work is similar of deriving the flux equation.

Until now, both the concentration profile and the flux function are prescribed with only one of the boundary nodal values. Unlike the flux value which is hard to observe everywhere, the concentration values can be obtained or interpolated at least at both ends of any element. Intuitively, more information should be able to be derived if the both nodal value of the concentration were provided. Similar to defining the parameter \mathbf{T} , the integrated value of \mathbf{T} , denoted as ε , is defined to simplify the later equations as

$$\varepsilon(x, x_s, t, \Delta) = \int_{x_s}^x \exp\left(-\frac{(x - x_0)^2 - (x_s - x_0)^2}{4t} ((\tilde{\mathbf{D}})^{-1})\right) \mathbf{d}\mathbf{x}'.$$

In a more explicit form,

$$\begin{aligned}
\varepsilon &= \begin{bmatrix} \cdot & & & & & 0 \\ & \cdot & & & & \\ & & \int_{x_s}^s dx' \exp\left(-\frac{(x-x_0)^2 - (x_s-x_0)^2}{4t} ((\tilde{\mathbf{d}}_i)^{-1})\right) & & & \\ & & & \cdot & & \\ 0 & & & & & 0 \end{bmatrix} \\
&= \begin{bmatrix} \cdot & & & & & 0 \\ & \cdot & & & & \\ & & \int_{x_s}^x dx' \exp\left(-\frac{(x-x_0)^2}{4td_i}\right) \cdot \exp\left(\frac{(x_s-x_0)^2}{4td_i}\right) & & & \\ & & & \cdot & & \\ 0 & & & & & \cdot \end{bmatrix} \\
&= \begin{bmatrix} \cdot & & & & & 0 \\ & \cdot & & & & \\ & & \sqrt{\pi td_i} \left(\operatorname{erf}\left(\frac{x-x_0}{2\sqrt{td_i}}\right) - \operatorname{erf}\left(\frac{x_s-x_0}{2\sqrt{td_i}}\right) \right) & & & \\ & & & \cdot & & \\ 0 & & & & & \cdot \end{bmatrix} \begin{bmatrix} \cdot & & & & & 0 \\ & \cdot & & & & \\ & & \exp\left(\frac{(x_s-x_0)^2}{4td_i}\right) & & & \\ & & & \cdot & & \\ & & & & & 0 \\ & & & & & \cdot \end{bmatrix}
\end{aligned}$$

Here, erf is the error function. By the definition of error function, $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$. Therefore, a normalization $\sqrt{\pi td_i}$ is desired to be multiplied. Convert the explicit form back to the matrix form, and one has

$$\varepsilon = \sqrt{\pi t} (\mathbf{\Delta})^{\frac{1}{2}} \cdot \left(\operatorname{erf}\left(\frac{\mathbf{x} - \mathbf{x}_0}{2\sqrt{t\mathbf{d}_i}}\right) - \operatorname{erf}\left(\frac{\mathbf{x}_s - \mathbf{x}_0}{2\sqrt{t\mathbf{d}_i}}\right) \right) \cdot \exp\left(\frac{(\mathbf{x}_s - \mathbf{x}_0)^2}{4t\mathbf{d}_i}\right) \quad (23)$$

As the error functions can be expanded by power series, one can perform similar transformation on ε and obtain

$$\mathbf{E}(x, x_s, t, \tilde{\mathbf{D}}) = \mathbf{P} \cdot \varepsilon \cdot \mathbf{P}^{-1} \quad (24)$$

As before, the inter-terms of $\mathbf{P} \cdot \mathbf{P}^{-1}$ are canceled as the exponential matrix \mathbf{E} is expanded explicitly.

Substituting the parameter \mathbf{E} in Eq.22, the concentration profile can be prescribed as

$$\mathbf{C}(\mathbf{x}, \mathbf{t}) = \mathbf{C}(\mathbf{x}_s, \mathbf{t}) - (\tilde{\mathbf{D}})^{-1} \cdot \mathbf{E} \cdot \mathbf{J}(\mathbf{x}_s, \mathbf{t}). \quad (25)$$

Equation 25 gives the general expression for the concentration profile in the element whose domain ranges from x_s to x_{s+1} . Therefore, this equation is also valid for the other nodal point which has the coordinate x_{s+1} . Thus one has

$$\mathbf{C}(\mathbf{x}_{s+1}, \mathbf{t}) = \mathbf{C}(\mathbf{x}_s, \mathbf{t}) - (\tilde{\mathbf{D}})^{-1} \cdot \mathbf{E}(\mathbf{x}_{s+1}, \mathbf{x}_s, \mathbf{t}, \tilde{\mathbf{D}}) \cdot \mathbf{J}(\mathbf{x}_s, \mathbf{t}). \quad (26)$$

Since the concentration values at two nodal points are assumed to be known, the flux value at x_s can be expressed in terms of the two nodal concentration values

$$\mathbf{J}(\mathbf{x}_s, \mathbf{t}) = -(\mathbf{C}(\mathbf{x}_{s+1}, \mathbf{t}) - \mathbf{C}(\mathbf{x}_s, \mathbf{t})) \cdot (\tilde{\mathbf{D}}) \cdot \mathbf{E}(\mathbf{x}_{s+1}, \mathbf{x}_s, \mathbf{t}, \tilde{\mathbf{D}})^{-1}. \quad (27)$$

Then Eq.25 becomes

$$\mathbf{C}(\mathbf{x}, \mathbf{t}) = \mathbf{C}(\mathbf{x}_s, \mathbf{t}) + (\tilde{\mathbf{D}})^{-1} \cdot \mathbf{E} \times [(\mathbf{C}(\mathbf{x}_{s+1}, \mathbf{t}) - \mathbf{C}(\mathbf{x}_s, \mathbf{t})) \cdot (\tilde{\mathbf{D}}) \cdot \mathbf{E}(\mathbf{x}_{s+1}, \mathbf{x}_s, \mathbf{t}, \tilde{\mathbf{D}})^{-1}]. \quad (28)$$

Consequently, the concentration profile in any element can be expressed in terms of the diffusion coefficient matrix and two nodal concentration values. Notice that the diagonal terms in the diffusion coefficient matrix can be simplified. The result is given as, by keeping t as a constant,

$$\mathbf{C} = \mathbf{C}(x_s) + \mathbf{P} \cdot \Phi \cdot \mathbf{P}^{-1} \cdot [\mathbf{C}(\mathbf{x}_{s+1}) - \mathbf{C}(\mathbf{x}_s)] \quad (29)$$

Where Φ is the diagonal matrix whose diagonal terms

$$\Phi_{ii} = \frac{\left(\operatorname{erf} \left(\frac{x-x_0}{2\sqrt{td_i}} \right) - \operatorname{erf} \left(\frac{x_s-x_0}{2\sqrt{td_i}} \right) \right)}{\left(\operatorname{erf} \left(\frac{x_{s+1}-x_0}{2\sqrt{td_i}} \right) - \operatorname{erf} \left(\frac{x_s-x_0}{2\sqrt{td_i}} \right) \right)}$$

Thus, for any region which has constant diffusion coefficients, the transfer matrix method is efficient to describe the concentration profile and the flux everywhere.

4.4 System of Equations

The former sections have introduced the procedure of deriving the concentration profile and flux. Although these two quantities are important to analyze the diffusion process, the main goal of the report is to calculate the diffusion coefficient matrix. The flux and concentration profile in a single element are given in Eq.19 and Eq.29. However, it has to be emphasized that these two equations are written in terms in the boundary values and the diffusion coefficients. Therefore, from the purely analytical perspective, the diffusion coefficient matrix has to be calculated first.

Recall that Sec 3 introduced a procedure of extracting information from raw experimental data. Thus, for every diffusion component in each element, the value of the concentration, the concentration gradient, and the flux are approximated for two end points. It is clear that for a ternary diffusion system, the diffusion coefficient contains four unknown functions of position and time. With the assumption that the diffusion coefficients are constant in each small element, there will be four unknown constants for each element to be determined to form the diffusion coefficient matrix.

The diagonalized diffusion coefficient matrix is given by Eq.9. The four unknown components in the matrix then could be calculated if its eigenvalues and eigenvectors were known. Notice that since the eigenvectors were normalized, so that $\alpha_1 = \beta_2 = 1$. It still requires a system of four equations to have a unique solution.

The first two equations come from Fick's first law. The flux of the first diffusion compo-

ment has the relation

$$J_1 = - \sum_j D_{1j} \frac{\partial C_j}{\partial x} \quad (30)$$

Apply the procedure of transfer matrix method for the above equation, and the flux for the first component can be expressed as

$$J_1 - \alpha_2 J_2 = -d_1 \frac{\partial}{\partial x} (C_1 - \alpha_2 C_2). \quad (31)$$

Here, the two unknowns are d_1 and α_2 .

Similarly, the flux equation for the second component is

$$J_2 - \beta_1 J_1 = -d_2 \frac{\partial}{\partial x} (C_2 - \beta_2 C_1). \quad (32)$$

Again, the two unknowns are d_2 and β_1 .

For the remaining two equations, the transfer matrix method provides several choices as the boundary conditions can come from either the flux values or the gradient concentration values. For example, the flux equation given by Eq.19 can be used to determine the coefficient matrix by substituting two boundary values of the flux. In short, the equations can be chosen from among any transferred flux or concentration equations given in the former sections. However, these choices are not the same since the values are approximated instead of the realistic value. The accuracy then becomes the primary concern here. There are two major sources of the error terms. The first kind is the error from the original approximation. Another source is from the numerical calculation process since the analytical solution is hard to obtain. Here we will briefly talk about reason of the choices this report uses. The error bound and the order of the accuracy will not be carefully analyzed.

For the first kind of error source, recall that the experiment supplies the discrete concentration values and the dividing method in this report is chosen to be equally spaced. The flux equation is derived based on the approximated concentration profile function by

integration. Thus the error of concentration profile could be potentially accumulated into the error of flux in each element. Consequently, the error in flux values is assumed to be larger than the error of the concentration values.

For the second kind of error, the error terms are assumed to be directly related to the complex relations of the equations. The complicity of the equations is defined as the how much different the undetermined parameters are from the linear equation. Therefore, the simplest equation is the flux equation, the most complicated equation is the equation of concentration based on two boundary values.

From above, it is not clear which equation is the best to choose since the lower the first kind error is, the higher the second kind error will be. One can of course calculate the order of error by expanding these equations and analyzing which equation has lowest error bound. The detail will not be provided in this report and the equation used here is Eq.27. After diagonalization, one has

$$(J_1 - \alpha_2 J_2)_{x_s} = \frac{[C_1 - \alpha_2 C_2]_{x_{s+1}} - [C_1 - \alpha_2 C_2]_{x_s}}{\sqrt{\frac{\pi t}{d_1}} \cdot \left[\operatorname{erf} \left(\frac{x_{s+1} - x_0}{2\sqrt{d_1 t}} \right) - \operatorname{erf} \left(\frac{x_s - x_0}{2\sqrt{d_1 t}} \right) \right]} \quad (33)$$

and

$$(J_2 - \beta_1 J_1)_{x_s} = \frac{[C_2 - \beta_1 C_1]_{x_{s+1}} - [C_2 - \beta_1 C_1]_{x_s}}{\sqrt{\frac{\pi t}{d_2}} \cdot \left[\operatorname{erf} \left(\frac{x_{s+1} - x_0}{2\sqrt{d_2 t}} \right) - \operatorname{erf} \left(\frac{x_s - x_0}{2\sqrt{d_2 t}} \right) \right]} \quad (34)$$

A system of equations of determining diffusion coefficients is formed by combining Eq.31, Eq.32 Eq.33, and Eq.34.

5 Solving for Diffusion Coefficients

A formalism of calculating the diffusion coefficients is established from Sec.3 and Sec.4. The next object is to calculate the diffusion coefficients for each element based on the system of equations derived in Sec.4.4. The value of α_2 and d_1 can be calculated from Eq.31 and Eq.33. Similarly, β_1 and d_2 can be calculated from Eq.32 and Eq.34. The analogical solution

is extremely hard to find for most of the case. Therefore, numerical approach will be chosen. From the physics perspective, it worth nothing to discuss the process of solving these parameters. However, several issues which were encountered during the solving process deserve to be discussed.

The first issue is due to the denominator in Eq.33 and Eq.34. If the size of the element were too large or too small, there will be an element whose two ends points x_s and x_{s+1} have very similar value in the error function term due to the symmetry property of the error function. In this case, the system of equations contains a singular point and consequently, there will be no answer for the diffusion coefficients in this element. The remedy for this case is simple. This situation happens only when the size of element is too large or too small. If the size of element were too large, one should apply a finer mesh on this element. If the size were too small, one can choose to simply ignore the diffusion coefficients in this element.

The second issue is related to the nature of the diffusion process. The areas close to boundaries of the diffusion domain have very similar concentration value and the flux value. Therefore, the solution of the above equations can be trivial or not unique. It still satisfies the physical condition because the flux value is very close to zero. If both the diffusion components had consistent concentration gradient, then the diffusion coefficients can be any number, or simply equal to zero. In other words, the assumption that the diffusion coefficients matrix is diagonalizable is violated. This situation happens in a certain range of region. There is no point to force ourselves to find a solution to such area. To avoid this issue, one should omit certain amount of elements in calculation and the number of elements ignored should depend on the size of elements.

For now, we will only provide the results of the calculated diffusion coefficient matrices from one data set with different partition. The discussion of these results will be given in Sec.7.

Table 3: Diffusion Coefficient Matrix I

Total Element Number = 10							
Excluded Element Number = 0							
Measured points = 281							
Element I		Element II		Element III		Element IV	
N/A	N/A	0.6547	-0.6540	0.0763	-0.0758	0.0192	-0.0188
N/A	N/A	0.6546	-0.6539	0.0762	-0.0757	0.0191	-0.0187
Element V		Element VI		Element VII		Element VIII	
0.0058	-0.0001	0.0028	0.0087	-0.0095	0.0803	-0.0088	0.4529
0.0017	0.0044	-0.00976	0.0307	-0.0093	0.0797	-0.0084	0.4521
Element IX		Element X					
0.8541	0.7311	0.0064	2.8795				
0.0009	2.2645	0.0059	2.8796				

Table 4: Diffusion Coefficient Matrix II

Total Element Number = 20							
Excluded Element Number = 3							
Measured points = 281							
Element I		Element II		Element III		Element IV	
0	0	1.2433	-1.2432	0.2936	-0.2935	0.0719	-0.0718
0	0	1.2433	-1.2432	0.2936	-0.2935	0.0719	-0.0718
Element V		Element VI		Element VII		Element VIII	
0.0201	-0.0200	0.0068	-0.0067	0.0029	-0.0027	0.0011	-0.0005
0.0201	-0.0200	0.0068	-0.0067	0.0029	-0.0027	0.0011	-0.0004
Element IX		Element X		Element XI		Element XII	
0.0004	0.0002	0.0003	0.0002	0.0000	0.0011	0.0001	0.0021
0.0004	0.0003	0.0002	0.0003	0.0000	0.0011	-0.0000	0.0023
Element XIII		Element XIV		Element XV		Element XVI	
-0.0002	0.0057	-0.0002	0.0151	-0.0003	0.0495	0.1151	-0.0562
-0.0000	0.0053	-0.0000	0.0148	-0.0000	0.0489	0.0000	0.1866
Element XVII							
0.0003	0.8233						
0.0001	0.8235						

Here, the total element number is the number of divided sub-domains, the Excluded element number are the total of elements which are not considered because of the issue mentioned above, the measured points are the number of observation from the data sheet. For ternary diffusion system, the diffusion coefficient matrices have dimension of 2×2 . Then for each element, there are four components which represent the four components of the diffusion coefficient matrix in that element.

6 Jump Condition

An important phenomenon in the diffusion process is that the concentration profile experiences a drastic drop or increase at interfaces. Mathematically, the value of concentration is not continuous at the position of interfaces. This section gives a brief explanation and introduces proper methods of deriving the flux and concentration functions for the element containing an interface.

6.1 Trivial explanation

Let two components be annealed and allowed to diffuse through each other. At the beginning of the diffusion process, the interface is located at the position of annealing. At anywhere else on the left side of the interface, the concentrations of two components will be 0% and 100%. Similarly, at the right side of the interface, concentrations should be 100% and 0%. Therefore, there is a jump for both components at $t = 0$ at the interface. The concentration is a function of time and position. If the position were fixed, then the change of the value concentration with respect time has to be continuous. However, if the time were fixed, the concentration profile does not have to be continuous, such as at $t = 0$. As the interface changes its position, this condition should still hold. For a two components diffusion system, the concentration value for each component approaches its final value at the interface from 0% and 100%. Therefore, mathematically the jump naturally exists. From the physical perspective, the jump condition has no meaning since the concentration does not describe the movement of particles. As the system goes towards its equilibrium state, the concentration value of each component will converge to its final value for each side and the two values do not necessarily to be same.

However, the jump condition will make numerical analysis much more complicated. Without the discontinuity, the concentration profile is a smooth function. Thus one can use standard finite element to obtain the approximate solution. But the jump condition will create

a considerable oscillation which starts from the interface and will not smooth out for a large size spatial interval. To conquer the issue from the jump condition, one can either adjust the numerical approach by using other methods such as discontinuous Galerkin's method or generate a smooth function to approximate the original situation.

6.2 Connecting the Jump

Based on Sec. 9.3, one approach of smoothing the jump condition around interfaces is to predefine the form of a function and to solve its parameters. The main idea here is to first find a function whose first derivative is continuous but experiences a purge rapidly increase or decrease in a small region. Fermi-function indeed satisfies this requirement. The form of the function is then chosen to be

$$f(x) = \frac{a}{\exp\left(\frac{x-b}{c}\right) + 1} + d \quad (35)$$

Where the undetermined parameters are a, b, c and d . The derivative of function f is

$$\frac{df(x)}{dx} = -\frac{a \cdot \exp\left(\frac{x-b}{c}\right)}{c \cdot (\exp\left(\frac{x-b}{c}\right) + 1)^2} \quad (36)$$

In the diffusion problem, the value of the function f will be the concentration value at the corresponding position. The boundary nodal concentration and concentration gradient values of the element across a interface are determined from the previous section. Therefore, these four values play roles analogous the conditions to provide a solution for the parameters in function f .

Suppose the element ranges from x_1 to x_2 . The concentration values at each points are Y_1 and Y_2 and the concentration gradient values are Y'_1 and Y'_2 . The system of equations is

then formed as

$$Y_1 = \frac{a}{\exp(\frac{x_1-b}{c}) + 1} + d; \quad (37)$$

$$Y_2 = \frac{a}{\exp(\frac{x_2-b}{c}) + 1} + d; \quad (38)$$

$$Y_1' = -\frac{a \cdot \exp(\frac{x_1-b}{c})}{c \cdot (\exp(\frac{x_1-b}{c}) + 1)^2}; \quad (39)$$

$$Y_2' = -\frac{a \cdot \exp(\frac{x_2-b}{c})}{c \cdot (\exp(\frac{x_2-b}{c}) + 1)^2}. \quad (40)$$

It is clear that the system of equations has no singularity issue. Then theoretically, these four equations should give a unique solution for these four parameters. However, it is not easy to have an analytical solution for such complex equations. Numerical methods would be the proper approach here.

The error and the difficulty of calculation should be considered at same time. The error can come from both the form of the function itself and the numerical calculation. Although the Fermi-function fits the requirements to a considerable extent, there is no theory to support the Fermi-function is the right choice. On the other hand, the more non-linear the parameters are in the system of equation, the more likely the error has a lower order of accuracy. Then we conclude here that reducing the difficulty of calculating these parameters by making reasonable assumptions may not increase the error.

The idea of reducing the difficulty here is to use the symmetry property of the Fermi-function. The location of interface can be detected from the experiment. However, not only that the interface does not necessarily locate at the middle of the element, but also the derivative values at two ends do not usually match. Consequently, the symmetry property cannot be applied to a single Fermi function here.

The alternate method is to create the symmetrical situation for the element across the interface by using two Fermi-functions. Since the domain and size of the element contains the interface is free for us to choose, one can then choose the interface location at the middle

of the element. This condition is not necessary to have, but it will make the explanation of our process simpler since it can be used as a reference point for which a Fermi function symmetrical is about.

Let us start to build a symmetrical situation for our calculation. First, comparing the absolute values of the concentration gradient value of two end points and finding the one with the lower value. For example, if the element ranges from $x_1 = 1$ to $x_2 = 2$ and the values of concentration gradient are $Y'_1 = -1$ and $Y'_2 = -1.2$, then the nodal point would be chosen to be x_1 . From here, assume that the value of concentration gradient at x_2 matches the value at x_1 . Under this assumption, one can obtain two relations

$$b = \frac{x_1 + x_2}{2} = L; \quad (41)$$

$$d = -\frac{a - (Y_1 + Y_2)}{2}. \quad (42)$$

where Y_i is the value of concentration at x_i and L is the location of the interface. Substituting these relations in to the system of equations above, one can obtain

$$Y_1 = \frac{a}{e^{-\frac{B}{c}} + 1} - \frac{a - (Y_1 + Y_2)}{2}; \quad (43)$$

$$Y'_1 = -\frac{a \cdot e^{-\frac{B}{c}}}{c \cdot (e^{-\frac{B}{c}} + 1)^2} \quad (44)$$

Where $B = L - x_1$ is a constant. It is clear that the parameters a and C are much easier to be solved from these two equations.

After solving the parameters a and c , the first Fermi-function is then formed. The next step is to find the point at the same side of x_1 and whose value of concentration derivative is equal to Y'_2 . Suppose this point has coordinate (x_3, Y_3) , then one can define another symmetrical point $(\frac{x_3+x_2}{2}, \frac{Y_3+Y_2}{2})$. Following same procedure, the second Fermi function will be generated.

It is trivial to check that both the Fermi functions and their concentration gradient

functions intersect at (x_3, Y_3) . Therefore, for the element across the interface, one can use two Fermi-functions for the concentration profile. The first function has the domain from x_1 to x_3 and the second one has the domain from x_3 to x_2 .

As a concrete example, let us assume that the boundary values of the element are

$$\begin{aligned} x_1 &= 2.98; & x_2 &= 3.02 \\ Y_1 &= 82; & Y_2 &= 70 \\ Y_1' &= -5; & Y_2' &= -7.5. \end{aligned}$$

Since the absolute value of Y_1' is smaller, the system of equation for the first Fermi function is

$$\begin{aligned} \frac{a}{e^{-\frac{0.02}{c}} + 1} - \frac{a - 152}{2} &= 82; \\ -\frac{a \cdot e^{-\frac{0.02}{c}}}{c \cdot (e^{-\frac{0.02}{c}} + 1)^2} &= -5. \end{aligned}$$

The calculated value is

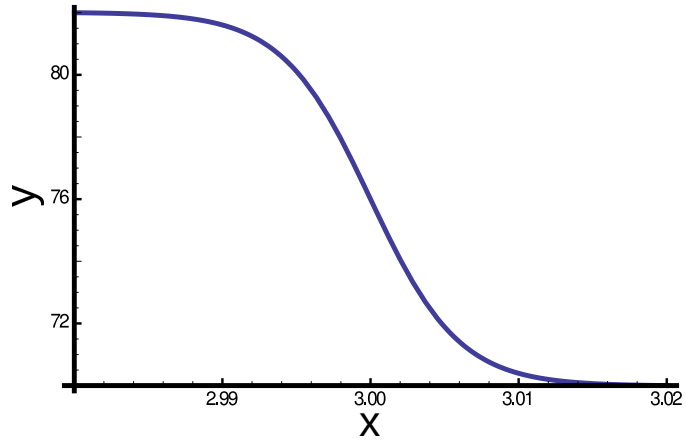
$$\begin{aligned} a &= 12.0299427; \\ c &= 0.00299053. \end{aligned}$$

Therefore, the first Fermi function is

$$f_1(x) = \frac{12.02994}{\mathbf{exp}\left(\frac{x-3}{0.00299}\right) + 1} + 69.98505 \quad (45)$$

The plot of the first function is

Figure 8: The First Fermi-Function

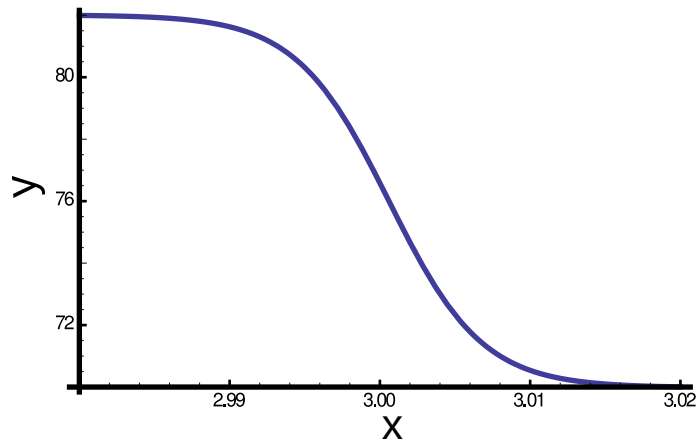


Next step is to determine the point which has same concentration gradient value as the value at $x = 3.02$. The point is found to be $p = (2.9812, 81.9926)$. Thus the new symmetrical point is $p_s = (3.0006, 75.9963)$. Following same procedure, the second Fermi function is

$$f_2(x) = \frac{12.0393}{\exp\left(\frac{x-3.0006}{0.0031}\right) + 1} + 69.9766 \quad (46)$$

The plot of the second function is

Figure 9: The Second Fermi-Function



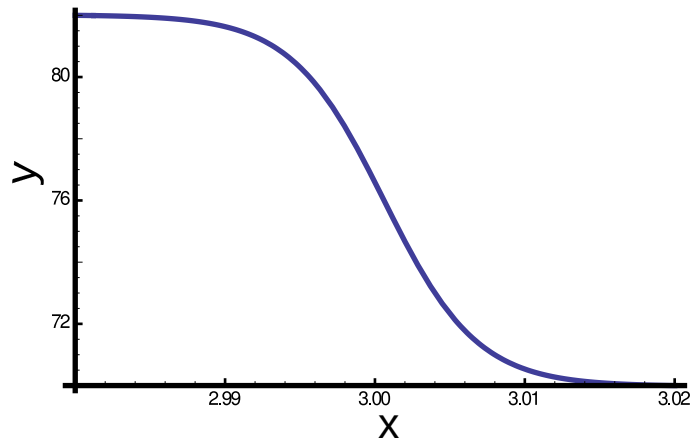
Combine the two functions and assign proper domain for each function, the concentration

profile in the interval of (2.98, 3.02) will be

$$\begin{aligned}
 F(x) &= \frac{12.02994}{\exp\left(\frac{x-3}{0.00299}\right) + 1} + 69.98505, & x \in (2.98, 2.9812); \\
 &= \frac{12.0393}{\exp\left(\frac{x-3.0006}{0.0031}\right) + 1} + 69.9766, & x \in (2.9812, 3.02).
 \end{aligned}$$

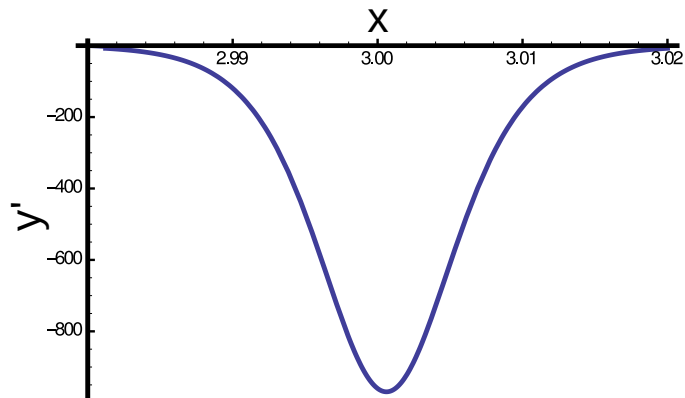
The plot of this piecewise function is

Figure 10: Example of Concentration Profile



The plot of its first position derivative is

Figure 11: Example of Concentration gradient



It should be emphasised that the domain of the first Fermi function is supposed to be small compared to the size of element as the gradient value changes rapidly towards the interface. This section has shown one way to connect the jump condition with a combination

of Fermi-functions. In principle, any function satisfying the condition introduced in Sec.6.2 can be potentially used to connect the jump.

6.3 Least Square Fitting by using Fermi-function

For an element which is very close to the interface and contains a limited number of experimental data, the connecting method introduced in previous section makes sense. However, the drawback of directly connecting the jump condition is that this method only uses the information from the two end points of the element. If a moderate amount of observation were made in the element at an interface, the information from the data are ignored besides the two nodal points. The other potential problem is that the symmetry is not guaranteed for the two sides of the interface. Most of time, different dominant diffusion components occupy each side of the interface. They do not necessarily have similar behavior in their rate of change with respect to the position.

If there were enough observation in the element, one can choose to use interpolation functions to connect the jump. This method uses all the information from measured points and the shape of the function is not constrained before hand. Recall Sec.3.2.2, Fermi-function has the property similar to the jump condition. Let us take a close look at Eq 7. Mathematically, the attributions of each parameters are

- a: the range of function value
- b: the symmetrical position
- c: the rate of change
- d: the shift of function value

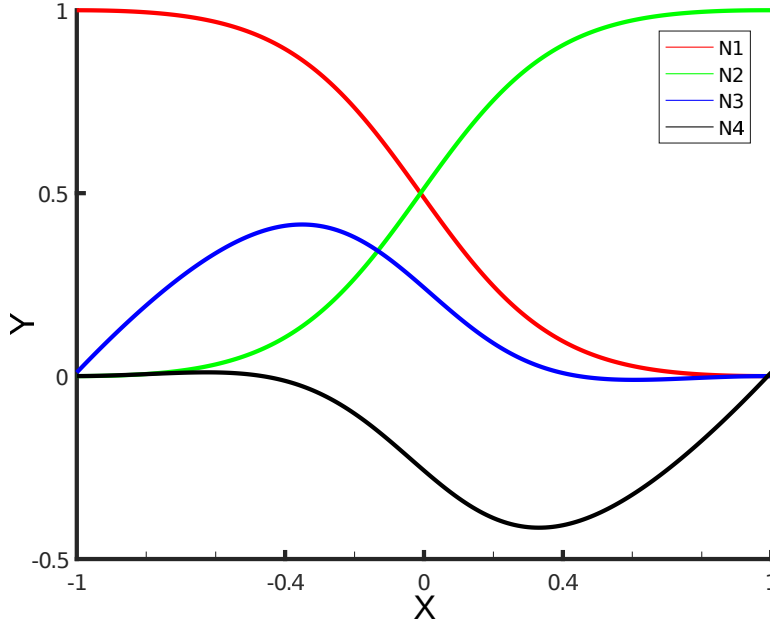
The Fermi function cannot be used along as the shape function since it is an odd function about its symmetrical point and therefore the derivative would be an even function. Whereas the condition for Hermite interpolation requires different values for derivative values of two

boundary points. Therefore, some supplemental work has to be considered. For any additional shape function, there must be at least one undetermined parameter. Then some parameters from the Fermi function have to be dropped. Fortunately in a diffusion process, although the values of certain parameters are not precisely defined, they can be guessed with small error. Since we wish to get rid of the non-linearity of the Fermi-function, one could consider the following shape function

$$f_1 = \frac{a}{e^{-kx} + 1} + bx^2 + cx + d \quad (47)$$

Here the undetermined parameters are $a, b, c,$ and $d.$ k is an assigned constant based on the width of the element. If the value of k were assigned to 5, The plot of the shape functions is given in Fig.12

Figure 12: Shape function of the 1st form



There are other kinds two shape functions based on similar idea given by

$$f_1 = \frac{a}{10^{-kx} + 1} + bx^2 + cx + d \quad (48)$$

$$f_3 = \frac{a}{(x+1)^{-k} + 1} + bx^2 + cx + d \quad (49)$$

The plot of these two kinds of shape functions are given in following figures

Figure 13: Base function of the 2nd form

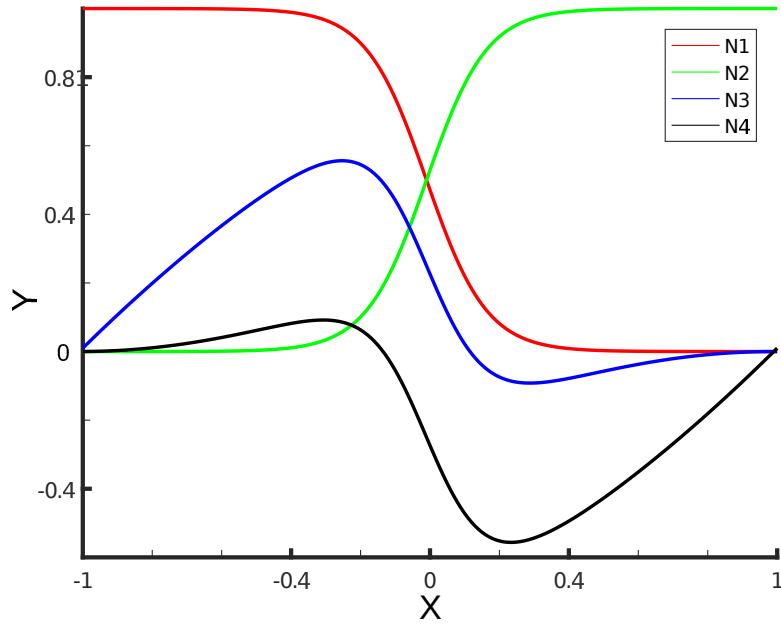
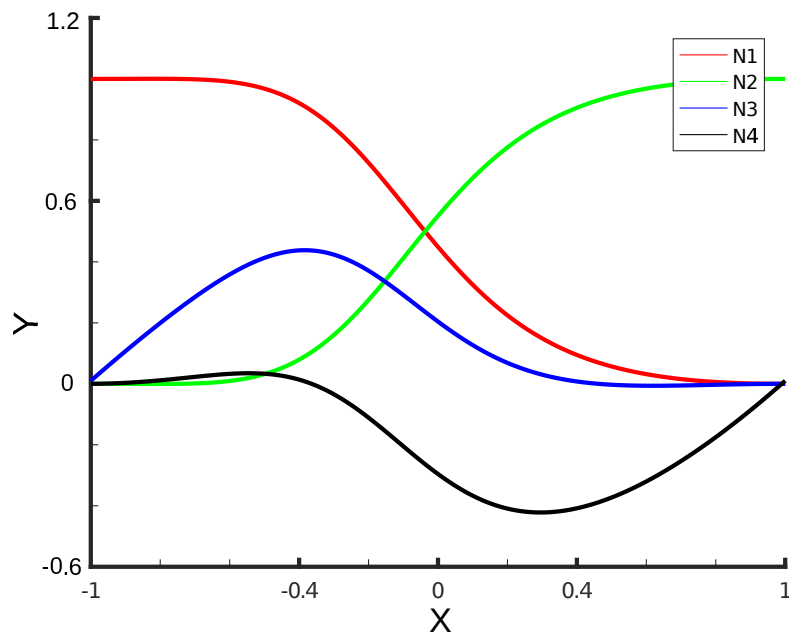
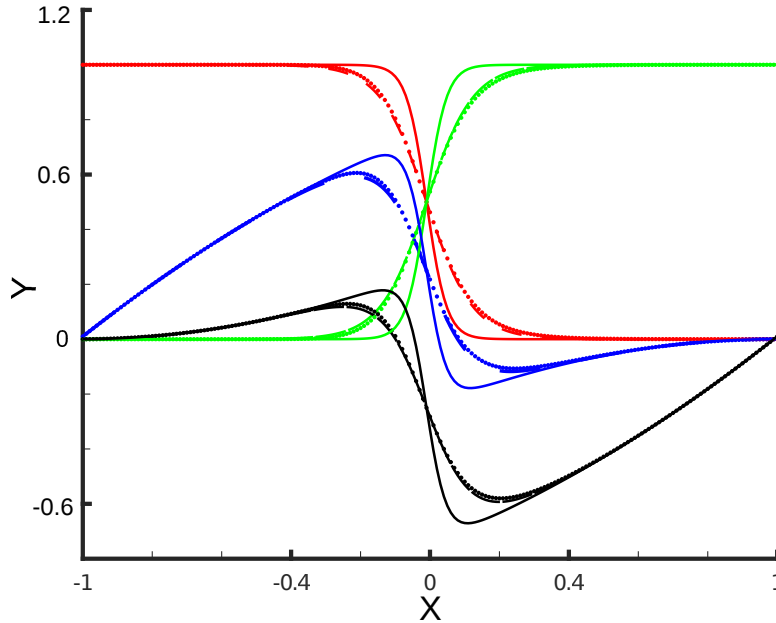


Figure 14: Base function of the 3rd form



If the value of k changes, these shape functions will also change. The following figure compares between the three kinds of shape functions with $k = 15$,

Figure 15: Comparison



In the figure above, the red lines are the function of N_1 , the green lines are the function of \overline{N}_1 , the blue lines are the function of N_2 , the black lines are the function of \overline{N}_2 . The solid line represents the first kind, the dash line represents the second kind, and the dot represents the third kind of shape function.

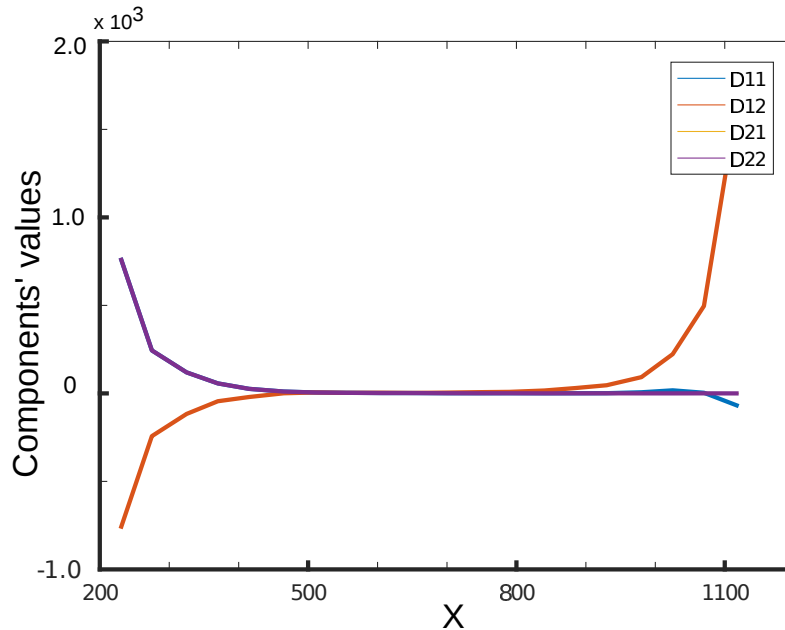
7 Trend of Diffusion Coefficients

As mentioned before, the diffusion coefficients should be a function of position for any given time. The result of diffusion coefficients' value is given in Sec.5. However, we have not discussed anything about the result yet. This section will first analyze the values for diffusion coefficients.

The first notable attribution of the diffusion coefficient matrix is that the values of D_{11} and D_{21} , D_{12} and D_{22} are close to each other in most of the region. As shown in Fig.16, the

two pairs of components have a big portion of overlapping.

Figure 16: Diffusion Coefficient versus Position
Element number = 30(21)

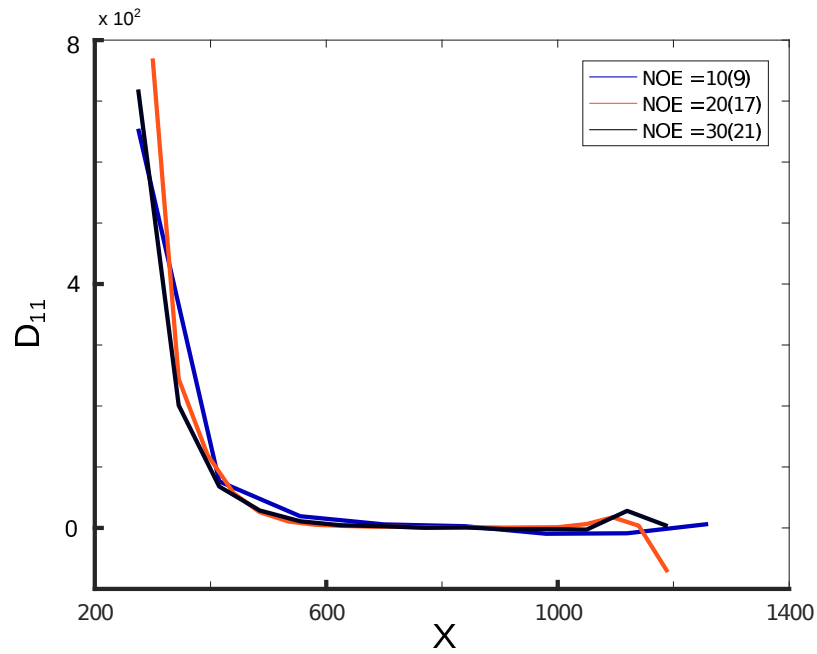


The above figure used 30 elements partition and omitted first 4 elements from each ends. From a overall view, recall that the concentration profile varies to a good extend from about $x = 400$ to $x = 1000$. The absolute diffusion coefficients' values and its changed values in this region are very small compared to the elements towards either end. This is agreed with that the shape of concentration gradient plots and the flux plots are similar in this range.

It would be pointless to discuss the behaviors of the diffusion coefficient matrix in general from one case. However, it still worth it to find relations from the plots of diffusion coefficients and the diffusion process itself.

The value of component D_{11} over the most diffusion domain from three different partitions is shown in the following figure

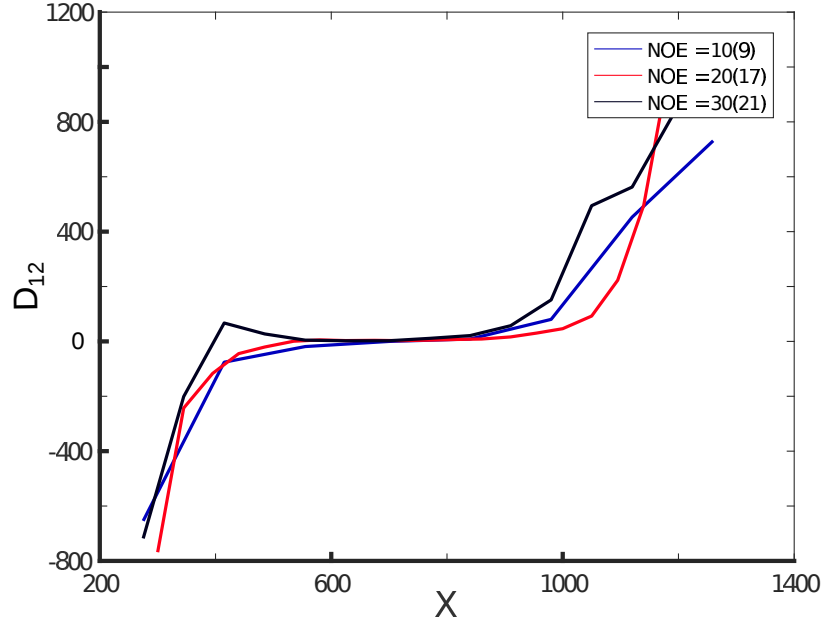
Figure 17: Diffusion Coefficient Component Plot 1



Here, the blue line represents the value of D_{11} from a 10 elements partition(9 elements are included), the red line represents the 20 elements partition(17 elements are included), and the yellow line represents the 30 elements partition(21 elements included)

The value of component D_{12} over the most diffusion domain from three different partitions is shown in the following figure

Figure 18: Diffusion Coefficient Component Plot 2



Here, the blue line represents the value of D_{12} from a 10 elements partition(9 elements are included), the red line represents the 20 elements partition(17 elements are included), and the yellow line represents the 30 elements partition(21 elements included).

Recall from the governing equation of diffusion process,

$$J_i = -D_{11} \frac{\partial C_1}{\partial x} - D_{12} \frac{\partial C_2}{\partial x}$$

In this specific case, it is clear that the first component of diffusion coefficient has a similar shape of the e^{-x} and the second component diverges out towards the boundary. The more interested topic is to find the relation between these two coefficients. For most of the region, these two coefficients seems to balance each other. Recall that the scale for both concentration and flux are 10^{-4} which is relatively small compare to the value of diffusion coefficients' values. For the region of which the coefficients' values become flatter, it would be more clear by checking the value from the tables given in Sec.5.

One important fact is that the parameters are not nondimensionlized. Therefore, the

units of each parameter cannot be changed. The concentration values are given in percentage in the original data sheet and the length is given in micrometer. If these values were re-scaled or given in other units, the shape of diffusion coefficients might not hold the same.

8 Conclusion

In this report, the flux function, the concentration profile, and the concentration gradients have been derived from the experimental data of concentration values for each component. These functions can be used to obtain values at any points in the diffusion domain. The derived values provide necessary information of calculating the diffusion coefficients in the ternary diffusion system. A system of equations which is derived from the transfer matrix method has been developed to calculate the eigenvalues and eigenvectors of the diffusion coefficient matrix. These eigenvalues and eigenvectors are used to form the diffusion coefficient matrix for each element.

The jump condition of the concentration profile has also been discussed in this report. A brief explanation is given and two proper methods of extracting information of concentration and flux in these special elements are introduced. Based on the procedure shown in this report, one can then obtain the value of flux, the concentration, and the concentration gradient everywhere in the diffusion domain. From there, a complete formalism has been developed to calculate the diffusion coefficients in all the elements.

Following by this report, future effort can be made towards either developing higher dimensional diffusion phenomena or including the contribution of time.

9 Appendix

9.1 Picard Iteration

The unique solution of this differential equation of the for $\dot{x} = Ax + b$. is

$$x(t) = \left(\exp \int_{\mathbf{t}_0}^{\mathbf{t}} \mathbf{A}(\tau) \mathbf{d}\tau \right) \left(x_0 + \int_{\mathbf{t}_0}^{\mathbf{t}} \exp \left(- \int_{\mathbf{t}_0}^{\sigma} \mathbf{A}(\sigma) \mathbf{d}\sigma \right) \mathbf{b}(\tau) \mathbf{d}\tau \right). \quad (50)$$

Here A denotes a family of matrices and b is a vector valued function. Let Φ_A denote the homogeneous part of the differential equation and from Volterra integral equation,

$$\Phi_A = \mathbf{I} + \int_{\mathbf{t}_0}^{\mathbf{t}} \mathbf{A}(\tau) \Phi_A(\tau, \mathbf{t}_0) \mathbf{d}\tau, \quad \Phi(\mathbf{t}_0, \mathbf{t}_0) = \mathbf{0}.$$

Here, \mathbf{I} is the identity matrix. Applying the mean of formal Picard iteration, one can show

$$\Phi_A = \mathbf{I} + \int_{\mathbf{t}_0}^{\mathbf{t}} \mathbf{A}(\tau) \mathbf{d}\tau + \int_{\mathbf{t}_0}^{\mathbf{t}} \int_{\mathbf{t}_0}^{\tau_1} \mathbf{A}(\tau_1) \mathbf{A}(\tau_2) \mathbf{d}\tau_1 \mathbf{d}\tau_2 \quad \dots \quad (51)$$

Here, for each integral, $\mathbf{A}(\tau_i)$ is independent of τ_j for $i \neq j$. Let I_n be

$$I_n = \int_{\mathbf{t}_0}^{\mathbf{t}} \int_{\mathbf{t}_0}^{\tau_1} \dots \int_{\mathbf{t}_0}^{\tau_{n-1}} \mathbf{A}(\tau_1) \mathbf{A}(\tau_2) \dots \mathbf{A}(\tau_n) \mathbf{d}\tau_1 \mathbf{d}\tau_2 \quad \dots \mathbf{d}\tau_n.$$

If I_0 equal to \mathbf{I} , Then for all n the following relation will be satisfied:

$$I_{n+1} = \int_{\mathbf{t}_0}^{\mathbf{t}} \mathbf{A}(\tau) I_n(\tau) \mathbf{d}\tau.$$

Thus Eq.51 can be write in a compact form as $\Phi_A = \mathbf{I} + \sum I_n$. If \mathbf{A} is continuous and differentiable on a interval, one can get

$$I_n = \frac{1}{n!} \left(\int_{\mathbf{t}_0}^{\mathbf{t}} \mathbf{A}(\tau) \mathbf{d}\tau \right)^n.$$

Extend the above analysis to the non-homogeneous case, one can obtain, for both \mathbf{A} and b continuous,

$$x = \Phi_{\mathbf{A}} * \left(\mathbf{x}_0 + \int_{t_0}^t \Phi_{\mathbf{A}} \mathbf{b}(\tau) d\tau \right) \quad (52)$$

Since the flux function and its first derivative has to be continuous, with the assumption of that the diffusion coefficients are constant, the solution of the flux function in Sec4 can be written in the desired form.

9.2 Marker plane

Kirkendall's experiment gives the evidence that the intrinsic diffusions between a diffusion couple do not usually equal to each other. If a marker has no diffusivity with both of the diffusion couple and is put at the conjunct plane of two materials at $t = 0$. Then the Kirkendall's effect makes the marker moves towards the sides of higher diffusivity due to the interchange of vacancies. The interface jump happens at the marker plane. The marker plane can be detected directly at any time. In the case of two component diffusion system, the difference between the diffusivity of two components and the concentration gradient developed in the interdiffusion zone give the velocity of marker which can be expressed as

$$v_m = -(V_B J_B + V_A J_A) = V_B (D_B - D_A) \frac{\partial C_B}{\partial x}. \quad (53)$$

Here, v_m is the velocity of the marker, V_i is the partial molar volume of component i , D_i is the diffusion coefficient of component i , and J_i is the intrinsic diffusion of component i . Another well-known expression of the velocity of marker is basic on the displacement of the marker and it gives

$$v_m = \frac{\partial x}{\partial t} = \frac{x_m - x_0}{2t} \quad (54)$$

Here, x_m is the position of the marker plane, x_0 is the position of the Matano plane, and t is the total experiment time.

Since these two relations both give the velocity of the marker, therefore one should be able to find the location of marker plane by finding the common point of two velocity curves versus $\frac{2t}{x}$. Notice that the number of intersection of two curve can be more than one which reflects the case of multiple marker planes.

Let us then consider the continuity of the flux. The continuity condition is given by

$$J_{A_+}^{\sim} - J_{A_-}^{\sim} = v_m \cdot (C_{A_+} - C_{A_-}) \quad (55)$$

Here, v_m is the velocity of the interface, $J_{A_+}^{\sim}$ and $J_{A_-}^{\sim}$ are the intrinsic flux of the component A of limit value from left and right side to the interface, that is

$$\begin{aligned} J_+ &= J|_x, & x &\rightarrow x_{m_+}; \\ J_- &= J|_x, & x &\rightarrow x_{m_-}. \end{aligned}$$

Similarly, the C_{A_+} and C_{A_-} are defined as

$$\begin{aligned} C_+ &= C|_x, & x &\rightarrow x_{m_+}; \\ C_- &= C|_x, & x &\rightarrow x_{m_-}. \end{aligned}$$

Then, by applying the Fick's equation, one obtains

$$D_{A_+}^{\sim} \frac{\partial C_A}{\partial x} - D_{A_-}^{\sim} \frac{\partial C_A}{\partial x} = -v_m \cdot (C_{A_+} - C_{A_-}) \quad (56)$$

One can modify the usual Matano-Boltzmann parameter with

$$\xi = \frac{x - x_0}{2\sqrt{\overline{D}t}}.$$

Where \overline{D} is the value of \tilde{D} and it is a number, and x_0 is the Matano plane position. Substitute

this in to Eq.56 one can obtain a dimensionless expression

$$-\xi \frac{\partial \hat{C}}{\partial \xi} = \frac{\partial}{\partial \xi} (\hat{D} \frac{\partial \hat{C}}{\partial \xi}) \quad (57)$$

Here, $\hat{D} = \frac{\tilde{D}}{D}$, with this transformation, the boundary condition becomes

$$\begin{aligned} \hat{C}_+ &= \hat{C} |_{\xi}, & \xi &\rightarrow \xi_{0+} \\ \hat{C}_- &= \hat{C} |_{\xi}, & \xi &\rightarrow \xi_{0-} \end{aligned}$$

Then the continuity flux condition gives

$$(\hat{D}_A |_{C_{A+}}) \frac{\partial \hat{C}_{A+}}{\partial \xi} - (\hat{D}_A |_{C_{A-}}) \frac{\partial \hat{C}_{A-}}{\partial \xi} = -\xi * (C_{A+} - C_{A-}). \quad (58)$$

One can expand the analysis to write down the expression of velocity of the marker plane and the displacement field, and obtain the singularity at $x = \frac{x_m - x_0}{2t}$ which is exactly one of the expression of the position of marker plane.

9.3 More constraints about connecting jump condition

During the diffusion process, there should be no particle lose for each component. If the shape and volume of the diffusion material remain same, then the number of particles can be represented by the concentration values. Mathematically, the total area under a concentration function should be a constant. Suppose the concentration profile has been calculated for all the elements except those contain an interface. The integrated concentration can then be calculated for the region outside the interface.

Suppose we are looking for a function F to represent the concentration profile in an element contains an interface. The besides the four constraints which come from the continuity condition, there is another constraints for F of which its integrated value over the interval should to be a desired number.

References

- [1] Santosh Kumar, Carol A. Handwerker, and Mysore A. Dayananda, *Intrinsic and Interdiffusion in Cu-Sn System*, 2011
- [2] P. G. Shewmon, *Diffusion in Solids*, McGraw-Hill Book
- [3] T. Heumann, *Z. Physik. Chem.* 201, p 168-189, 1952
- [4] M. A. Dayananda, *Average Effective Interdiffusion Coefficients in Binary and Multicomponent Alloys*, *Defect Diffus. Forum*, 95-98, p 521-536 Company, Inc, New York, 1993
- [5] C. Wagner, *Evaluation of Data Obtained with Diffusion Couples of Binary Single-Phase and Multiphase Systems*, *Acta Metall.*, 17(2), p 99-107,1969
- [6] A. G. Guy, *Treatment of Diffusion Considering Changes in Atomic Volume*, *Scripta Metall.*, 5(4), p 279-281,1971
- [7] M. A. Dayananda and C. W. Kim, *Zero-Flux Planes and Flux Reversals in Cu-Ni-Zn Diffusion Couples*, *Metall. Trans. A*, 10(9), p 1333-1339,1979
- [8] M. A. Dayananda, *Atomic Mobilities in Multicomponent Diffusion and Their Determination*, *Trans. Met. Soc. AIME*, 242,1968 p 1369-1372

- [9] P. C. Tortorici and M. A. Dayananda, *Growth of Silicides and Interdiffusion in the Mo-Si System*, *Metall. Mater. Trans. A*, 30A, p 545-550,1999
- [10] L. R. Ram-Mohan, *Finite Element and Boundary Element Applications in Quantum Mechanics*, Oxford University Press, Oxford, UK, 2002.